

รายงานวิจัยฉบับสมบูรณ์

การพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

(ความเห็นในรายงานฉบับนี้เป็นของผู้วิจัย สกว. ไม่จำเป็นต้องเห็นด้วยเสมอไป)

บทคัดย่อ

การพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์มีความสำคัญอย่างยิ่งสำหรับอนาคตอุตสาหกรรมวัสดุก่อสร้างของประเทศไทย กระบวนการผลิตปูนซีเมนต์เป็นกระบวนการที่ใช้พลังงานมากและปลดปล่อยก๊าซคาร์บอนไดอ็อกไซด์สูงมาก การผลิตปูนซีเมนต์ 1 ตันปลดปล่อยก๊าซคาร์บอนไดอ็อกไซด์เกือบ 1 ตัน การใช้ปูนซีเมนต์ผสมสารปอซโซลานสามารถลดการใช้ปูนซีเมนต์ปอร์ตแลนด์ลงได้ วัสดุปอซโซลานเป็นวัสดุที่มีซิลิกาและอะลูมินาเป็นองค์ประกอบหลัก งานวิจัยนี้ได้ศึกษา เถ้าลอย, เถ้าก้นเตา, ดินขาวเผา, เถ้าแกลบ, เถ้าแกลบ-เปลือกไม้, เถ้าปาล์มน้ำมัน, และเถ้าชานอ้อย การลดปริมาณปูนซีเมนต์ปอร์ตแลนด์และแทนที่ด้วยสารปอซโซลานทำให้ปริมาณแคลเซียมไฮดรอกไซด์ในส่วนผสมลดลง ส่งผลให้คอนกรีตมีความทนทานขึ้น การต้านทานการซึมผ่านของคลอไรด์, การต้านทานการทำลายของสารซัลเฟต, และความสามารถในการป้องกันการเกิดสนิมของเหล็กเสริมดีขึ้น ได้ศึกษาและพัฒนาวัสดุซีเมนต์ชนิดใหม่คือจีโอโพลิเมอร์ โดยใช้วัตถุดิบที่มีในประเทศ ได้แก่ เถ้าลอยแคลเซียมสูง ในการผสมใช้โซเดียมไฮดรอกไซด์ความเข้มข้นสูงและสารโซเดียมซิลิเกตเป็นของเหลว ซึ่งพบว่าจีโอโพลิเมอร์เถ้าลอยแคลเซียมสูงมีสมบัติทางกลที่ดี ให้กำลังรับแรงสูง การหดตัวต่ำ มีความคงทนต่อการทำลายของสารซัลเฟตและกรด ได้ใช้วัสดุไมโครซิลิกา, นาโนซิลิกา, ซิงค์ออกไซด์, ไทเทเนียมออกไซด์ และสารประกอบอื่นผสมเข้ากับสารเชื่อมประสาน ผลการทดสอบแสดงให้เห็นว่าการผสมออกไซด์เหล่านี้สามารถปรับปรุงสมบัติทางไฟฟ้าและทางแม่เหล็กของสารซีเมนต์แต่มีผลกระทบต่อสมบัติทางกลอยู่บ้าง ผลที่ได้จากการวิจัยสามารถใช้เป็นข้อมูลพื้นฐานที่สำคัญสำหรับนำวัสดุเหล่านี้ไปใช้ประโยชน์และใช้ในการพัฒนาอุตสาหกรรมก่อสร้างที่ยั่งยืนในประเทศไทย

คำหลัก: ปูนซีเมนต์, จีโอโพลิเมอร์, คาร์บอนไดอ็อกไซด์, สารปอซโซลาน, ซิลิกา, อะลูมินา, เถ้าลอย, เถ้าก้นเตา, ดินขาวเผา, เถ้าแกลบ, เถ้าแกลบ-เปลือกไม้, เถ้าปาล์มน้ำมัน, เถ้าชานอ้อย, ความทนทาน, การซึมผ่านของคลอไรด์, การทำลายจากซัลเฟต, การเกิดสนิมของเหล็ก, แคลเซียมไฮดรอกไซด์, โซเดียมไฮดรอกไซด์, โซเดียมซิลิเกต, ไมโครซิลิกา, นาโนซิลิกา, ซิงค์ออกไซด์, ไทเทเนียมออกไซด์, การกัดกร่อนของกรด

Abstract

The development of blended cement and geopolymer is very important to the future of construction industry of Thailand. The process of manufacturing of Portland cement uses a large amount of energy and emits huge quantity of carbon dioxide. In making 1 ton of Portland cement, almost 1 ton of carbon dioxide is released. The use of blended Portland pozzolana cement can reduce the use of Portland cement. Pozzolans are materials containing silica and alumina as major oxides. In this research, fly ash bottom ash, calcined kaolin, rice husk ash, rice husk-bark ash, palm oil fuel ash, and bagasse ash were studied. The partial replacement of Portland cement with these pozzolans reduced calcium hydroxide in the mixture and resulted in the improvement of concrete durability. The resistance to chloride penetration, resistance to sulfate attack, and resistance to corrosion of steel reinforcement were improved. The research and development of new binder called 'geopolymer' was undertaken. The source material available in Thailand was high calcium fly ash. Sodium hydroxide and sodium delicate were used as liquid for the mix. The results indicated that high calcium geopolymer gave good mechanical properties with high compressive strength, low shrinkage, and good resistances to sulfate and acid attack. Microsilica, nanosilica, zinc oxide, titanium oxide, and other composite oxides were incorporated into the binder system. The results showed that the incorporation of these oxides improved the electrical and magnetic properties of the cement composites but with some effects on the mechanical properties of the binder. The results obtained from this research can be used as important basic information for the utilization and development of the sustainable construction material industry in Thailand.

Key words: cement, geopolymer, carbon dioxide, pozzolans, silica, alumina, fly ash, bottom ash, calcined kaolin, rice husk ash, rice husk-bark ash, palm oil fuel ash, bagasse ash, durability, chloride penetration, sulfate attack, steel corrosion, calcium hydroxide, sodium hydroxide, sodium silicate, microsilica, nanosilica, zinc oxide, titanium oxide, acid attack

Executive summary

This research, Development of Portland cement and geopolymer composite material, was funded by the Thailand Research Fund (TRF) under the TRF Senior Research Scholar Contract No. RTA5480004. The project period is three years, 31 August 2011 – 30 August 2014, with the total budget of 7.5 million baht. The project was led by Professor Dr. Prinya Chindaprasirt, Department of Civil Engineering, Khon Kaen University with the support from 11 other researchers; two from Suranaree University of Technology, one from Burapha University, one from Rajamangala University of Technology Phra Nakhon, two from Chiang Mai University, one form MTEC and four from Khon Kaen University. The expertise covers both engineering and science including civil engineering, physics, material science, and industrial chemistry.

The project studied the use of blended Portland pozzolana cements. Fly ash, bottom ash, calcined kaolin, rice husk ash, rice husk-bark ash, palm oil fuel ash, and bagasse ash were studied. The partial replacement of Portland cement with these pozzolans reduced calcium hydroxide in the mixture and resulted in the improvement of resistance to chloride penetration, resistance to sulfate attack, and resistance to corrosion of steel reinforcement. New binder 'high calcium fly ash geopolymer' was also developed with high compressive strength, low shrinkage, and good durability. The project also studied the incorporation of microsilica, nanosilica, zinc oxide, titanium oxide and composite oxides incorporated to the binder system. The results showed that the incorporation of these compounds improved the electrical and magnetic properties of the cement composites but with some effects on the mechanical properties of the binder.

The project output is significant and can be summarized as follows:

1. A total of 45 papers were published in the international peer-reviewed journal with impact factor of 0.362-3.398 (IF 2013).
2. The number of researchers in this project was twelve including the project leader. Three master degree and three Ph.D. students obtained their degrees with the help with this project funding. The cooperation among the researchers in Thailand was very good. In addition, the project also enabled the linkages with foreign experts. The collaborations were between our researchers and students with researchers overseas from CSIRO, Melbourne, School of Arts and Sciences (NSW), Mie University and Curtin University.
3. The seminars organized at the end of the year during the project implementation were very helpful in getting the researchers to consult and to have discussions with the other interested parties.

4. A book entitled ‘Cement and Geopolymer Composite Materials” was published as a result of the research of this project. It was distributed to all research and academic institutions in Thailand. It will serve as an important handbook on this subject.

It can be concluded that the results obtained from this research and the output can be used as important information for the utilization and development of the sustainable construction material industry in Thailand.

กิตติกรรมประกาศ

โครงการวิจัยเรื่อง “การพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์” สามารถดำเนินการจนสำเร็จได้ด้วยดีตามวัตถุประสงค์ที่ตั้งไว้ เนื่องจากได้รับความอนุเคราะห์และสนับสนุนจากบุคคลและหน่วยงานต่างๆ ซึ่งคณะผู้ทำวิจัย

ขอขอบคุณ บุคคลต่างๆ ที่มีส่วนเกี่ยวข้องกับงานวิจัยและข้อมูลผลงานวิจัย อันได้แก่ ผู้ช่วยวิจัย นักศึกษา เจ้าหน้าที่ของภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่นและสถาบันอื่นๆ ที่ผู้ร่วมวิจัยสังกัดอยู่

ขอขอบคุณศูนย์วิจัยและพัฒนาโครงสร้างมูลฐานอย่างยั่งยืน และภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น ซึ่งหัวหน้าโครงการสังกัดในการสนับสนุนการดำเนินงานตลอดจนเครื่องมือและอุปกรณ์ที่ใช้ในงานวิจัยตั้งแต่ต้นจนเสร็จสิ้นโครงการ

การดำเนินงานวิจัยในครั้งนี้จะไม่สามารถดำเนินการได้ หากขาดการสนับสนุนทุนวิจัยจากสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) ภายใต้โครงการเมธีวิจัยอาวุโส สกว. ประจำปี พ.ศ. 2554 (RTA5480004) ซึ่งคณะผู้วิจัยขอบคุณเป็นอย่างสูงมา ณ โอกาสนี้

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บทที่ 1
วัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์

1.1 บทนำ

ตามที่ทางสำนักงานกองทุนสนับสนุนการวิจัย (สกว.) ได้สนับสนุนให้นายปริญญา จินดาประเสริฐ เป็นหัวหน้าโครงการวิจัยผู้รับทุนวิจัย เรื่อง "การพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์" ตามสัญญาเลขที่ RTA5480004 โดยเริ่มโครงการตั้งแต่วันที่ 31 สิงหาคม 2554 เป็นต้นไปเป็นระยะเวลา 3 ปี คณะดำเนินการวิจัยขอเสนอรายงานวิจัยฉบับสมบูรณ์ ซึ่งเป็นผลการดำเนินงาน ตั้งแต่วันที่ 31 สิงหาคม 2554 ถึง 30 สิงหาคม 2557

1.2 ความสำคัญของโครงการ

วัสดุก่อสร้างที่ใช้มากสุดในงานก่อสร้าง คือ ผลิตภัณฑ์ซีเมนต์และคอนกรีต โดยใช้ปูนซีเมนต์ปอร์ตแลนด์เป็นวัสดุประสานหลัก การศึกษาและพัฒนาสมบัติของปูนซีเมนต์และคอนกรีตให้ดีขึ้นและเหมาะสมกับการใช้งานจึงมีความจำเป็นอย่างยิ่ง นอกจากนี้การลดการปล่อยก๊าซคาร์บอนไดออกไซด์จากอุตสาหกรรมนี้เป็นสิ่งจำเป็นสำหรับการใช้ผลิตภัณฑ์ซีเมนต์และคอนกรีตในอนาคต การใช้วัสดุปอซโซลานแทนที่ปูนซีเมนต์ปอร์ตแลนด์บางส่วนในการผลิตคอนกรีต และการใช้วัสดุประสานชนิดอื่นที่เป็นมิตรกับสิ่งแวดล้อมทดแทนการใช้ปูนซีเมนต์ จึงมีความสำคัญเป็นอย่างยิ่ง

วัสดุปอซโซลาน คือวัสดุที่มีซิลิกาหรืออะลูมินาเป็นองค์ประกอบหลัก และสามารถทำปฏิกิริยากับแคลเซียมไฮดรอกไซด์ ($Ca(OH)_2$) ที่ได้จากปฏิกิริยาไฮเดรชัน ทำให้ได้สารประกอบที่มีสมบัติในการยึดประสาน และได้ผลิตภัณฑ์ซีเมนต์และคอนกรีตที่มีสมบัติทางกลดีขึ้นได้ วัสดุปอซโซลานที่สำคัญได้แก่ เถ้าลอย (Fly ash) ซึ่งมีการนำมาใช้งานอุตสาหกรรมคอนกรีตอย่างแพร่หลาย นอกจากนี้ยังมี เถ้าก้นเตา ดินขาว เผา เถ้าแกลบ (หรือเถ้าแกลบ-เปลือกไม้) เถ้าปาล์มน้ำมันและเถ้าชานอ้อย วัสดุปอซโซลานเหล่านี้นับวันจะมีความสำคัญมากขึ้น

วัสดุประสานอื่นที่เริ่มมีการวิจัยกันมากขึ้น ได้แก่ จีโอโพลิเมอร์ เกิดจากปฏิกิริยาเคมีระหว่างสารที่มีซิลิกา (SiO_2) และอะลูมินา (Al_2O_3) กับสารละลายซึ่งอาจเป็นด่างความเข้มข้นสูงหรือเกลือ ที่นิยมใช้กันเป็นด่างความเข้มข้นสูงและสารซิลิเกต ปฏิกิริยาของจีโอโพลิเมอร์แตกต่างจากปฏิกิริยาไฮเดรชั่นของปูนซีเมนต์ แต่มีสมบัติเป็นวัสดุประสานที่ดี มีสมบัติทางกลและมีความทนทานต่อการกัดกร่อนของสารเคมีดีกว่าวัสดุประสานจากปูนซีเมนต์

นอกจากนี้การใช้วัสดุอนุภาคระดับไมโครและนาโนเมตรเป็นวัสดุผสมเพิ่ม เช่น ไมโครซิลิกา นาโนซิลิกา และเส้นใยนาโนคาร์บอน สามารถปรับปรุงหรือเปลี่ยนแปลงสมบัติของวัตถุเชื่อมประสานให้มีสมบัติดีขึ้น เช่นทำปฏิกิริยาเคมีได้เร็วขึ้น มีความแข็งแรงมากขึ้น ทำให้สมบัติทางไฟฟ้า สมบัติทางแม่เหล็ก และ

สมบัติอื่น เปลี่ยนไป โดยผลิตภัณฑ์ซีเมนต์และคอนกรีตในอนาคตต้องมีประสิทธิภาพสูง ฉลาด ใช้งานได้หลายรูปแบบ มีความสามารถตอบสนองเป็นพิเศษ หรือมีความสามารถพิเศษ

โครงการวิจัยนี้จึงมุ่งเน้นการศึกษาในการนำเถ้าถ่านหิน ดินขาวเผา และเถ้าชนิดอื่นมาเป็นวัสดุปอซโซลานสำหรับแทนที่ปูนซีเมนต์บางส่วนในงานคอนกรีต และใช้เป็นวัสดุหลักในการผลิตจีโอโพลิเมอร์ นอกจากนั้นยังใช้วัสดุผสมเพิ่มที่เป็นวัสดุไมโครและนาโน เพื่อให้สารซีเมนต์มีสมบัติทางกล ทางฟิสิกส์ และทางไฟฟ้าที่ต้องการ ทั้งนี้เพื่อจะให้ได้ผลิตภัณฑ์คอนกรีตที่มีความทนทาน ใช้งานได้หลากหลาย ผลที่ได้จะเป็นข้อมูลพื้นฐานที่สำคัญสำหรับนำวัสดุเหล่านี้ไปใช้ประโยชน์สำหรับอุตสาหกรรมก่อสร้างในอนาคต

1.3 วัตถุประสงค์ของโครงการ

1) ศึกษาและพัฒนาเถ้าลอย เถ้าก้นเตา ดินขาวเผา และ เถ้าจากโรงงานอุตสาหกรรมและเกษตรกรรมอื่นๆเพื่อใช้เป็นวัสดุปอซโซลาน
2) พัฒนาสารซีเมนต์ผสมสารปอซโซลานและจีโอโพลิเมอร์ที่มีสมบัติทางวิศวกรรมที่ดี
3) ศึกษาการใช้วัสดุไมโครและนาโนในการปรับปรุงสมบัติทางวิศวกรรม ทางฟิสิกส์ และทางไฟฟ้าของสารซีเมนต์และสารจีโอโพลิเมอร์ เพื่อให้ได้ผลิตภัณฑ์คอนกรีตฉลาดที่มีความทนทานและใช้งานได้หลากหลาย

1.4 ขอบเขตของโครงการ

วัสดุปอซโซลานที่ศึกษาได้แก่ เถ้าลอย เถ้าก้นเตา ดินขาวเผา เถ้าแกลบ เถ้าแกลบเปลือกไม้ เถ้าปาล์มน้ำมัน และเถ้าชานอ้อย ได้ศึกษาสารซีเมนต์ผสมสารปอซโซลานดังกล่าว ส่วนวัสดุประสานอื่นที่ได้ศึกษาวิจัยได้แก่ จีโอโพลิเมอร์ที่ทำจากเถ้าลอยแคลเซียมสูงและเถ้าหนักเป็นองค์ประกอบหลัก โดยมีเถ้าแกลบ ดินขาวเผา และไมโครซิลิกาเป็นสารผสมเพิ่ม และใช้สารละลายโซเดียมไฮดรอกไซด์และโซเดียมซิลิเกตเป็นตัวทำละลาย นอกจากนี้ได้ศึกษาการใช้วัสดุอนุภาคระดับไมโครและนาโนเมตร ได้แก่ ไมโครซิลิกา นาโนซิลิกา นาโนอะลูมินา ซิงค์ออกไซด์ และนาโนไทเทเนียมออกไซด์ เป็นวัสดุผสมเพิ่มเพื่อปรับปรุงหรือเปลี่ยนแปลงสมบัติของวัตถุเชื่อมประสานให้มีสมบัติดีขึ้น

1.5 เนื้อหาของรายงาน

รายงานฉบับนี้ประกอบด้วย 4 บท และภาคผนวก โดยบทที่ 1 กล่าวถึง สังเขปของโครงการวิจัยการพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์ ส่วนบทที่ 2 กล่าวถึงการดำเนินงานโครงการ บทที่ 3 เป็น OUPUT ที่ได้จากโครงการ แสดงผลงานที่ได้เปรียบเทียบกับผลที่คาดว่าจะได้เมื่อเริ่มต้นโครงการ โดยแสดงในรูปตารางและมีรายละเอียดด้านท้ายบท และนำเสนอในรูปแบบของการเผยแพร่ผลงานในรูปแบบบทความที่ได้จากโครงการ และบทที่ 4 เป็นบทสรุป

ภาคผนวกมี 4 ภาคผนวก ภาคผนวก ก. แสดงผลงานการตีพิมพ์ในวารสารวิชาการระดับนานาชาติ ส่วนภาคผนวก ข. แสดงรายการสร้างเครือข่ายเชื่อมโยงงานวิจัยกับต่างประเทศ ภาคผนวก ค. แสดงการจัด

ประชุมวิชาการ ภาคผนวก ง. แสดงรางวัลที่ได้รับและการเชิดชูเกียรติ และภาคผนวก จ. แสดงสำเนาบทความฉบับเต็ม

บทที่ 2
การดำเนินงานโครงการ

2.1 การพัฒนาเครื่องมือสำหรับงานวิจัยที่ยั่งยืน

ได้พัฒนาเครื่องมือสำหรับงานวิจัยด้านนี้ เช่น เครื่องมือวัดการซึมผ่านได้ของน้ำของคอนกรีตพรุน เครื่องมือวัดการขัดสีที่ผิวของวัสดุซีเมนต์, เครื่องอัดขึ้นรูปชิ้นงานขนาดเล็กสำหรับการศึกษาด้านไฟฟ้าและฟิสิกส์ของวัสดุเชื่อมประสานผสมวัสดุนาโน, เครื่องมือทดสอบการนำความร้อน และเครื่องทดสอบการส่งผ่านเสียง การพัฒนาเครื่องมือเหล่านี้นับเป็นส่วนสำคัญของการวิจัย เนื่องจากงานวิจัยมีห้องปฏิบัติการวิจัยที่ร่วมวิจัยอยู่หลายที่ ดังนั้นการพัฒนาเครื่องมือในการวิจัยที่มีราคาไม่แพง แต่มีความแม่นยำและสามารถทำงานวิจัยได้ จะช่วยทำให้ห้องปฏิบัติการต่างๆ สามารถรองรับการวิจัยได้หลากหลายและมากขึ้น และเป็นการเตรียมความพร้อมเพื่อที่จะให้ห้องปฏิบัติการนั้นสามารถปรับตัว ทำงานได้ดีและอยู่ได้อย่างยั่งยืน

นอกจากนี้ยังได้เตรียมความพร้อมในการใช้เครื่องมือที่มีขีดความสามารถสูงเพื่อศึกษาในระดับไมโคร และนาโนเนื่องจากทางมหาวิทยาลัยขอนแก่นได้ลงทุนพัฒนา Beam line ของเครื่อง Synchrotron ซึ่งจะเพิ่มขีดความสามารถในการวิจัยในระดับลึกต่อไป

2.2 การทดสอบสมบัติทางกายภาพและสมบัติทางเคมีของวัสดุ

ได้ทำการทดสอบสมบัติด้านต่าง ๆ ของวัสดุซีเมนต์ที่ใช้ในโครงการนี้ คือ ปูนซีเมนต์ วัสดุปอซโซลาน และวัสดุไมโครและนาโน วัสดุปอซโซลาน ได้แก่ เถ้าลอย เถ้าก้นเตา ซิลิกาฟูม ดินขาวเผา เถ้าแกลบ เถ้าแกลบ-เปลือกไม้ เถ้าปาล์มน้ำมัน และเถ้าชานอ้อย วัสดุไมโครและนาโน ได้แก่ ไมโครซิลิกา นาโนซิลิกา นาโนอะลูมินา ซิงค์ออกไซด์ นาโนไทเทเนียมออกไซด์ และได้ทำการทดสอบสมบัติของมวลรวม วัสดุก่อสร้างที่ใช้งานแล้วนำกลับมาใช้ใหม่ (Recycling) และ เศษแก้วทั้งนี้เพื่อให้ได้ข้อมูลพื้นฐานที่พอเพียงสำหรับการวิจัย มีความจำเป็นที่จะต้องทดสอบสมบัติด้านต่าง ๆ ของวัสดุอย่างต่อเนื่อง เนื่องจากความแปรเปลี่ยนของวัสดุ นอกจากนี้ยังได้ศึกษาเบื้องต้นการทำวัสดุกราไฟต์ (Graphite) ที่สังเคราะห์ขึ้นเองจากเศษวัสดุทางการเกษตร คาดว่าจะสามารถนำมาใช้ในการปรับปรุงคุณสมบัติของสารซีเมนต์ในอนาคต

2.3 การทดสอบสมบัติของวัสดุผสมปูนซีเมนต์

ได้วิจัยปูนซีเมนต์ผสมสารปอซโซลานและคอนกรีต ใช้เถ้าถ่านหินและสารปอซโซลานประเภทอื่นโดยเฉพาะสิ่งที่ยังไม่ได้นำมาใช้ประโยชน์ เช่น เถ้าแกลบ เถ้าหนัก เถ้าชีวมวลอื่น โดยนำมาทดแทนปูนซีเมนต์บางส่วน ได้ทดสอบสมบัติด้านต่างๆ เช่น การก่อตัว กำลังรับแรง ความทนทานในรูปของ ความทนทานต่อสารซัลเฟต ความทนทานต่อการกัดกร่อนของกรด ความทนทานต่อการทำลายโดยคาร์บอเนชัน ทดลองการใช้สารปอซโซลานสองชนิดร่วมกัน ทดสอบอิทธิพลของความละเอียดของสารปอซโซลาน ได้ทดลองทำ

คอนกรีตที่ทำจากสารปอซโซลานและวัสดุนำกลับมาใช้ (Recycled materials) ได้ทดลองคอนกรีตพรุนที่มีส่วนผสมของสารปอซโซลาน ได้ทดลองคอนกรีตเบาที่ผสมสารปอซโซลาน

2.4 การทดสอบสมบัติของจีโอโพลิเมอร์

ได้ศึกษาและพัฒนาวัสดุซีเมนต์ชนิดใหม่คือจีโอโพลิเมอร์ โดยใช้วัตถุดิบที่มีในประเทศ ได้แก่ เถ้าลอยแคลเซียมสูง ในการผสมใช้โซเดียมไฮดรอกไซด์ความเข้มข้นสูงและสารโซเดียมซิลิเกตเป็นของเหลว ได้ทดสอบสมบัติทางกล กำลังรับแรง การหดตัว ความคงทนต่อการทำลายของสารซัลเฟตและกรด ได้ทดลองใช้เถ้าแกลบ และซิลิกาฟูมในการปรับปรุงสมบัติของจีโอโพลิเมอร์ ศึกษาสมบัติของการยึดเกาะระหว่างเหล็กเสริมและจีโอโพลิเมอร์คอนกรีต ศึกษาปัจจัยต่างๆที่มีผลต่อการเตรียมจีโอโพลิเมอร์คอนกรีตพรุน ศึกษาจีโอโพลิเมอร์ทำจากวัสดุนำกลับมาใช้ Recycled materials มีการพัฒนานำเถ้าเหลือทิ้งจากอุตสาหกรรมต่างๆ มาใช้เป็นวัสดุตั้งต้นในการเตรียมวัสดุจีโอโพลิเมอร์ มีการเติมสารผสมเพิ่ม เช่น ยิปซัม เพื่อปรับปรุงสมบัติของวัสดุจีโอโพลิเมอร์

2.5 การทดสอบสมบัติทางไฟฟ้าและฟิสิกส์

ได้ศึกษาสมบัติทางไฟฟ้าและฟิสิกส์ของวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์ ได้ศึกษาผลของอนุภาคระดับนาโน เช่น นาโนซิลิกา และนาโนอะลูมินาที่มีต่อสมบัติทางกายภาพ ได้ศึกษาสมบัติของวัสดุผสมนาโนและปูนซีเมนต์ปอร์ตแลนด์ (Portland cement nano-material composites) และศึกษาเรื่องคอนกรีตที่ไม่ต้องทำความสะอาด เนื่องจากมีความสามารถในการทำความสะอาดให้ตัวเอง (Self cleaning) โดยใช้ไทเทเนียมออกไซด์ ได้ใช้วัสดุซิงค์ออกไซด์และสารประกอบออกไซด์อื่นผสมเข้ากับสารเชื่อมประสาน

บทที่ 3
OUTPUT ที่ได้จากโครงการ

3.1 ผลงานวิจัยโดยรวม

ได้ทดสอบสมบัติของวัสดุผสมปูนซีเมนต์ การใช้ปูนซีเมนต์ผสมสารปอซโซลานสามารถลดการใช้ปูนซีเมนต์ปอร์ตแลนด์ลงได้ วัสดุปอซโซลานเป็นวัสดุที่มีซิลิกาและอะลูมินาเป็นองค์ประกอบหลัก งานวิจัยนี้ได้ศึกษาการลดปริมาณปูนซีเมนต์ปอร์ตแลนด์และแทนที่ด้วยสารปอซโซลาน จากการวิจัยพบว่าสมบัติของซีเมนต์และคอนกรีตมีความสัมพันธ์โดยตรงกับการเปลี่ยนแปลงโครงสร้างโพรงในซีเมนต์เพสต์ การแทนที่ปูนซีเมนต์ปอร์ตแลนด์ด้วยสารปอซโซลาน ทำให้ปริมาณแคลเซียมไฮดรอกไซด์ลดลง การใช้วัสดุปอซโซลานแทนที่ในปูนซีเมนต์บางส่วนที่เหมาะสมทำให้คอนกรีตมีกำลังดีขึ้น ลดการซึมผ่าน ลดปริมาตรและขนาดของโพรงในซีเมนต์เพสต์ ทำให้ความทนทานดีขึ้น การผสมวัสดุปอซโซลานละเอียดที่ได้จากการแยกขนาดทำให้ซีเมนต์เพสต์มีความสม่ำเสมอและแน่นขึ้น เนื่องมาจากอนุภาคของวัสดุปอซโซลานที่มีขนาดเล็กเมื่อกระจายตัวในเพสต์ ทำหน้าที่เป็นศูนย์กลาง (Nucleation) กระตุ้นให้เกิดปฏิกิริยามากขึ้น นอกจากนี้ยังช่วยอุดช่องว่าง (Filling) ภายในเพสต์ทำให้เกิดปฏิกิริยาปอซโซลาน (Pozzolanic reaction) ได้ดีกว่าวัสดุปอซโซลานที่ไม่ได้แยกขนาด การใช้วัสดุปอซโซลานสองชนิดให้คอนกรีตที่มีค่ากำลังอัดที่สูงและมีการต้านทานคลอไรด์ดี เมื่อเทียบกับการใช้วัสดุปอซโซลานชนิดเดียว เนื่องมาจากการประสานจุดเด่น (Synergy) ของวัสดุปอซโซลานทั้งสองชนิด

ได้ศึกษาและพัฒนาวัสดุซีเมนต์ชนิดใหม่คือจีโอโพลิเมอร์ โดยใช้วัตถุดิบที่มีในประเทศ ได้แก่ เถ้าลอยแคลเซียมสูง ในการผสมใช้โซเดียมไฮดรอกไซด์ความเข้มข้นสูงและสารโซเดียมซิลิเกตเป็นของเหลว ซึ่งพบว่าจีโอโพลิเมอร์เถ้าลอยแคลเซียมสูงมีสมบัติทางกลที่ดี ให้กำลังรับแรงสูง การหดตัวต่ำ มีความคงทนต่อการทำลายของสารซัลเฟตและกรด ได้ทดลองใช้เถ้าแกลบและซิลิกาฟูมในการปรับปรุงสมบัติของจีโอโพลิเมอร์ ศึกษาสมบัติของการยึดเกาะระหว่างเหล็กเสริมและจีโอโพลิเมอร์คอนกรีต ศึกษาปัจจัยต่างๆที่มีผลต่อการเตรียมจีโอโพลิเมอร์คอนกรีตพรุน ศึกษาจีโอโพลิเมอร์ทำจากวัสดุนำกลับมาใช้ Recycled materials มีการพัฒนานำเถ้าเหลือทิ้งจากอุตสาหกรรมต่างๆ มาใช้เป็นวัสดุตั้งต้นในการเตรียมวัสดุจีโอโพลิเมอร์ มีการเติมสารผสมเพิ่ม เช่น ยิปซัม เพื่อปรับปรุงสมบัติของวัสดุจีโอโพลิเมอร์ ทำให้ขณะนี้งานวิจัยด้านจีโอโพลิเมอร์ของกลุ่มนักวิจัยไทยมีการเผยแพร่ออกมาเป็นจำนวนมากอย่างต่อเนื่อง โดยถูกจัดให้อยู่ในระดับชั้นนำและเป็นที่ยอมรับในระดับนานาชาติ

ได้วิจัยวัสดุซีเมนต์และจีโอโพลิเมอร์ให้มีประสิทธิภาพที่ดียิ่งขึ้น โดยศึกษาการใช้วัสดุที่มีอนุภาคขนาดเล็กระดับนาโนเมตร (วัสดุนาโน) มาเป็นวัสดุผสมเพิ่ม เช่น นาโนซิลิกา นาโนอะลูมินา และนาโนออกไซด์ วัสดุนาโนเหล่านี้สามารถปรับปรุงหรือเปลี่ยนแปลงสมบัติของวัสดุเชื่อมประสานให้มีสมบัติดีขึ้น เช่น ทำปฏิกิริยาเคมีได้เร็ว มีความแข็งแรง ทำให้สมบัติทางไฟฟ้า ทางแม่เหล็ก และทางแสงของวัสดุเชื่อม

ประสานเปลี่ยนจากเดิมและ สามารถประยุกต์ใช้งานได้หลากหลาย ผลที่ได้จะใช้เป็นข้อมูลพื้นฐานที่สำคัญสำหรับนำวัสดุเหล่าไปใช้ในอุตสาหกรรมก่อสร้างในอนาคต

นอกจากนี้โครงการยังได้สร้างนักวิจัยรุ่นใหม่และพัฒนาศักยภาพของนักวิจัย และห้องปฏิบัติการเพื่อให้มีผลงานที่เป็นประโยชน์และมีขีดความสามารถทางการวิจัยที่ทัดเทียมกับต่างประเทศ ได้ช่วยวางรากฐานการวิจัยด้านซีเมนต์และจีโอโพลิเมอร์ของไทยให้อยู่ในระดับนานาชาติ พื้นฐานการวิจัยด้านนี้เป็นเรื่องสำคัญสำหรับการพัฒนาวัสดุเชื่อมประสานและวัสดุก่อสร้างของไทย

3.2 ผลงาน

ผลที่ได้จากการดำเนินงานของโครงการวิจัยในช่วงของโครงการ พ.ศ. 2555 ถึง พ.ศ. 2557 เปรียบเทียบกับความคาดหมายที่วางไว้ในข้อเสนอโครงการในช่วงต้น มีรายละเอียดดังนี้

3.2.1 ผลงานที่ได้เปรียบเทียบกับแผน

ผลที่ได้จากโครงการเมื่อเปรียบเทียบกับความคาดหมายที่วางไว้ในข้อเสนอโครงการในช่วงต้น แสดงดังตารางที่ 4.1 ซึ่งพบว่า ผลงานที่ได้สูงกว่าแผนประกอบด้วย จำนวนนักศึกษาจบปริญญาเอก, และจำนวนผลงานตีพิมพ์วารสารวิชาการระดับนานาชาติ ผลงานที่เป็นไปตามแผนประกอบไปด้วย จำนวนนักวิจัยที่สร้างจากโครงการทั้งสถาบันเดียวกันและจากต่างสถาบัน, จำนวนนักศึกษาจบปริญญาโท, จำนวนหนังสือที่มีการพิมพ์เผยแพร่ และการจัดงานประชุมสัมมนาวิชาการเพื่อเผยแพร่ผลงานวิจัย ส่วนงานอื่นๆ ที่ไม่ได้กำหนดจำนวนแต่ได้ผลงานที่โดดเด่นคือ คือ การสร้างเครือข่ายงานวิจัย และผู้ร่วมวิจัยได้ตำแหน่งทางวิชาการเพิ่ม

3.2.2 บทความในวารสารวิชาการระดับนานาชาติ

จากการดำเนินงานโครงการวิจัยตามที่ได้แสดงไว้ในบทที่ 2 เมื่อได้ข้อมูลการวิจัยที่สำคัญและเป็นประโยชน์ จึงได้เขียนบทความที่จะลงตีพิมพ์ในวารสารวิชาการระดับนานาชาติ ทั้งนี้เพื่อเป็นการยืนยันในความสำคัญของงานที่ได้ช่วยกันวิจัยออกมา รายละเอียดตามภาคผนวก ก. โดยผลงานวิจัยที่ได้รับการตีพิมพ์ในวารสารวิชาการระดับนานาชาติที่มี Impact Factor มีจำนวนทั้งหมด 45 บทความ โดยแบ่งเป็นบทความที่ได้รับการตีพิมพ์แล้ว 43 บทความ บทความที่รอเลขหน้า (in press) 1 บทความ และบทความที่ได้รับการพิสูจน์อักษร (galley proof) 1 บทความ โดยมีค่า Impact Factor (2013) ในช่วง 0.362-3.398 สามารถจัดหมวดหมู่เป็น ทางด้านวัสดุผสมปูนซีเมนต์ 14 บทความ ทางด้านจีโอโพลิเมอร์ 20 บทความ และ ทางด้านสมบัติไฟฟ้าและฟิสิกส์ 11 บทความ

ตารางที่ 4.1 เปรียบเทียบผลงานกับความคาดหมายที่ได้วางแผนไว้

ลักษณะของผลงาน	แผน	ผลที่ได้	ผลประเมิน
1. จำนวนนักวิจัยที่สร้างจากโครงการ (คน)			
1.1 สถาบันเดียวกัน	4	4	ตรงตามแผน
1.2 ต่างสถาบัน	7	7	ตรงตามแผน
1.3 นักศึกษาจบปริญญาเอก	2	3	สูงกว่าแผน
1.4 นักศึกษาจบปริญญาโท	3	3	ตรงตามแผน
2. จำนวนผลงานตีพิมพ์วารสารวิชาการระดับนานาชาติ (บทความ)	16	45	สูงกว่าแผน
3. จำนวนหนังสือ (เล่ม)	1	1	ตรงตามแผน
4. อื่นๆ			
4.1 สร้างเครือข่ายงานวิจัย (สถาบัน)	ไม่ระบุ	6	ตรงตามแผน
4.2 การจัดประชุมวิชาการ (ครั้ง)	3	3	ตรงตามแผน
4.3 ผู้ร่วมวิจัยได้ตำแหน่งวิชาการเพิ่ม (คน)	ไม่ระบุ	5	ตรงตามแผน
ผลประเมินในภาพรวม	**สูงกว่าแผน**		

3.2.2.1 บทความด้านวัสดุผสมปูนซีเมนต์

ได้ตีพิมพ์บทความด้านวัสดุผสมปูนซีเมนต์ จำนวน 14 บทความ ดังนี้

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3.2.2.2 บทความด้านจีโอโพลิเมอร์

ได้ตีพิมพ์บทความด้านจีโอโพลิเมอร์ จำนวน 20 บทความ ดังนี้

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3.2.2.3 บทความด้านสมบัติไฟฟ้าและฟิสิกส์

ได้ตีพิมพ์บทความด้านสมบัติไฟฟ้าและฟิสิกส์จำนวน 11 บทความ ดังนี้

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5. Chaipanich A., Rianyoi R., Potong R., Jaitanong N., Chindaprasirt P., Compressive strength and microstructure of 0-3 lead zirconate titanate ceramic-portland cement composites, Ferroelectrics 457, 2013, pp. 53-61 (IF 0.415)
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8. Hanjitsuwan S., Hunpratub S., Thongbai P., Maensiri S., Sata V., Chindaprasirt P., Effects of NaOH concentrations on physical and electrical properties of high calcium fly ash geopolymer paste, Cement and Concrete Composites 45, 2014, pp. 9-14 (IF 2.523)
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3.2.3 จำนวนนักวิจัยที่สร้างจากโครงการ

3.2.3.1 นักวิจัยสถาบันเดียวกัน

นอกจากหัวหน้าโครงการแล้วยังมีผู้ร่วมวิจัยในสถาบันเดียวกันไม่รวมหัวหน้าโครงการ รวม 4 ท่าน ดังนี้

1. รศ. ดร.วิทยา อมรกิจบำรุง มหาวิทยาลัยขอนแก่น
2. ผศ.ดร.วันชัย สะตะ มหาวิทยาลัยขอนแก่น
3. ผศ.ดร.สุปรีดิ์ พินิจสุนทร มหาวิทยาลัยขอนแก่น
4. ดร.ประสิทธิ์ ทองใบ มหาวิทยาลัยขอนแก่น

3.2.3.2 นักวิจัยต่างสถาบัน

ผู้ร่วมวิจัยต่างสถาบัน รวม 7 ท่าน ดังนี้

1. ศ.ดร.สันติ แม้นศิริ มหาวิทยาลัยเทคโนโลยีสุรนารี
2. ผศ.ดร.อุบลลักษณ์ รัตนศักดิ์ มหาวิทยาลัยบูรพา
3. ผศ.ดร.ธีรวัฒน์ สินศิริ มหาวิทยาลัยเทคโนโลยีสุรนารี
4. ผศ.ดร.เกศรินทร์ พิมรักษา มหาวิทยาลัยเชียงใหม่
5. ผศ.ดร.สำเริง รักซ้อน มหาวิทยาลัยเทคโนโลยีราชมงคลพระนคร
6. ผศ.ดร.อานนท์ ชัยพานิช มหาวิทยาลัยเชียงใหม่
7. ดร.ธีรพนธ์ แย้มวงษ์ National Metal and Materials Technology Center (MTEC)

3.2.3.3 นักศึกษาปริญญาเอกที่จบการศึกษา

1. ดร.ชัยชาญ โชติถนอม ปัจจุบันเป็นอาจารย์ประจำคณะวิศวกรรมศาสตร์ มหาวิทยาลัยมหาสารคาม
2. ดร.ยุวดี แซ่ตั้ง ปัจจุบันเป็นอาจารย์ประจำคณะวิทยาศาสตร์และวิศวกรรมศาสตร์ มหาวิทยาลัยเกษตรศาสตร์ วิทยาเขตเฉลิมพระเกียรติ จังหวัดสกลนคร
3. ดร.กรกนก บุญเสริม ปัจจุบันเป็นอาจารย์ประจำคณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยราชภัฏมหาสารคาม

3.2.3.4 นักศึกษาปริญญาโทที่จบการศึกษา

1. นายธวัชชัย โทอินทร์
2. นายแสงสุรีย์ พังแดง
3. นายอำพล วงศ์ษา

3.2.4 หนังสือ

เพื่อเป็นการเผยแพร่ผลงานวิจัยในโครงการนี้ ศ.ดร.ปริญญา จินดาประเสริฐ และผศ.ดร.วันชัย สะตะ จึงได้รวบรวมและเรียบเรียงข้อมูลการผลงานวิจัยที่เกียวข้องกับการพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์จัดทำเป็นหนังสือ “วัสดุผสมซีเมนต์และจีโอโพลิเมอร์” ขึ้น โดยได้ส่งมาพร้อมกับรายงานฉบับสมบูรณ์

3.2.5 ผลงานอื่น

3.2.5.1 การสร้างเครือข่ายงานวิจัยด้านคอนกรีตและจีโอโพลิเมอร์

ตลอดระยะของการดำเนินโครงการวิจัย นอกจากมีการสร้างเครือข่ายการวิจัยภายในประเทศโดยการมีผู้ร่วมงานวิจัยจากหลายๆสถาบันแล้ว ยังมีการสร้างเครือข่ายด้านคอนกรีตและจีโอโพลิเมอร์ในต่างประเทศโดยเชิญนักวิจัยต่างชาติมาบรรยายพิเศษในงานจัดประชุมวิชาการประจำปี ดังนี้ (รายละเอียดเพิ่มเติมตามภาคผนวก ข. และภาคผนวก ค.)

1) ปี 2555

1. Dr. K. Sagoe-Crentsil

   CSIRO Materials Science and Engineering, Melbourne, Australia

2. Dr. Pre De Silva

   School of Art and Sciences (NSW/ACT), Australian Catholic University, North Sydney, NSW, Australia

2) ปี 2556

1. Prof. J.B. Aguiar

   Department of Civil Engineering, University of Minho, Guimarães, Portugal

2. Prof. S. Hatanaka

   Division of Architecture, Graduate School of Engineering, Mie University, Japan

3) ปี 2557

1. Prof. Dr. V. Vimonsatit

   Department of Civil Engineering, Curtin Univeristy, Western Australis

2. Prof. J. Sanjayan

   Director, Centre for Sustainable Infrastructure, Faculty of Science, Engineering & Technology, Swinburne University of Technology, Melbourne, Australia

3.2.5.2 การจัดประชุมวิชาการ

การจัดการประชุมสัมมนาวิชาการเพื่อเผแพร่ผลงานวิจัยที่เกี่ยวข้องกับการพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์ ได้มีการจัดขึ้นทุกปี รวม 3 ครั้งดังนี้ (รายละเอียดเพิ่มเติมตามภาคผนวก ค.)

ครั้งที่ 1 จัดวันศุกร์ที่ 20 กรกฎาคม 2555 เวลา 8.30-16.30 น. ณ ห้องสัมมนา 2 ชั้น 9 ตึกเพียรวิจิตร คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น มีผู้เข้าร่วมประชุม จำนวน 100 ท่าน ประกอบด้วย_คณาจารย์และผู้ช่วยวิจัยภายใต้ทุนเมธีวิจัย 12 ท่าน, อาจารย์จากมหาวิทยาลัยต่างๆ 21 ท่าน, นักวิจัย ผู้ประกอบการและผู้สนใจจากภาคอุตสาหกรรม 24 ท่าน, นักศึกษามหาวิทยาลัยต่างๆ 17 ท่าน, อาจารย์และนักศึกษามหาวิทยาลัยขอนแก่น 26 ท่าน

ครั้งที่ 2 จัดวันศุกร์ที่ 2 สิงหาคม 2556 เวลา 8.30-16.30 น. ณ ห้องสัมมนา 2 ชั้น 9 ตึกเพียรวิจิตร คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น มีผู้เข้าร่วมประชุม จำนวน 98 ท่าน ประกอบด้วย คณาจารย์และผู้ช่วยวิจัยภายใต้ทุนเมธีวิจัย 10 ท่าน, อาจารย์จากมหาวิทยาลัยต่างๆ 22 ท่าน, นักวิจัย ผู้ประกอบการและผู้สนใจจากภาคอุตสาหกรรม 11 ท่าน, นักศึกษามหาวิทยาลัยต่างๆ 24 ท่าน, อาจารย์และนักศึกษามหาวิทยาลัยขอนแก่น 31 ท่าน

ครั้งที่ 3 จัดวันจันทร์ที่ 25 สิงหาคม 2557 เวลา 8.30-16.30 น. ณ ห้องสัมมนา 2 ชั้น 9 ตึกเพียรวิจิตร คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น มีผู้เข้าร่วมประชุม จำนวน 127 ท่าน ประกอบด้วย คณาจารย์และผู้ช่วยวิจัยภายใต้ทุนเมธีวิจัย 10 ท่าน, อาจารย์จากมหาวิทยาลัยต่างๆ 21 ท่าน, นักวิจัย ผู้ประกอบการและผู้สนใจจากภาคอุตสาหกรรม 20 ท่าน, นักศึกษามหาวิทยาลัยต่างๆ 29 ท่าน, อาจารย์และนักศึกษามหาวิทยาลัยขอนแก่น 47 ท่าน

3.2.5.3ผู้ร่วมวิจัยได้ตำแหน่งวิชาการเพิ่มในระหว่างดำเนินโครงการ

ผู้ร่วมวิจัยได้ตำแหน่งวิชาการเพิ่มในระหว่างดำเนินโครงการ ประกอบด้วย

1. ผู้ร่วมวิจัยที่ได้ตำแหน่งศาสตราจารย์ คือ ศ.ดร.สันติ แม้นศิริ
2. ผู้ร่วมวิจัยที่ได้ตำแหน่งผู้ช่วยศาสตราจารย์ คือ ผศ.ดร.สำเริง รักซ้อน และผศ.ดร.สุปรีดิ์ พินิจสุนทร
3. ผู้ร่วมวิจัยที่ได้ขอกำหนดตำวิชาการเพิ่ม คือ ผศ.ดร.อุบลลักษณ์ รัตนศักดิ์ (ขอตำแหน่งรองศาสตราจารย์) และผศ.ดร.วันชัย สะตะ (ขอตำแหน่งรองศาสตราจารย์)

บทที่ 4
สรุปผลการศึกษาวิจัย

จากการศึกษาวิจัยโครงการ “การพัฒนาวัสดุผสมปูนซีเมนต์และจีโอโพลิเมอร์” สามารถสรุปได้ว่า สารปอซโซลานที่ศึกษาได้แก่ เถ้าลอย เถ้าก้นเตา ซิลิกาฟูม ดินขาวเผา เถ้าแกลบ เถ้าแกลบ-เปลือกไม้ เถ้าปาล์มน้ำมัน และเถ้าชานอ้อย เป็นวัสดุที่ประกอบด้วย ซิลิกาและ/หรืออะลูมินาเป็นองค์ประกอบหลัก สามารถใช้แทนที่ปูนซีเมนต์ปอร์ตแลนด์ได้ การแทนที่ปูนซีเมนต์ปอร์ตแลนด์ด้วยสารปอซโซลาน ทำให้ปริมาณแคลเซียมไฮดรอกไซด์ในระบบลดลง การใช้วัสดุปอซโซลานในปริมาณที่เหมาะสม ทำให้คอนกรีตมีสมบัติทางกลที่ดี กำลังรับแรงดี การซึมผ่านลดลง ความทนทานดีขึ้น วัสดุปอซโซลานละเอียดสามารถทำปฏิกิริยาได้ดีขึ้น และให้เพสต์และคอนกรีตที่มีสมบัติดี อนุภาคเล็กของวัสดุปอซโซลานทำหน้าที่เป็น Nucleation site สำหรับการเกิดปฏิกิริยาและเป็นตัวที่อุดช่องว่าง (Filler) การใช้วัสดุปอซโซลานสองชนิดให้คอนกรีตที่มีค่ากำลังอัดที่สูงและมีการต้านทานคลอไรด์ดีขึ้น เนื่องมาจากการประสานจุดเด่น (Synergy) ของวัสดุปอซโซลานสองชนิด

วัสดุซีเมนต์ชนิดใหม่คือจีโอโพลิเมอร์สามารทำจากเถ้าลอยแคลเซียมสูง โดยใช้โซเดียมไฮดรอกไซด์ความเข้มข้นสูงและสารโซเดียมซิลิเกตเป็นของเหลว จีโอโพลิเมอร์เถ้าลอยแคลเซียมสูงมีสมบัติทางกลที่ดี ให้กำลังรับแรงสูง การหดตัวต่ำ มีความคงทนต่อการทำลายของสารซัลเฟตและกรด สามารถใช้เถ้าแกลบและซิลิกาฟูมในการปรับปรุงสมบัติของจีโอโพลิเมอร์ การวิจัยยังแสดงให้เห็นว่าการยึดเกาะระหว่างเหล็กเสริมและจีโอโพลิเมอร์คอนกรีต ศึกษาการเตรียมจีโอโพลิเมอร์คอนกรีตพรุน จีโอโพลิเมอร์ทำจากวัสดุนำกลับมาใช้ และนำเถ้าเหลือทิ้งจากอุตสาหกรรมต่างๆ มาใช้เป็นวัสดุตั้งต้นในการเตรียมจีโอโพลิเมอร์ มีการเติมสารผสมเพิ่มเช่น ยิปซัม เพื่อปรับปรุงสมบัติของวัสดุจีโอโพลิเมอร์ ผลการทดลองแสดงให้เห็นว่าโอโพลิเมอร์เถ้าลอยแคลเซียมสูงมีสมบัติที่ดี สามารถพัฒนาเป็นวัสดุเชื่อมประสานได้

ได้วิจัยวัสดุซีเมนต์และจีโอโพลิเมอร์ให้มีประสิทธิภาพที่ดี โดยใช้วัสดุนาโน เช่น นาโนซิลิกา นาโนอะลูมินา และนาโนออกไซด์อื่นมาเป็นวัสดุผสมเพิ่ม วัสดุนาโนเหล่านี้สามารถปรับปรุงสมบัติของวัสดุเชื่อมประสาน ทำให้สมบัติทางไฟฟ้าและทางฟิสิกส์เปลี่ยนไป

นอกจากนี้โครงการยังได้สร้างนักวิจัยรุ่นใหม่และพัฒนาศักยภาพของนักวิจัย ให้มีผลงานที่ทัดเทียมกับต่างประเทศ โครงการนี้ได้ช่วยวางรากฐานการวิจัยด้านซีเมนต์และจีโอโพลิเมอร์ของไทยให้อยู่ในระดับนานาชาติ

ภาคผนวก ก.
การตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

ภาคผนวก ก. การตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

ผลงานวิจัยที่ได้รับการตีพิมพ์ในวารสารวิชาการระดับนานาชาติที่มี Impact Factor มีจำนวนทั้งหมด 45 บทความ รายชื่อพร้อมรายละเอียด Impact Factor และสำเนาบทความฉบับเต็ม ดังนี้

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ภาคผนวก ข.
การสร้างเครือข่ายงานวิจัยกับต่างประเทศ

ภาคผนวก ข. การสร้างเครือข่ายงานวิจัยกับต่างประเทศ

ในช่วงของโครงการ หัวหน้าโครงการได้ต้อนรับนักวิจัยต่างประเทศดังนี้

1) ปี 2555

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ภาคผนวก ค.
การจัดประชุมวิชาการ

ภาคผนวก ค. การจัดประชุมวิชาการ

ในช่วงของโครงการ มีการจัดการประชุมวิชาการเพื่อเผยแพร่ผลงานวิจัย จำนวน 3 ครั้ง ดังนี้

ค.1 การประชุมวิชาการครั้งที่ 1

ผู้เข้าร่วมประชุม จำนวน 100 ท่าน ประกอบด้วย

1. คณาจารย์และผู้ช่วยวิจัยภายใต้ทุนเมธีวิจัย 12 ท่าน
2. อาจารย์จากมหาวิทยาลัยต่างๆ 21 ท่าน
3. นักวิจัย ผู้ประกอบการและผู้สนใจจากภาคอุตสาหกรรม 24 ท่าน
4. นักศึกษามหาวิทยาลัยต่างๆ 17 ท่าน
5. อาจารย์และนักศึกษามหาวิทยาลัยขอนแก่น 26 ท่าน

เวลาและสถานที่ในการจัดประชุม

วันศุกร์ที่ 20 กรกฎาคม 2555 เวลา 8.30-16.30 น. ณ ห้องสัมมนา 2 ชั้น 9 ตึกเพียรวิจิตร คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น

วิทยากร

1. ศ.ดร.ปริญญา จินดาประเสริฐ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น
   หัวข้อ “Blended Portland cement and high calcium fly ash composites”
2. ผศ.ดร.เกศรินทร์ พิมรักษา ภาควิชาเคมีอุตสาหกรรม คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่
   หัวข้อ “Synthesis of low temperature cements; belite and ye’elimite cements”
3. ผศ.ดร.ธีรวัฒน์ สินสิริ สาขาวิศวกรรมโยธา สำนักวิชาวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีสุรนารี หัวข้อ “Microstructure of bended cement paste”
4. ผศ.ดร.อานนท์ ชัยพานิช ภาควิชาฟิสิกส์และวัสดุศาสตร์ คณะวิทยาศาสตร์ มหาวิทยาลัยเชียงใหม่
   หัวข้อ “Development of Piezoelectric-cement Composites”
5. ผศ.ดร.อุบลลักษณ์ รัตนศักดิ์ ภาควิชาเคมี คณะวิทยาศาสตร์ มหาวิทยาลัยบูรพา
   หัวข้อ “Geopolymer : An alternative green cementitious material”

ผลที่ได้จากการจัดประชุม

การจัดประชุมครั้งนี้ได้รับการตอบรับที่ดี มีผู้สนใจเข้าร่วมประชุมจากหน่วยงานรัฐและเอกชนจำนวนมาก นอกจากนี้ยังเป็นการสร้างเครือข่าย ต่อยอดงานวิจัย และสร้างโอกาสให้กับผู้เข้าร่วมประชุมเป็นอย่างดี

ภาพบรรยากาศภายในงานประชุมวิชาการครั้งที่ 1








ค.2 การประชุมวิชาการครั้งที่ 2

ผู้เข้าร่วมประชุม จำนวน 98 ท่าน ประกอบด้วย

1. คณาจารย์และผู้ช่วยวิจัยภายใต้ทุนเมธีวิจัย 10 ท่าน
2. อาจารย์จากมหาวิทยาลัยต่างๆ 22 ท่าน
3. นักวิจัย ผู้ประกอบการและผู้สนใจจากภาคอุตสาหกรรม 11 ท่าน
4. นักศึกษามหาวิทยาลัยต่างๆ 24 ท่าน
5. อาจารย์และนักศึกษามหาวิทยาลัยขอนแก่น 31 ท่าน

เวลาและสถานที่ในการจัดประชุม

วันศุกร์ที่ 2 สิงหาคม 2556 เวลา 8.30-16.30 น. ณ ห้องสัมมนา 2 ชั้น 9 ตึกเพียรวิจิตร คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น

วิทยากร

1. Prof. Dr. Shigemitsu Hatanaka, Department of Architecture, Faculty of Engineering, Mie University Japan หัวข้อ “Water-Related Attractive Properties of Small Particle Size Porous Concrete”

2. ศ.ดร.สันติ แม้นศิริ สาขาวิชาฟิสิกส์ สำนักวิชาวิทยาศาสตร์ มหาวิทยาลัยเทคโนโลยีสุรนารี หัวข้อ “Nanostructured materials for cement-based nanocomposites ”
3. ผศ.ดร.สำเริง รักซ้อน ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีราช มงคลพระนคร หัวข้อ “Durability of concrete using of two kinds of pozzolanic materials”
4. Assoc. Prof. Dr. José Barroso de Aguiar, C-TAC Research Centre, School of Engineering University of Minho, Portugal หัวข้อ “Eco-Concrete: One-Part Geopolymer Mixes”
5. ผศ.ดร.วันชัย สะตะ ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น หัวข้อ“Effect of coarse aggregate sizes and liquid to ash ratio on pervious geopolymer concrete properties”

ผลที่ได้จากการจัดประชุม

การจัดประชุมครั้งนี้ได้รับการตอบรับที่ดี มีผู้สนใจเข้าร่วมประชุมจากหน่วยงานรัฐและเอกชนจำนวนมาก นอกจากนี้ยังเป็นการสร้างเครือข่ายต่อยอดงานวิจัย และสร้างโอกาสให้กับผู้เข้าร่วมประชุมเป็นอย่างดี

ภาพบรรยากาศภายในงานประชุมวิชาการครั้งที่ 2








ค.3 การประชุมวิชาการครั้งที่ 3

ผู้เข้าร่วมประชุม จำนวน 127 ท่าน ประกอบด้วย

1.	คณาจารย์และผู้ช่วยวิจัยภายใต้ทุนเมธีวิจัย	10 ท่าน
2.	อาจารย์จากมหาวิทยาลัยต่างๆ	21 ท่าน
3.	นักวิจัย ผู้ประกอบการ และผู้สนใจจากภาคอุตสาหกรรม	20 ท่าน
4.	นักศึกษามหาวิทยาลัยต่างๆ	29 ท่าน
5.	อาจารย์และนักศึกษามหาวิทยาลัยขอนแก่น	47 ท่าน

เวลาและสถานที่ในการจัดประชุม

วันจันทร์ที่ 25 สิงหาคม 2557 เวลา 8.30-16.30 น. ณ ห้องสัมมนา 2 ชั้น 9 ตึกเพียรวิจิตร คณะวิศวกรรมศาสตร์ มหาวิทยาลัยขอนแก่น

วิทยากร

1. Prof. Jay Sanjayan Swinburne University of Technology
   หัวข้อ “Geopolymer: alternative eco-binder”
2. ดร.ประสิทธิ์ ทองใบ คณะวิทยาศาสตร์ มหาวิทยาลัยขอนแก่น
   หัวข้อ “Nanostructured materials for cement-based nanocomposites”
3. รศ.ดร.วิทยา อมรกิจบำรุง คณะวิทยาศาสตร์ มหาวิทยาลัยขอนแก่น
   หัวข้อ “Nanotechnology for enhancement of cement-based composites”
4. ผศ.ดร.สหลาภ หอมวุฒิวงศ์ คณะวิศวกรรมศาสตร์ มหาวิทยาลัยมหาสารคาม
   หัวข้อ “ความต้านทานต่อการสึกกร่อนของปอซโซลานคอนกรีต Abrasion resistance of pozzolan concrete”
5. ผศ.ดร.สำเริง รักซ้อน คณะวิศวกรรมศาสตร์ มหาวิทยาลัยเทคโนโลยีราชมงคลพระนคร
   หัวข้อ “ความทนทานของคอนกรีตผสมวัสดุปอซโซลานสองชนิด Durability of concrete incorporating two pozzolans”
6. ดร.ธนากร ภูเงินขำ และ ศ.ดร.ปริญญา จินดาประเสริฐ ศูนย์วิจัยและพัฒนาโครงสร้างมูลฐานอย่างยั่งยืน หัวข้อ “การใช้จีโอโพลิเมอร์สำหรับเป็นวัสดุซ่อมแซม”

ภาพบรรยากาศภายในงานประชุมวิชาการครั้งที่ 3








ภาคผนวก ง.
รางวัลที่ได้รับและการเชิดชูเกียรติ

ภาคผนวก ง. รางวัลที่ได้รับและการเชิดชูเกียรติ

ในช่วงของโครงการ หัวหน้าโครงการได้รับรางวัลและการเชิดชูเกียรติดังนี้

ง.1 รางวัล

ในช่วงของโครงการ หัวหน้าโครงการได้รับรางวัลดังนี้

1) รางวัลนักวิจัยดีเด่นระดับทอง ปี 2555 สาขาวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยขอนแก่น
2) รางวัลเชิดชูเกียรติ นักวิจัยที่มีผลงานวิจัยระดับดีเลิศ ปี 2555 มหาวิทยาลัยขอนแก่น
3) รางวัลพระธาตุพนมทองคำ ม.ขอนแก่น ปี 2556 รับพระราชทานจากสมเด็จพระเทพรัตนราชสุดาฯ สยามบรมราชกุมารีในงานพระราชทานปริญญาบัตร

ง.2 การเชิดชูเกียรติ

ในช่วงของโครงการ หัวหน้าโครงการได้รับการเชิดชูเกียรติดังนี้

1) ศาสตราภิชาน บริษัท เอสซีจี ซิเมนต์ จำกัด พ.ศ. 2555-2557
2) ภาคีสมาชิก สาขาวิชาวิศวกรรมศาสตร์ สำนักวิทยาศาสตร์ ราชบัณฑิตยสถาน ปี 2556
3) ได้รับเชิญเสนอบทความองค์ปาฐก 4 ครั้ง
    3.1 Chindaprasirt, P. Blended Portland Cement and Geopolymer Technology for Green and Durable Cementitious Materials Composite, Thai-German Symposium on Nanoscience and Nanotechnology (GTSNN2011), 13-16 September 2011, Suranaree University of Technology, P.13
    3.2 Chindaprasirt, P. Engineering and technological responses to the global challenges: Low carbon footprint cement and concrete, The 5th KKU International Engineering Conference (KKU-IENC 2014)
    3.3 ปริญญา จินดาประเสริฐ วัสดุซีเมนต์และคอนกรีตที่เป็นมิตรกับสิ่งแวดล้อม การประชุมวิชาการวิศวกรรมโยธาแห่งชาติ ครั้งที่ 19, 14-16 พฤษภาคม 2557 จ. ขอนแก่น
    3.4 Chindaprasirt, P. High calcium fly ash geopolymer - Alternative cement for Thailand, Advances in Civil Engineering for Sustainable Development 2014, Suranaree University of Technology, 27-29 August 2014

ภาคผนวก จ.
สำเนาบทความฉบับเต็ม
(ตามรายชื่อในภาคผนวก ก.)

Efficiency factor of high calcium Class F fly ash in concrete

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Abstract. This paper studied the cement efficiency factor (k factor) of high calcium Class F fly ash. This k factor represents a unit of fly ash with efficiency equivalent to k unit of cement. The high calcium Class F fly ash was used to replace cement in concrete. The modified Bolomey's law with linear relationship was used for the analysis of the result of compressive strength, cement to water ratio (c/w) and fly ash to water ratio (f/w) by using the multi-linear regression to determine the k factor and other constants in the equations. The results of analysis were compared with the results from other researcher and showed that the k factor of high calcium Class F fly ash depends on the fineness of fly ash, replacement level and curing age. While the amount of CaO content in Class F fly ash not evident. Furthermore, necessary criteria and variables for the determination of the k factor including the use of the k factor in concrete mix design containing fly ash were proposed.

Keywords: efficiency factor; fly ash; Class F; concrete; multi-linear regression analysis.

1. Introduction

Fly ash is a by-product of coal-burning in power plants. It is widely used as a cementitious material and a pozzolanic ingredient in concrete. The use of fly ash in concrete is constantly increasing because it improves the properties of concrete, namely workability, durability, and long term strength in hardened concrete. Fly ash consists mainly of SiO_2, Al_2O_3, Fe_2O_3 and CaO and some impurities. According to ASTM C618 (2003), fly ash are specified in two major classes and are designated as Class F and Class C. Class F is fly ash normally produced from the burning of anthracite or bituminous coal and has the $SiO_2+Al_2O_3+Fe_2O_3$ content higher than 70%. Class C is fly ash normally produced from the burning of lignite or sub-bituminous coal with the $SiO_2+Al_2O_3+Fe_2O_3$ content higher than 50%. Usually, Class F fly ash has a low CaO content and exhibits pozzolanic properties. Class C fly ash, on the other hand, may contain higher than 10% CaO and exhibits both pozzolanic and cementitious properties. However, the variations in coal composition and combustion condition have significant effects on the heterogeneity of chemical and mineralogical compositions of fly ash. The Class F fly ash can also contain a high amount of CaO.

In Thailand, Mae Moh power plant in Lampang province produces around 3 million tons of lignite fly ash annually. The $SiO_2+Al_2O_3+Fe_2O_3$ content of this fly ash is usually higher than 70%.

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The CaO varies generally between 10-20%. It is being used quite extensively for construction in Thailand.

There are many methods for designing or predicting the behaviors of fly ash in mortar and concrete (Hwang and Hsieh 2007, Chakraverty *et al.* 2008, Rukzon and Chindaprasirt 2008). One specific method for strength predicting is known as the fly ash cementing efficiency factor concept proposed by Smith (1967). The efficiency factor (k) is defined as a number representing a part of the fly ash in concrete mixture which can be considered as equivalent to Portland cement. The equivalent fly ash produces concrete with the same properties as the concrete without fly ash (Ganesh Babu and Siva Nageswara Rao 1996, Papadakis and Tsimas 2002). From this concept, the term of water to cement ratio (w/c) of the conventional concrete without fly ash is adjusted to the equivalent water to cement ratio $(w/c)_{eq}$ for the fly ash concrete as shown in Eq. (1).

$$\left(\frac{w}{c}\right)_{eq} = \frac{w}{c+kf} \tag{1}$$

Where:

w = water content
c = Portland cement content
k = fly ash cementing efficiency factor
f = fly ash content

Many researchers in this field have considered the efficiency factor of various type of fly ash and others pozzolan. Ganesh Babu and Siva Nageswara Rao (1996) studied the efficiency factor of fly ash in concrete and found that the overall cementing factor (k) of fly ash could be established through a general efficiency factor (k_e) and percentage efficiency factor (k_p) depending on the testing age and amount of replacement, respectively. The BS EN 206 (2000) recommends that fly ash can be introduced as a pozzolanic addition in designed concrete mixture with an equivalent k = 0.2 or 0.4 depending on the cement class.

Papadakis and Tsimas (2002) and Papakadis *et al.* (2002) studied the efficiency factor of supplementary cementitious materials (SCM) such as silica fume, fly ash, slag, and natural pozzolan and reported that these values were valid for a content of SCM in concrete and depended on the concerned properties such as strength and durability. Oner *et al.* (2005) investigated the efficiency and the maximum Class F fly ash content for maximum compressive strength using Bolomey and Feret strength equation and showed that the optimum fly ash was about 40% of cement and fly ash/ cement ratio was an important factor determining the efficiency of fly ash. Yamamoto *et al.* (2006) studied the pozzolanic reaction of Class F fly ash in mortar and found that the K-value from Feret's law is useful for the estimation of the degree of reaction. In addition, Tang (2010) studied the degree of pozzolanic reaction using factor in term α_p to replace the k factor and found that the degree of cement hydration in the blended cement pastes can be calculated.

In spite of all these investigations, there is still a lack of investigation on the efficiency of high calcium Class F fly ash. In this paper, an experimental investigation of efficiency factor of high calcium Class F Mae Moh fly ash in concrete was carried out using modified Bolomey's law. The mix proportions of concrete were designed at various compressive strengths. The amounts of fly ash were replaced of cement at rate of 0, 20, 40, and 60% by weight of binder. The compressive strengths of concrete were tested at the age of 14 and 28 days. An expression predicting compressive strength including the parameters mentioned above was proposed. In addition, the analysis results were compared to those of other researches.

2. Calculation of *k* factor

The famous formula that shows relationship between compressive strength of concrete and *w/c* ratio is Abrams' law (Abrams 1918) as follow

$$R = \frac{k_1}{(k_2)^x} \tag{2}$$

Where:

R = compressive strength of concrete
x = ratio between volume of water and volume of cement
k_1, k_2 = empirical constants for a given materials, age of curing and test conditions

In 1927, Bolomey (1927) proposed a linearized form Feret's formula as shown in Eq. (3). This gives the results very similar to Abrams' law.

$$R = p_1\left(\frac{1}{w/c} - p_2\right) \tag{3}$$

Where:

p_1, p_2 = empirical factor materials
c = cement content in concrete mixture
w = water content in concrete mixture

Hedegaard and Hansen (1992) suggested that strength development of fly ash concrete may be due to the hydration of cement and reaction of fly ash independent of pore-filler mechanism in the concrete. Therefore a linear relation between ordinary concrete compressive strength and cement to water ratio as shown in Eq. (4) can be expressed with fly ash cementing efficiency factor concept in term of a modified Bolomey's law as

$$\sigma_c = A_1\left(\frac{c}{w}\right) + A_3 \tag{4}$$

$$\sigma_c = A_1 + \frac{(c+kf)}{w} + A_3 = A_1\left(\frac{c}{w}\right) + A_1\left(\frac{kf}{w}\right) + A_3 \tag{5}$$

Then, it follows that

$$\sigma_c = A_1\left(\frac{c}{w}\right) + A_2\left(\frac{f}{w}\right) + A_3 \tag{6}$$

Hence

$$k = \frac{A_2}{A_1} \tag{7}$$

Where:

σ_C = compressive strength of concrete (MPa)
c = cement content in concrete mixture (kg/m^3)
w = water content in concrete mixture (kg/m^3)
f = fly ash content in concrete mixture (kg/m^3)
k = fly ash cementing efficiency factor
A_1, A_2, A_3 = empirical constants for a given materials, age of curing and test conditions.

3. Experimental programs

3.1 Materials

The materials used in this study consisted of Portland cement type I (PC), Lignite fly ash (FA) from the Mae Moh power station in northern Thailand, coarse and fine aggregates, and tap water.

Physical properties of materials are given in Table 1. The specific gravity of PC was 3.15 with Blaine fineness of 3580 cm^2/g. FA had 42.5% retained on a sieve No. 325 (opening 45 mm), specific gravity of 2.33, and Blaine fineness of 3045 cm^2/g. Local river sand with specific gravity of 2.67 and fineness modulus of 2.73 was used as fine aggregate and crushed limestone with a fineness modulus of 7.51 and specific gravity of 2.70 was used as coarse aggregate in concrete mixture.

Chemical compositions of PC and FA are listed in Table 2. The oxides of PC were CaO (62.7%), SiO_2 (21.5%), Al_2O_3 (4.5%), and Fe_2O_3 (3.1%) and SO_3 (3.5%). The loss on ignition (LOI) was 1.2%. FA was a high calcium Class F pozzolan according to ASTM C618-08a (2008) 74.8% of the sum SiO_2, Al_2O_3, and Fe_2O_3, 2.6% of SO_3, 16.6% of CaO and 0.1% of LOI.

3.2 Mixture proportions and testing

Four groups of main concrete mixtures were designed according to ACI 211 (2000). For all main mixtures, PC was replaced by FA at rates of 20, 40, and 60% by weight of binder. The mixture

Table 1 Physical property of materials

Properties	Portland cement type I	Fly ash	Fine aggregate	Coarse aggregate
– Specific gravity	3.15	2.33	2.67	2.70
– Absorption (%)	-	-	0.52	0.38
– Fineness modulus	-	-	2.73	7.51
– Retained on No. 325 sieve	-	42.4	-	-
– Blaine fineness (cm^2/g)	3580	3045	-	-

Table 2 Chemical composition of cement and fly ash

Oxides	Cement	Fly ash
SiO_2	21.5	38.7
Al_2O_3	4.5	20.8
Fe_2O_3	3.1	15.3
CaO	62.7	16.6
MgO	1.1	1.5
Na_2O	1.5	1.2
K_2O	0.7	2.7
SO_3	3.5	2.6
LOI	1.2	0.1
$SiO_2 + Al_2O_3 + Fe_2O_3$	-	74.8

Table 3 Concrete mix proportions

Symbol	Proportions (kg/m^3)					
	PC	FA	Water	Fine aggregate	Coarse aggregate	Slump (mm)
20PC	346	0	217	864	910	50
25PC	380	0	217	831	909	50
30PC	409	0	217	801	908	55
35PC	447	0	217	771	903	70
20PC20FA	299	75	206	863	907	70
25PC20FA	327	82	206	828	907	50
30PC20FA	355	89	206	797	897	50
35PC20FA	386	96	206	766	804	55
20PC40FA	242	161	192	865	909	50
25PC40FA	265	176	192	829	908	50
30PC40FA	287	191	192	797	903	50
35PC40FA	312	208	192	764	850	60
20PC60FA	182	272	182	851	895	75
25PC60FA	199	298	182	813	891	85
30PC60FA	215	323	182	780	883	65
35PC60FA	234	351	182	745	872	65

proportions of concrete and slumps of fresh concretes are listed Table 3.

The fresh concretes were prepared using a rotating drum mixer. The concrete specimens were cast in cubes of 150 mm. After casting for 24 h, the concrete samples were removed from the moulds and immersed in water at 23±2°C until testing. The compressive strengths of concretes were determined at 14 and 28 days. For each age, the average of experimental results from three specimens was reported.

4. Results and discussion

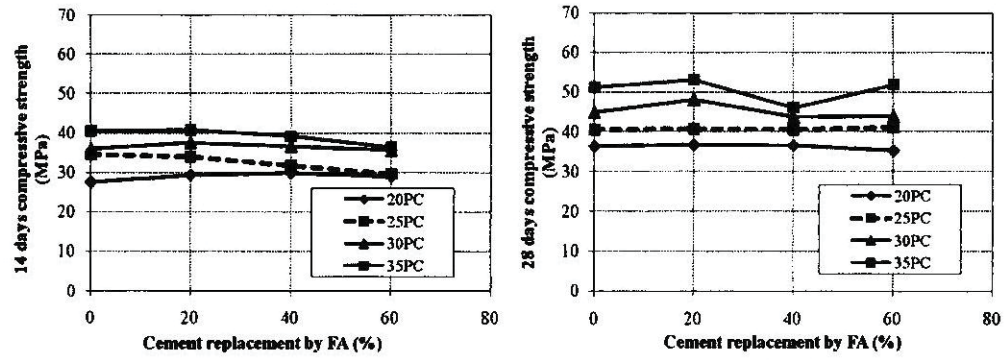
4.1 Compressive strength of concretes

Table 4 presents cement to binder ration (*w/b*), cement to water ratio (*c/w*), water to fly ash ratio (*f/w*), and compressive strengths of concretes. The 14 and 28 days compressive strengths varied from 27.5-40.8 MPa and 35.2-53.1 MPa, respectively. The mixes were designed to obtain similar slumps of 50-85 mm. Fig. 1 shows the relationship between compressive strength of concrete and FA replacement rate. The compressive strengths of fly ash concretes were approximately the same as those of normal concrete. This is due to reduction of water to binder ratio (*w/b*) of the mixes containing fly ash as a result of the ball bearing effect of the spherical FA particles. Additional pozzolanic reaction and the packing effect of the small fly ash particles contributed to the compressive strength development. The concretes with 20% cement replacement by FA give slightly higher compressive strength than those of 40 and 60% due to the small reduction in Portland cement.

Table 4 Compressive strengths

Symbol	*w/b* ratio	*c/w* ratio	*f/w* ratio	Compressive strength (MPa)	
				14 days	28 days
20PC	0.63	1.59	0.00	27.5	36.4
25PC	0.57	1.75	0.00	34.5	40.6
30PC	0.53	1.88	0.00	36.0	44.9
35PC	0.49	2.06	0.00	40.6	51.2
20PC20FA	0.55	1.45	0.36	29.3	36.7
25PC20FA	0.50	1.59	0.40	34.0	40.7
30PC20FA	0.46	1.72	0,43	37.6	48.1
35PC20FA	0.43	1.87	0.47	40.8	53.1
20PC40FA	0.48	1.26	0.84	29.8	36.6
25PC40FA	0.44	1.38	0.92	31.8	40.6
30PC40FA	0.40	1.49	0.99	36.6	43.7
35PC40FA	0.37	1.63	1.08	39.2	46.1
20PC60FA	0.40	1.00	1.49	28.9	35.2
25PC60FA	0.37	1.09	1.64	29.7	41.1
30PC60FA	0.34	1.18	1.77	35.6	43.9
35PC60FA	0.31	1.29	1.93	36.5	51.8

Note: w = water, b = binder (cement + fly ash), c = cement, f = fly ash.



(a) 14 days (b) 28 days

Fig. 1 Variation of compressive strength with replacement of FA

4.2 Determination of k factor

In this study, the *c/w* ratio, and *f/w* ratio varied between 1.00 to 2.06, and 0 to 1.93, respectively. The combination of *c/w* ratio and f/w ratio of 16 concrete mixes are showed in Fig. 2. The graph indicated a good coverage of the tests. From the Eq. (6), a multi-linear regression analysis based on least squares method was applied to obtain the relationship between *c/w* ratio, *f/w* ratio, and compressive strength as well as to calculate the constants A_1, A_2 and A_3 at each age. The results at the age of 14 and 28 days based on the compressive strength of 16 mixes are shown in Eqs. (8) and

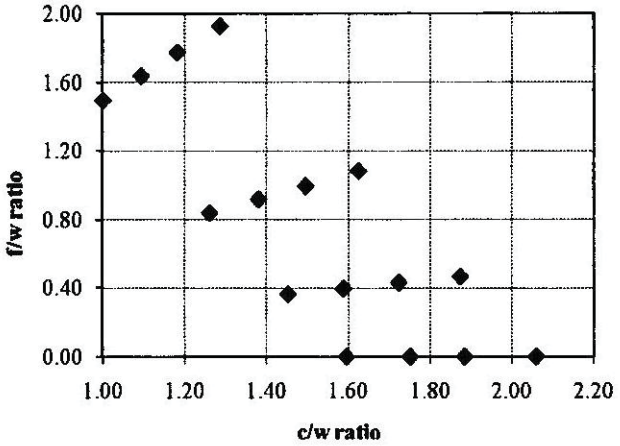


Fig. 2 The combinations of *c/w* and *f/w* ratios of concretes in this study

(9). The correlation coefficient (R^2) of 0.92 and 0.93 indicates the goodness of fit. To further examine how well the developed model fits the tested data, the predicted values from Eqs. (8) and (9) versus experimental compressive strengths at 14 and 28 days were plotted as shown in Fig. 2. The predicted data were within the line of ±10% of experimental values. The modified Bolomey equation (Eq. (6)), therefore, accurately predicts the compressive strengths. Therefore, the present model is expected to provide a good level for compressive strength estimate of high calcium Class F fly ash concrete.

$$\sigma_c(14D) = 23.53\frac{c}{w} + 8.01\frac{f}{w} - 7.56, \quad R^2 = 0.92 \tag{8}$$

$$\sigma_c(28D) = 32.32\frac{c}{w} + 12.26\frac{f}{w} - 13.96, \quad R^2 = 0.93 \tag{9}$$

From Eqs. (8) and (9), the k factor of fly ash at 14 and 28 days can be obtained as;

$$k(14D) = \left(\frac{A_2}{A_1}\right)_{14} = \frac{8.01}{23.53} = 0.34 \tag{10}$$

$$k(28D) = \left(\frac{A_2}{A_1}\right)_{28} = \frac{12.26}{32.32} = 0.38 \tag{11}$$

The results show that the k factors of fly ash at 14 and 28 days are 0.34 and 0.38, respectively. The k factor tends to increase with age of concrete owing mainly to the pozzolanic reaction. Thus, it is essential that fly ash concrete requires prolonged curing (Bharatkumar *et al.* 2001). This result agrees with the experimental of Rajamane *et al.* (2007) which showed that the k factors of Class F fly ash when used as a partial replacement for both Portland cement and fine aggregate increased with the age of concrete.

Table 5 summarizes the replacement rate, the constants A_1, A_2 and A_3, R^2, and k factors of fly ash at the age of 14 and 28 days. The k factors of fly ash varied from 0.49-0.35 and 0.50-0.39 for fly ash replacement levels of 20-60% at the age of 14 and 28 days, respectively. The factor decreased slightly with the increasing level of replacement as shown in Fig. 4. The level of replacement of fly ash is an important factor determining the efficiency factor (Oner *et al.* 2005). From the above

Table 5 Results of the multi-linear regression analysis of this experimental data

Age of curing	Fly ash replacement (%)	A_1	A_2	A_3	R^2	$k = A_2/A_1$
14	0-60	23.53	8.01	-7.56	0.92	0.34
28	0-60	32.32	12.26	-13.96	0.93	0.38
14	20	24.46	11.36	-11.24	0.96	0.46
	40	23.14	8.83	-8.77	0.95	0.38
	60	22.21	7.67	-7.04	0.91	0.35
28	20	32.63	16.18	-17.87	0.99	0.50
	40	25.61	8.44	-4.89	0.96	0.33
	60	31.87	12.55	-16.39	0.99	0.39

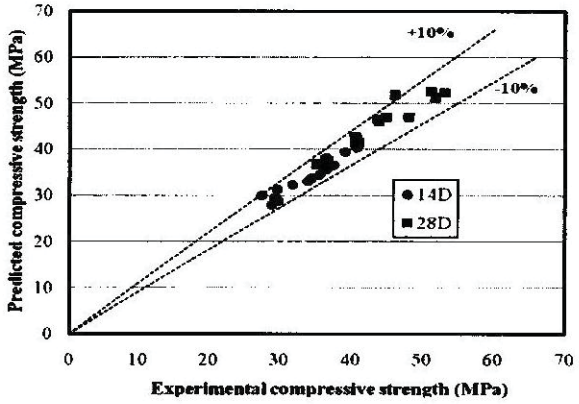


Fig. 3 Relationship between experimental and predicted compressive strength

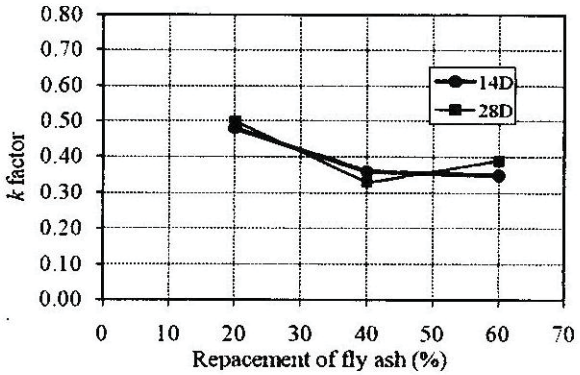


Fig. 4 Variation of level of fly ass replacement with k factor

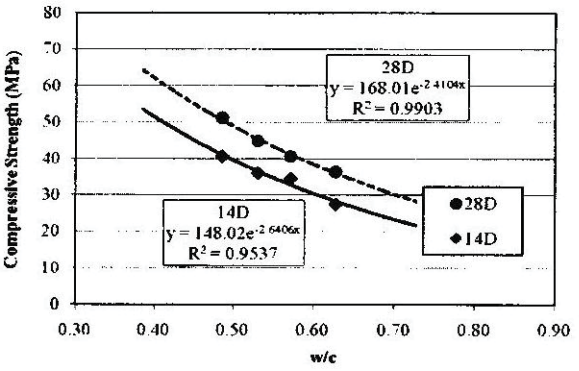


Fig. 5 Variation of compressive strength with w/c of normal concrete with out fly ash

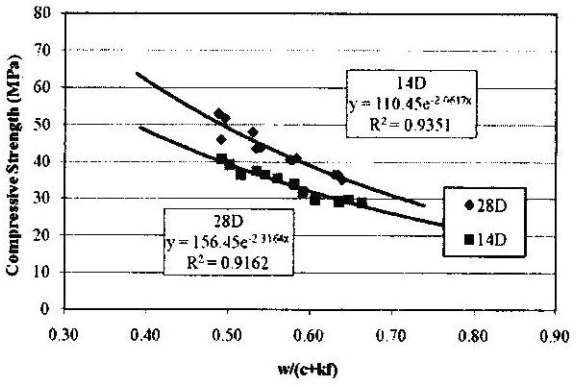


Fig. 6 Variation of compressive strength with $w/(c+kf)$ of fly ash concrete

results, it can be recognized that k factor depend on both age of curing and level of replacement.

Fig. 5 shows the normal relationship between the compressive strength of normal concrete at 14

and 28 days with *w/c* ratio. For the fly ash concrete, the *w/b* and compressive strength relations had to be modified to give a good fit with the aid of *k* factor. The plot of compressive strength of fly ash concrete at 14 and 28 days with *w/(c+kf)* shown in Fig. 6 gave similar relationship to those of *w/c* to compressive strength relations of normal concrete. Therefore, test results indicated that the compressive strength of high calcium Class F fly ash concrete can be predicted using *k* factor concept, which was based on modified Bolomey equation.

4.3 Comparison of k factor of concrete from other researches

In order to compare the *k* factors of Class F fly ash concretes from the other researches, the compressive strength data of concretes containing Class F fly ash with various CaO contents were used for the comparison. The details of concrete and the multi-linear regression analysis results are presented in Table 6. The CaO contents of the Class F fly ashes varied between 2.1-16.6% and the Blaine fineness ranged from 2208-6645 cm^2/g. The range of slump of fresh concrete of 3.0-12.5 cm. was selected. From the multi-linear regression analysis with *c/w* between 0.2 and 2.9, *f/w* between 0-2.0, the *k* factors of fly ash were found to be between 0.09-0.86 and the R^2 of analysis results at each data ranged from 0.90-0.99 indicating good correlations of result obtained from Eq. (6). However, the *k* factor depends on various properties of fly ash and concrete.

The plot of the *k* factor and age of curing with fly ash of similar fineness as shown in Fig. 7 indicated that *k* factors increase with curing ages. For example, the *k* factor of fly ash with Blaine

Table 6 The general details of concretes evaluated and results of references data comparison with this study

References	Fly ash			Cement Replacement (%)	Range of		Slump (cm)	Results		
	Source	Class F (% CaO)	Fineness (cm^2/g)		*c/w*	*f/w*		R^2	*k*	Curing (days)
Slanicka (1990)	Czech	2.8	5327	0-30	1.2-2.5	0.0-1.1	8.5-10	0.98	0.86	28
	Slovakia	3.1	2208	0-29	1.2-2.5	0.0-0.6	8.5-10	0.99	0.09	28
Hedegaard and Hasen (1992)	Asnaes (Denmark)	3.2	-	0-91	0.2-2.6	0.0-2.0	3-9	0.96	0.21	28
	Try (Denmark)	2.8	-	0-91	0.2-2.6	0.0-2.0	3-9	0.98	0.22	28
Oner *et al.* (2005)	Turkey	2.1	3355	0-37	0.9-1.7	0.0-0.7	11-12.5	0.90 0.90	0.48 0.54	28 180
Boonlualoah (2001)	Mae Moh (Thailand)	9.6	3233	0-60	0.5-2.9	0-1.7	8-10	0.95	0.42	28
Songpiriyakij (2002)	Mae Moh (Thailand)	9.0	6645	0-60	0.6-2.5	0.0-1.5	-	0.96	0.62	28
		11.3	3485	0-60	0.6-2.5	0.0-1.5	-	0.98 0.97 0.96 0.94	0.44 0.48 0.58 0.62	7 28 90 180
		10.1	2665	0-60	0.6-2.5	0.0-1.5	-	0.98	0.21	28
This study	Mae Moh (Thailand)	16.6	3045	0-60	1.0-2.1	0.0-1.9	5-8.5	0.92 0.93	0.34 0.38	14 28

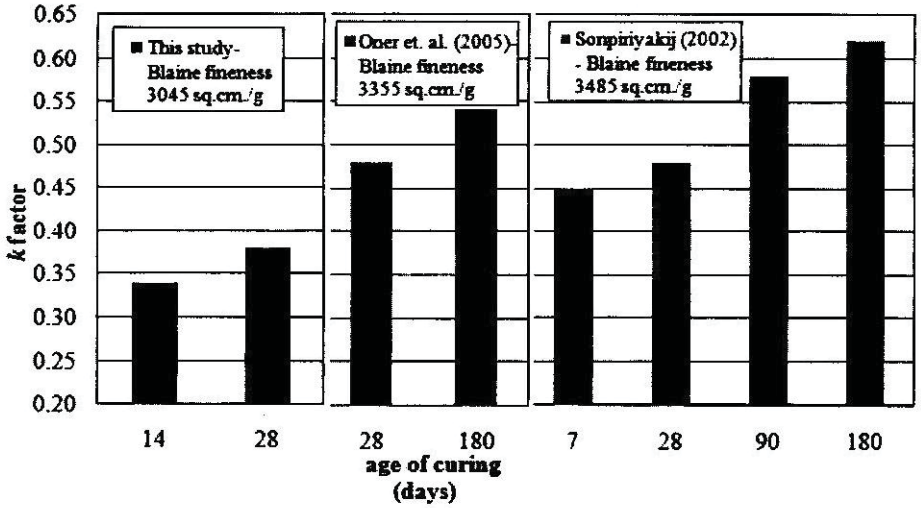


Fig. 7 Relationship between k factor of fly ash and age of curing

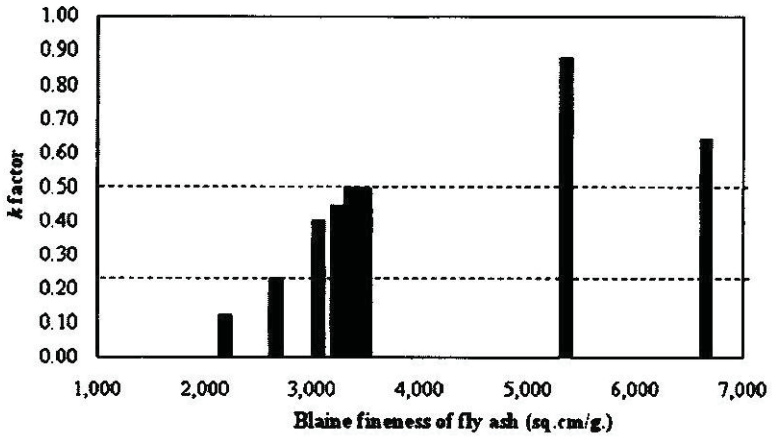


Fig. 8 Variation of k factor of fly ash at 28 days with various fly ash finenesses

fineness of 3485 cm^2/g (Songpiriyakij 2002) at 7, 28, 90, and 180 days were 0.44, 0.48, 0.58, and 0.62 respectively. The k factor of fly ash with Blaine fineness of 3355 cm^2/g (Oner *et al.* 2002) at 28 and 180 days were 0.48 and 0.54 respectively. These results conforms with the tested results (Blaine fineness of 3045 cm^2/g) which showed the k factor of high calcium Class F fly ash was 0.34 at the age of 14 days and increased to 0.38 at the age of 28 days. The k factor of fly ash improved with age as a result of the pozzolanic reaction.

Comparison the k factor and age of curing using various literatures data as shown in Fig. 7 showed that besides the age of curing, the k factor depends on fineness of fly ash. The plot of k factor of fly ash at the age of 28 days with various Blaine finenesses is shown in Fig. 8.

The k factor increases with the increase in the fineness. At the low fineness of 2208-2665 cm^2/g, the k factors were between 0.09-0.21. For the medium finenesses of 3045-3485 cm^2/g, the k factors were between 0.38-0.48. For the high fineness of 5327 and 6645 cm^2/g, the k factors were 0.86 and

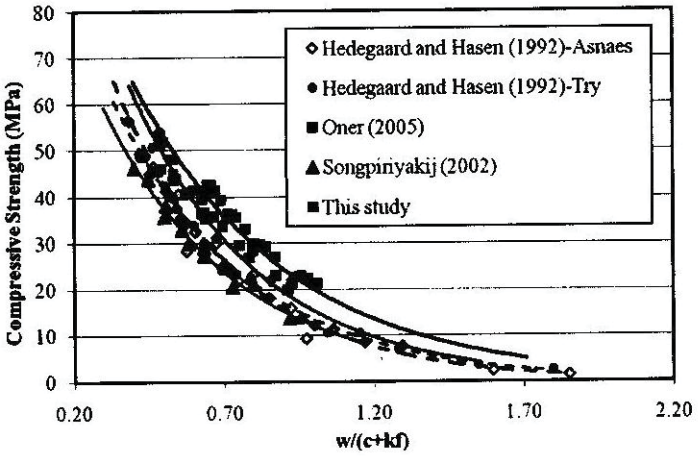


Fig. 9 Variation of compressive strength with $w/(c+kf)$ of fly ash concrete at 28 days

0.62. The increasing of k factor with fineness of fly ash is due a higher pozzolanic reaction from a higher surface area of fly ash particle and a small fly ash particle that filled the voids (Chindaprasirt *et al.* 2005). In addition, Yamamoto *et al.* (2006) also found that all types of fine fly ash (CaO amount up to 8.4%) with high fineness showed higher k factor, and also suggested the linear relationship between gaining rate of k factor and logarithmic time.

From the 28 day k factor of this study, the variation of compressive strength with $w/(c+kf)$ ratio of fly as concrete were plotted compare with various references data in Fig. 9. This shows that the high calcium Class F fly ash concretes can be represented by the compressive strength and the $w/(c+kf)$ ratio similar to the other Class F fly ash with various amount of CaO.

For fly ashes of similar fineness with different CaO contents, the effect of CaO content is not observable. The k factors at the age of 28 days of fly ashes with CaO content of 2.1% and fineness of 3355 cm^2/g; CaO content of 11.3% and fineness of 3485 cm^2/g; and CaO content of 16.6% and fineness of 3045 cm^2/g were 0.48, 0.48 and 0.38, respectively. Although, the high CaO content gave low k factor of 0.38, this may be the results of the fineness and the experimental variation. This aspect needs further research and clarification.

For Mae Moh high calcium Class F fly ash in Thailand, the 28 days k factor varied from 0.38 to 0.62 depending on the fly ash fineness. However for the design purpose, it can be recommended that the k factor should be 0.30-0.60 for fly ash replacement between 20-60%.

5. Conclusions

In this experimental, the cement efficiency factor (k factor) of high calcium Class F fly ash was tested. The modified Bolomey's law with linear relationship was used for the analysis of the result of compressive strength of concrete, cement to water ratio (c/w), and fly ash to water ratio (f/w) by using the multi-linear regression to determine the k factor and other constants in the equations. In addition, the results were compared with those of Class F fly ash concretes of other researches. Based on the above results and discussions, the conclusions can be listed as follow.

1. The k factor concept is suitable for high calcium Class F fly ash. It is useful for estimating the

degree of the pozzolanic activity of high calcium Class fly ash and compressive strength of concrete.

2. The *k* factor of Class F fly ash depends on the characteristics of fly ash and concrete. The important factors are fly ash fineness, age of curing and replacement level. While the effect of the CaO content in Class F fly ash on *k* factor is small and inconclusive. This subject needs further i3. nvestigation.

3. Finally, for the design of high calcium Class F Mae Moh fly ash concrete, it is recommended that the *k* factor should be about 0.30 to 0.60 for fly ash replacement between 20-60% depending on the fly ash fineness.

Acknowledgements

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Resistance of lignite bottom ash geopolymer mortar to sulfate and sulfuric acid attack

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ABSTRACT

This paper presents an investigation of the compressive strength and the durability of lignite bottom ash geopolymer mortars in 3% sulfuric acid and 5% sodium sulfate solutions. Three finenesses of ground bottom ash viz., fine, medium and coarse bottom ash were used to make geopolymer mortars. Sodium silicate, sodium hydroxide and curing temperature of 75 °C for 48 h were used to activate the geopolymerization. The results were compared to those of Portland cement and high volume fly ash mortars. It was found that the fine bottom ash was more reactive and gave geopolymer mortars with higher compressive strengths than those of the coarser fly ashes. All bottom ash geopolymer mortars were less susceptible to the attack by sodium sulfate and sulfuric acid solutions than the traditional Portland cement mortars.

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1. Introduction

It is known that 0.7–1.1 ton of CO_2 is emitted for every ton of cement produced. Approximately 50% of carbon dioxide emission by cement industry is from the calcination of limestone and the other 40% from combustion of fuel in the kiln, and 10% from transportation and manufacturing operations [1]. In order to reduce the amount of CO_2 emission from the cement industry, the manufacturing process has been improved and the growth in the Portland cement usage has to be reduced. For cement consumption, there are several efforts to reduce the use of cement in concrete. These include the utilization of supplementary cementitious materials such as fly ash, blast-furnace slag, silica fume, metakaolin, natural pozzolans, and biomass ash [2–4]. In the last decade, geopolymer binders have emerged as one of the possible alternative to conventional cement binders for concrete industry [5,6]. Geopolymer is an inorganic binder material and can be produced by a geopolymeric reaction of alkali activating solution with silica and alumina rich source materials from geological origin or pozzolanic materials such as metakaolin, fly ash, and rice husk ash [7]. Geopolymers exhibit many excellent properties such as high early strength, low creep, low shrinkage, and good resistance against acid and sulfate attack in addition to its environment friendliness [8–12].

Bottom ash (BA) is a by-product of the combustion of pulverized coal in the power plants. It is generated from the coagulation of the melting fly ash particles. The BA particles are therefore relatively large. The world production of coal ash was approximately 459 million tons in 1992 [13]. The BA comprises approximately 20% of the coal ash and almost all of it is disposed of as landfill. The annual output of lignite BA at Mae Moh power plant in the north of Thailand is about 0.8 million tons and is disposed of in the landfill and ash ponds which causes an environmental problem. BA contains high silica and alumina contents similar to fly ash. Several researchers [14,15] found that grinding of BA increases its pozzolanic activity and makes it suitable for use as partial replacement in Portland cement. In addition, BA is a suitable source material for making geopolymer [16–18]. Previous researches [19] studied the effects of fineness of BA, sodium hydroxide, sodium silicate, water, and naphthalene-based superplasticizer on workability and strength of geopolymer mortars. The results indicated that the flow and strength of geopolymers were improved with an increase in the fineness of BA.

In this study, the effect of BA fineness on compressive strength and the durability of BA geopolymer mortars in 5% sodium sulfate and 3% sulfuric acid solutions were presented. The results were compared to those of Portland cement mortar, and mortar containing 40% fly ash and ground BA. The obtained data of this work would be beneficial for the utilization of BA in the geopolymer mortar and concrete. This should lay a good foundation for the increased use of BA and thus lead to the reduction in the cement consumption and environmental problems.

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2. Experimental details

2.1. Materials

Materials used in this study consisted of Portland cement Type I (OPC), fly ash (FA), and lignite bottom ash (BA) from Mae Moh power plant in northern Thailand. The chemical and mineral compositions are summarized in Table 1 and Fig. 1, respectively and the physical properties of these materials are shown in Table 2.

The specific gravity of cement was 3.18 with the median particle size (d_{50}) of 17.3 μm. The major oxide ($SiO_2 + Al_2O_3 + Fe_2O_3$) of the FA was 74.7% which is higher than the minimum requirement (70%) specified by ASTM C 618 [20] for Class F fly ash. The XRD pattern of FA shows substantial amorphous phase with some peaks of crystals of anhydrite, lime, magnesioferrite, quartz, and mullite. In order to study the effect of BA fineness, three finenesses of ground BA viz., fine BA (FBA), medium BA (MBA) and coarse BA (CBA) with corresponding median particle sizes of 15.7, 24.5 and 32.2 μm and Blaine finenesses of 5300, 3400 and 2100 cm^2/g, respectively were used. The mineral compositions of FBA, MBA, and CBA were similar suggesting that the grinding of BA had little effect on the crystallinity. Sodium silicate solution (NS) with 13.8% Na_2O, 32.2% SiO_2 and 54.0% H_2O, and 10 molar (M) sodium hydroxide (NH) solution were used as alkaline activators. A local river sand with specific gravity of 2.62 and fineness modulus of 2.85 was used for making the mortar.

2.2. Mix proportions and mixing

In order to study the resistance of lignite BA geopolymer mortars on sulfuric acid attack and to compare the results to cement mortar, three Portland cement mortars and three geopolymer mortars were used. The mix proportions are shown in Table 3.

For cement mortar (PC, PFA40, and PFBA40), the ratio of a binder material to fine aggregate was set at 1–2.75 by weight. The PC mortar consisted of only OPC as cementitious materials. The PFA40 and PFBA40 mixes were Portland cement mortars with OPC replaced by FA and FBA at the dosage of 40% by weight of binder. The mortars were mixed and the flows were determined in accordance with the procedure given in ASTM C 1437 [21].

The BA to sand ratio of 1–2.75, liquid alkaline/BA ratio of 0.597 and NS/NH ratio of 1.50 were the geopolymer mortar mix proportions used. GFBA, GMBA, and GCBA were geopolymer mortars made from FBA, MBA, and CBA, respectively. The mixing of geopolymer mortar was done in a controlled room at 25 °C. The BA was mixed with NH for 5 min to allow the leaching of silica and alumina ions [22]. Sand was then incorporated and mixing was done for 5 more minutes. This was followed by the addition of NS with a final mixing of 5 min. After mixing, the flows of BA geopolymer mortars were tested.

Table 1
Chemical composition of materials.

Chemical composition (%)	OPC	FA	FBA	MBA	CBA
SiO_2	21.5	38.7	39.3	40.3	35.5
Al_2O_3	4.5	20.7	21.3	17.4	16.8
Fe_2O_3	3.1	15.3	13.5	13.6	15.1
CaO	62.7	16.6	16.5	11.8	13.3
MgO	1.1	1.5	2.6	7.6	8.4
Na_2O	1.5	1.2	1.0	2.8	3.8
K_2O	0.7	2.7	2.1	1.5	1.8
TiO_2	0.1	0.4	0.4	0.3	0.3
P_2O_5	–	0.2	0.2	0.2	0.2
SO_3	3.5	2.6	1.5	–	–
LOI	1.3	0.1	1.4	4.4	4.7

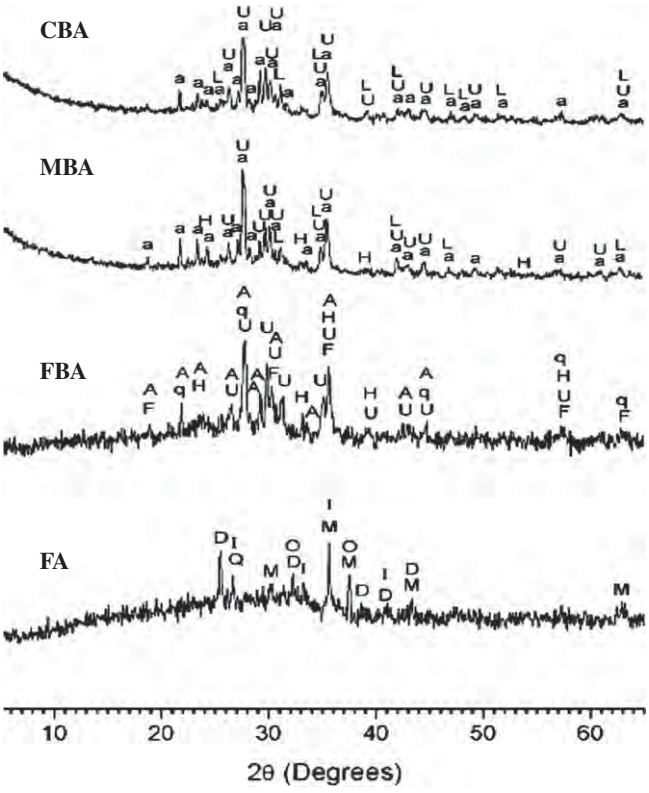


Fig. 1. The XRD pattern of materials; D-anhydrite; $CaSO_4$; O-lime: CaO; A-anorthite, Na-rich intermediate: $(Ca,Na)(Si,Al)_4O_8$; F-magnetite: Fe_3O_4; H-hematite: Fe_2O_3; Q-quartz: SiO_2; U-augite, Al-rich: $Ca(Mg,Fe,Al)(Si,Al)_2O_6$; I-Mullite: $3Al_2O_3.2SiO_2$.

Table 2
Physical properties of materials.

Sample	Specific gravity	Median particle size, d_{50} (μm)	Blaine fineness (cm^2/g)	Retained on a sieve No. 325 (%)
OPC	3.18	17.3	3400	9
FA	2.51	37.1	2100	33
FBA	2.89	15.7	5000	3
MBA	2.87	24.5	3400	18
CBA	2.86	32.2	2100	33

2.3. Testing detail

2.3.1. Compressive strength test

The cement mortars were cast in 50 × 50 × 50 mm cube molds. The specimens were cover with damped cloth and polyurethane sheet for moist curing. They were demolded at one day and stored in water at 23 ± 2 °C until the testing age. For geopolymer mortars, they were placed into the 50 × 50 × 50 mm cube molds and wrapped with cling film to avoid the moisture lost and left in the laboratory for 1 h and then temperature cured at 75 °C for 48 h [19]. The specimens were demolded and kept in the controlled room at 23 ± 2 °C and 50% RH until the testing age. All samples were tested for compressive strength at 7, 28, 90, 180 and 360 days in accordance with ASTM C 109 [23]. The reported compressive strengths were the average of three samples.

2.3.2. Sulfate resistance

In order to determine the durability of geopolymer mortar, the expansions of mortar bars immersed in sodium sulfate solution were tested. Mortar bars with 25 × 25 × 285 mm in dimension

Table 3
Mix proportions of mortars.

Mix	Type of fly ash	OPC (g)	FA (g)	BA (g)	NS (g)	NH (g)	Water (g)	Sand (g)	Flow (%)
PC	–	100	0	0	0	0	47	275	114
PFA40	FA	60	40	0	0	0	47	275	146
PFBA40	FBA	60	0	40	0	0	47	275	112
GFBA	FBA	0	0	100	35.8	23.9	0	275	62
GMBA	MBA	0	0	100	35.8	23.9	0	275	51
GCBA	CBA	0	0	100	35.8	23.9	0	275	35

Note: 10 M of NH, liquid alkaline/BA = 0.597, NS/NH = 1.50.

were prepared in accordance with the procedures given in Section 2.3.1 and ASTM C 1012 [24]. The mortar bars were immersed in 5% sodium sulfate solution and were tested for expansions. The sulfate solution was replaced with fresh solution after the immersion of 7, 14, 28, 56, 84, 120 and 240 days.

2.3.3. Sulfuric acid resistance

The sulfuric acid resistances of mortars were tested by modified test method B in accordance with ASTM C 267 [25]. The 50 × 50 × 50 mm cube mortar specimens were immersed in 3% sulfuric acid solution. After immersed time of 7, 14, 28, 56, 84, and 120 days in the sulfuric acid, the samples were brushed softly under water with a nylon brush to remove loose surface debris before weighting. The weight losses of specimens after immersion in the acid were evaluated. The sulfuric acid solution was replaced with fresh solution after the immersions of 7, 14, 28, 56, 84, and 120 days.

3. Results and discussion

3.1. Compressive strength

The results of the compressive strength tests of mortars are summarized in Table 4 and Fig. 2. The compressive strength of cement mortars (PC, PFA40, and PFBA40) increased with the curing age in accordance with the strength development of Portland cement. For example, the compressive strengths of PFBA40 mortar at 7, 28, 90, 180, and 360 days were 31.5, 43.5, 63.5, 68.5, and 71.5 MPa, respectively. The strength development of geopolymer mortars (GFBA, GMBA, and GCBA) increased at a lower rate compared to those of Portland cement mortars. This was due to the fact that the curing at temperature of 75 °C for 48 h increased the early age compressive strengths [26].

The development of compressive strength was also affected by the BA fineness. The use of FBA in geopolymer mortar seemed to give higher compressive strengths than those of the coarser ones. Since, the BA with high finenesses and high surface areas could dissolve more silica and alumina [19] and thus resulted in the increase in geopolymerization and compressive strength. In addition, a large portion of as-received BA particles were porous and contributed to the low strength of geopolymer mortars [12]. Grinding helped destroy the pores of BA particles and thus improved the strength of geopolymer mortars [19]. The compressive strengths

Table 4
Compressive strengths of mortars.

Mix	Compressive strength (MPa)				
	7 D	28 D	90 D	180 D	360 D
PC	44.7	47.4	54.0	68.0	68.5
PFA40	23.0	44.5	57.5	58.5	71.5
PFBA40	31.0	43.5	63.5	68.6	71.5
GFBA	48.5	54.5	51.5	61.5	55.5
GMBA	46.0	48.0	46.5	49.5	39.5
GCBA	43.0	40.0	32.5	35.0	36.5

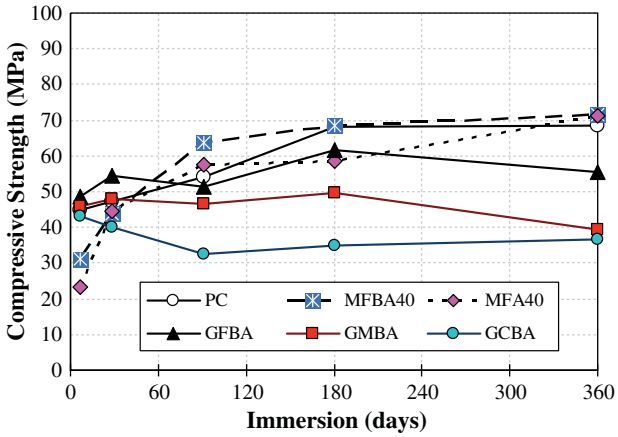


Fig. 2. Compressive strength of mortars and time of curing.

of GFBA mortars at 7, 28, 90, 180 and 360 days were 48.5, 54.5, 51.5, 61.5 and 55.5 MPa, respectively. For the coarser BA, the compressive strengths of GCBA mortars at the same ages were 43.0, 40.0, 32.5, 35.0 and 36.5 MPa, respectively.

3.2. Resistance to sodium sulfate attack

The results of the length change of mortars bars subjected to 5% Na_2SO_4 solution are shown in Fig. 3. The early-age expansions of PFA and PFBA mortars immersed in sodium sulfate solution were higher than that of OPC mortar due to the lower strengths of the PFA and PFBA mortars compared to that of OPC mortar. After 105 days of immersion, the expansions of PC mortar exceeded those of the PFA40 and PFBA40 mortars. This was due to the incorporation of pozzolanic materials in the mixture which helped

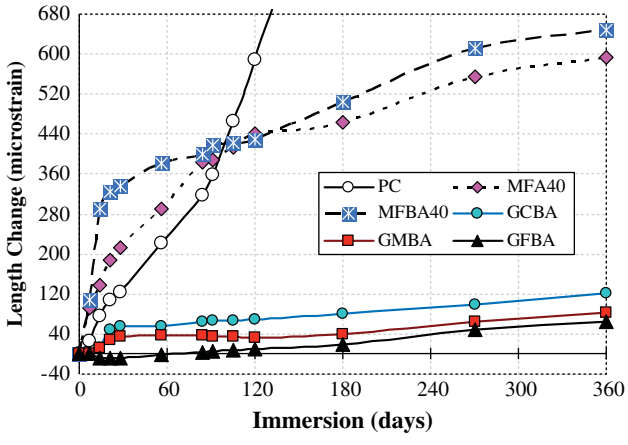


Fig. 3. Length change of mortars after immersion in 5% Na_2SO_4 solution.

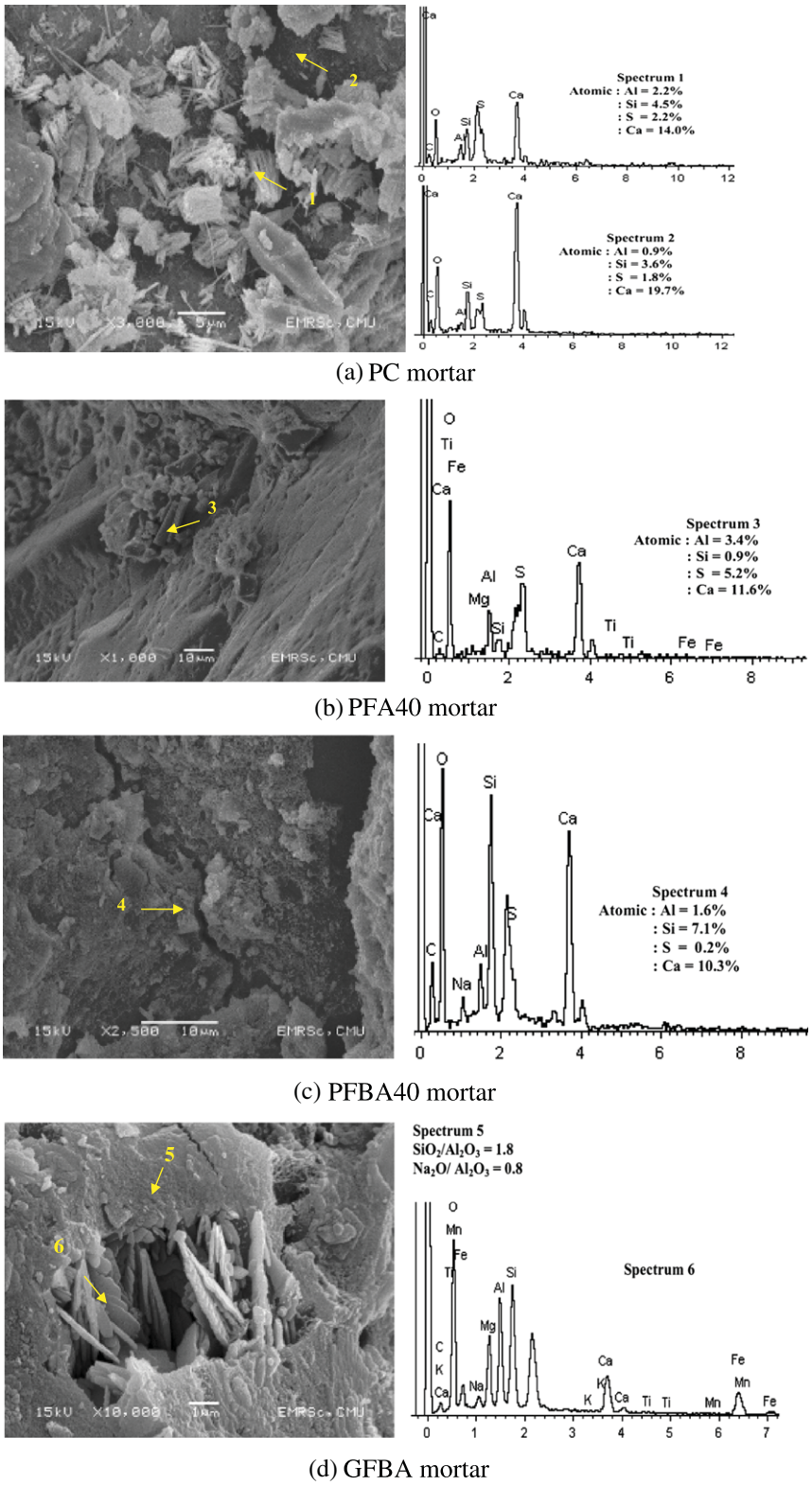
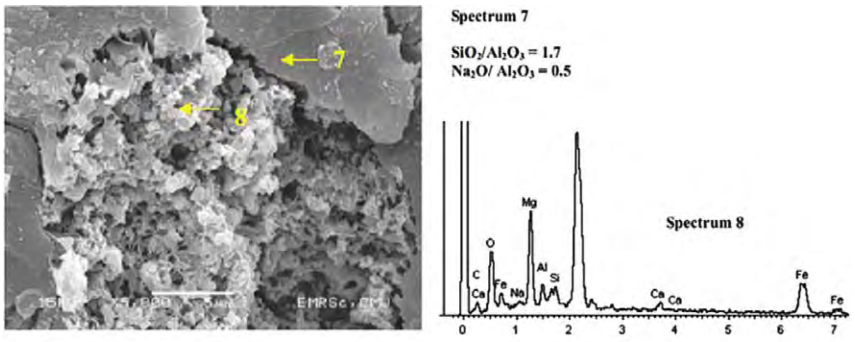


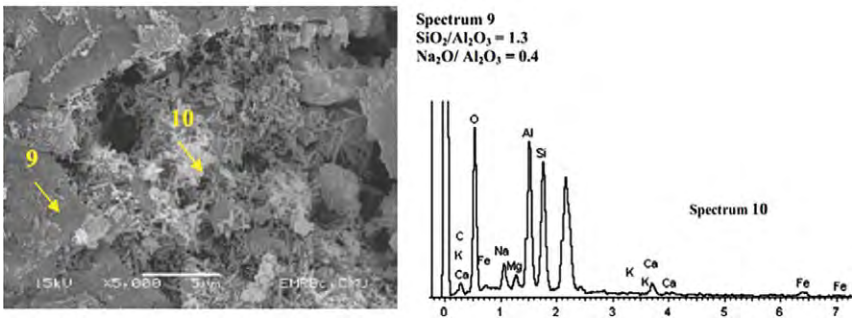
Fig. 4. SEM image and EDX spectrum of mortars after 270-day immersion in 5% Na_2SO_4 solution.

decrease the amount of $Ca(OH)_2$ and the total amount of calcium in the matrices of the PFA40 and PFBA40 mortars.

In case of the geopolymer mortars, the BA geopolymer mortars gave excellent resistance to sodium sulfate attack. After exposure to 5% Na_2SO_4 solution for 360 days, the length changes of geopolymer mortars were only 65–121 microstrain, while those of the PFA40 and PFBA40 mortars were 595 and 648 microstrain, respectively. The PC mortar exhibited the highest expansion of 7600 microstrain. The high deterioration of cement based mortars were due to the reaction of sulfate with calcium hydroxide and calcium monosulfoaluminate to form gypsum and ettringite which could lead to strength loss, expansion, cracking, and scaling of



(e) GMBA mortar



(f) GCBA mortar

Fig. 4 (*continued*)

the surface layers in mortar [27,28]. The geopolymer mortars, however, exhibited a different mechanism. The main geopolymerization products were different from Portland cement hydration products and were less susceptible to sulfate attack compared to the normal cement hydration product. Bakharev [10] found the good performance of fly ash based geopolymer in sodium and magnesium sulfate solutions and attributed this to a more stable cross-linked aluminosilicate polymer structure.

The microstructures of the matrices near the external surface of mortars after 270 days of immersion in 5% Na_2SO_4 solution were studied using Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDX) and the results are shown in Fig. 4. The SEM of cement based mortars (Fig. 4a) showed some cracks and the presence of ettringite in the samples. The EDX spectrum at area 1 showed the existence of the ettringite which could be observed in substantial quantity. The EDX spectrum at area 2 showed the background of the normal hydration products of calcium silicate and calcium aluminate hydrate. The sulfate attack on the cement matrix was associated with the ettringite and gypsum formation and the decalcification. At pH of 12–12.5 only ettringite formation took place and at pH of 8.0–11.5 gypsum formation and decalcification occurred [29]. For the PFA40 and PFBA40 mortars (Fig. 4b and c), the needle-like crystals of ettringite were not easily seen. The mass of hydration products of calcium silicate and aluminate hydrates remained intact. The contents of Ca were slightly lower at around 10.3–11.6% as compared to the values of 14–19.7% for the normal Portland cement hydration products. The attack on the $Ca(OH)_2$, calcium sulfoaluminates, and the CSH with a high C/S ratio in hardened PC paste resulted in a very porous layer whereas the attack on the low C/S CSH resulted in a protective layer of silica gel [30]. The Portland cement mortars containing pozzolans such as fly ash and rice husk ash with low calcium content, therefore, were more durable to the sulfate attack than the conventional Portland cement mortars [31].

The microstructure of BA geopolymer mortars are shown in Fig. 4d–f. The EDX spectrum showed the presence of unreacted BA particles (with the usually observed Al, Si, Fe, O, Ca, Mg, and

Table 5
Weight change of mortars after immersion in 3% of H_2SO_4.

Mix	Weight loss (%)						
	0 D	7 D	14 D	28 D	56 D	84 D	120 D
PC	0.0	−9.8	−23.1	−42.2	−66.5	−85.9	−95.7
PFA40	0.0	−1.7	−7.7	−26.1	−48.4	−71.7	−91.8
PFBA40	0.0	−0.1	−1.4	−7.3	−28.5	−52.5	−77.2
GFBA	0.0	−1.2	−2.0	−2.5	−2.8	−3.2	−3.6
GMBA	0.0	0.0	−0.4	−0.9	−1.0	−1.3	−1.7
GCBA	0.0	−0.1	−0.4	−0.8	−0.9	−1.1	−1.4

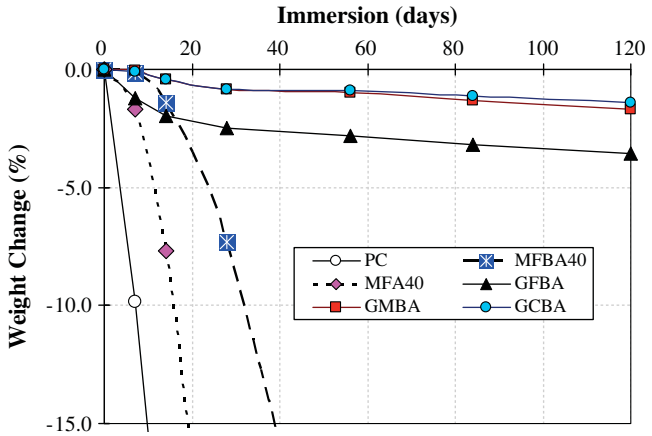


Fig. 5. Weight loss of mortar specimens after 120-day immersion in 3% H_2SO_4 solution.

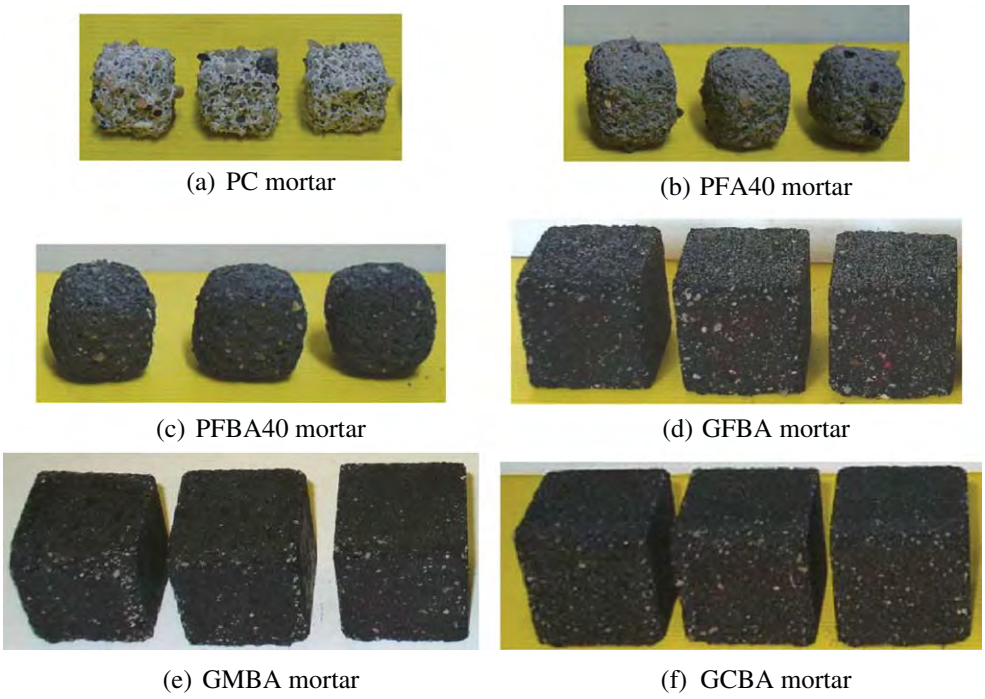


Fig. 6. Physical appearance of mortar specimens after 120-day immersion in 3% H_2SO_4 solution.

Na elements) embedded in the geopolymer matrix. These elements were the basic elements of the source BA. As compare to Portland cement mortar, this system contained significantly lower Ca content. The needle-shape like particles were also presented but only in a limited amount and could be observed in the some of the available space as shown in Fig. 4f. These needle-shape like particles were from the calcium presented in the source material as the BA was a high calcium lignite coal ash. The results confirmed that the main geopolymerization products were less susceptible to sulfate attack compared to the normal Portland cement product.

3.3. Resistance to sulfuric acid attack

Table 5 and Fig. 5 show the relationship between the weight change due to sulfuric acid attack on mortars and the immersed time. As for cement based mortars, their weight losses were due primarily on the reaction between calcium hydroxide ($Ca(OH)_2$) presented in the specimens and the acid, which can induce tensile stress, resulting in cracking and scaling of mortar. Among the cement based mortars, the PFA40 and PFBA40 mortars exhibited higher acid resistance than that of PC mortar. After 120 days of immersion in sulfuric acid solution, the weight loss of PFA40 and PFBA40 mortars were 91.8% and 77.2%, respectively, while that of PC mortar was 95.7%. The small particles of these ashes allowed a denser packing of the mixture. In addition, the siliceous compounds in FA and FBA reacted with free lime to form a more stable product of C–S–H that further filled the pores in mortars [32]. Therefore, mortars containing FA and FBA yielded lower weight loss than PC mortar.

Compared to the cement based mortars, the weight losses of all of geopolymer mortars were much lower. After 120 days of immersion, GFBA, GMBA and GCBA mortars had lost only 3.6%, 1.7%, and 1.4% of their weights, respectively. The geopolymer mortars had low weight loss under acid attack due to the low water absorption of these binders and also to their low calcium (Ca) contents compared to those of cement based mortars [33]. This result conformed with that of Thokchom et al. [34] who reported that after exposure in sulfuric acid solution for 18 weeks, the fly ash based geopolymer mortars showed a very low weight loss in the range from 0.41% to 1.23% of the initial weight. In addition, Bakharev [9] studied the resistance of fly ash geopolymer materials against 5% acetic and sulfuric acids up to 5 months exposure and found that geopolymer materials had better resistance than cement based specimens. Fig. 6 shows the physical appearance of the mortar specimens after 120 days of immersion. The cement mortars were severely deteriorated, while the geopolymer mortars seemed to be slightly damaged at the surface and around the edges of specimens.

The SEM and EDX spectrum of mortars after 120 days of immersion in 3% sulfuric acid solution are shown in Fig. 7. The EDX spectrums at areas 1 and 2 of Fig. 7a–c revealed the presence of elongated crystalline structures of gypsum ($CaSO_4 \cdot 2H_2O$) as indicated by the large presences of Ca, O, and S. The PC mortar had soft white depositions on the surface and became very porous after exposure to sulfuric acid. In the PFA40 mortar after the acid attack (Fig. 7b), abundant gypsum crystals could be seen in the morphological features similar to PC mortar. For the PFBA40 mortar (Fig. 7c), the results confirmed that the low calcium hydration products were more durable in the acid environment compared to that of high calcium hydration products in PC mortar.

The geopolymer mortars showed some delaminations at the surface, but the damage was significantly less than the cement based mortars as shown in Fig. 7d–f. The presence of $CaSO_4$ was also observed at the surface. The geopolymer mortars showed better performance than the cement based mortars when exposed to sulfuric solution due to difference in chemical and phase compositions [35]. The major components from the EDX spectrum of geopolymer mortars in the deterioration area were Si, Ca, Al, Mg, and O. The ratios of SiO_2/Al_2O_3 and Na_2O/Al_2O_3 varied between 11.5–15.7 and 0.2–0.3, respectively. The high SiO_2/Al_2O_3 and low Na_2O/Al_2O_3 ratio after deterioration were due to the leaching of Al and Na from geopolymer structure in the presence of sulfuric acid solution. This result conformed to the work of Bakharev [9] which reported that after the exposure to sulfuric acid, there was an increase of the Si/Al ratio in the fly ash based geopolymer.

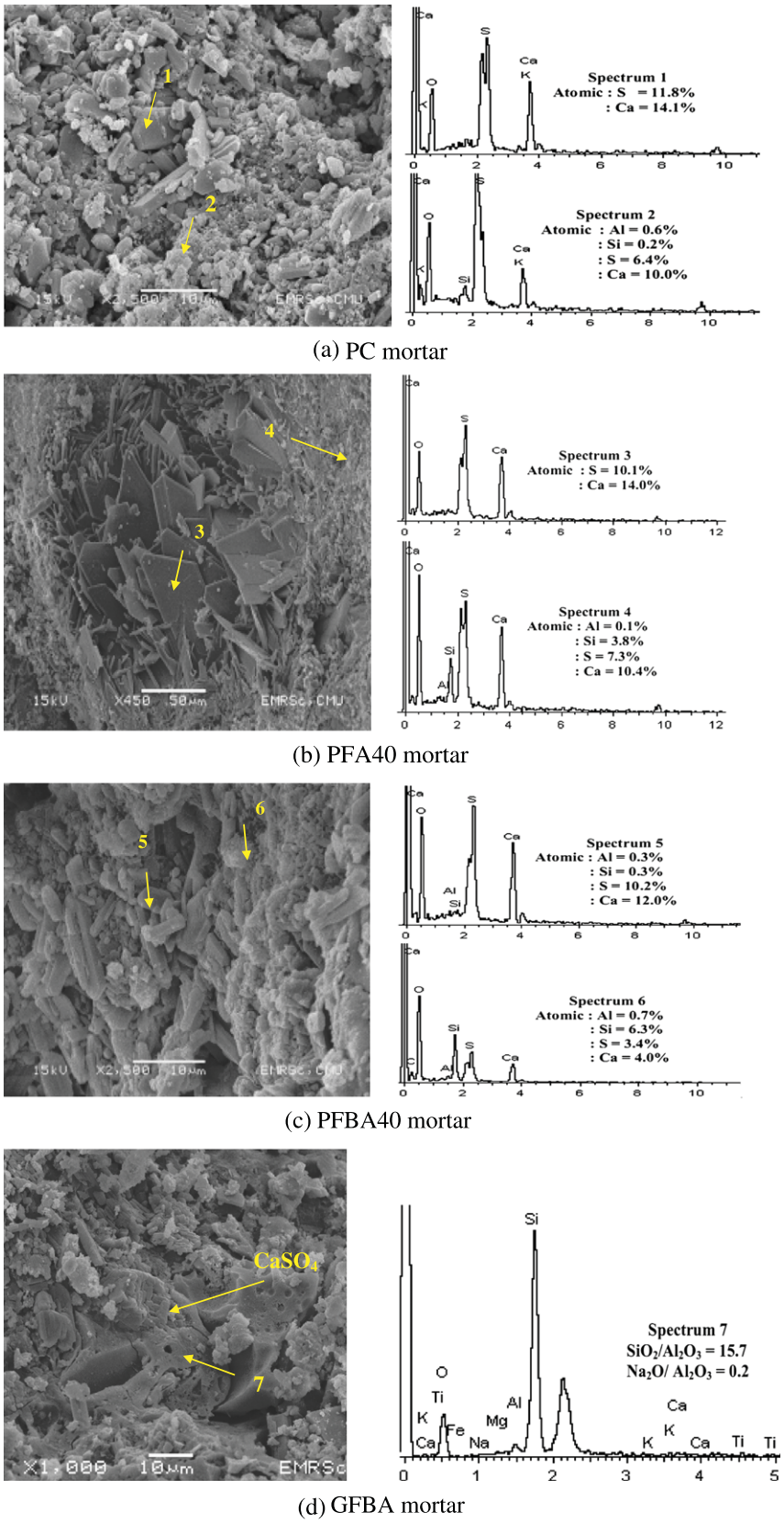
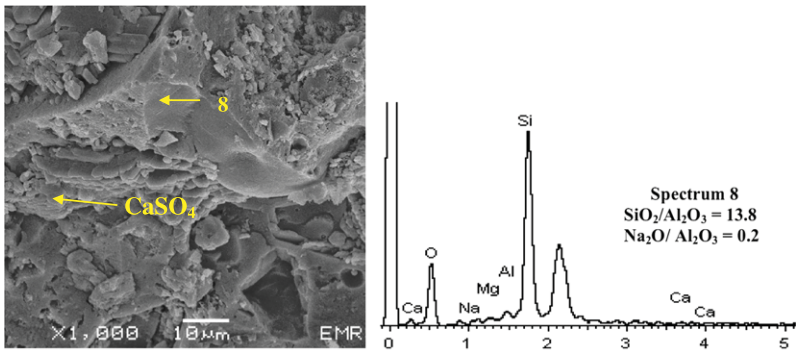
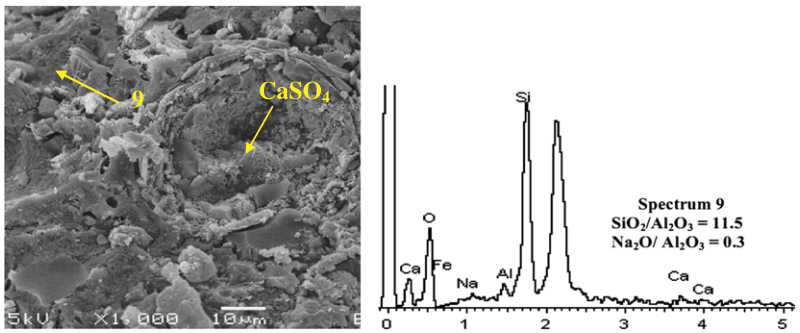


Fig. 7. SEM images and EDX spectrum of mortars after 120-day immersion in 3% H_2SO_4 solution.

Among geopolymer mortars, GCBA mortar performed significantly better than the others and showed the lowest SiO_2/Al_2O_3 ratio of 11.5. The fine BA with high surface area was more susceptible to the attack in sulfuric acid solution and thus GFBA mortar seems to deteriorate more as compared with GMBA and GCBA mortars. It is likely that the coarse BA underwent less geopolymerization and less hydration associated with the calcium as compared to those of the fine BA as indicated by the strength results. The



(e) GMBA mortar



(f) GCBA mortar

Fig. 7 (*continued*)

calcium hydration product was susceptible to the attack of the acid solution and if present in large quantity should cause the deterioration of the mortar. Hence the coarse BA geopolymer mortars performed better in the acid solution as compared to the fine BA geopolymer mortars. The good performance of Portland cement mortars containing coarse fly ash immersed in sulfuric acid as compared to that containing fine fly ash was also reported [36].

4. Conclusions

This study presents the investigations of the resistance on sulfuric acid and sulfate solutions of OPC and FA mortars, and BA geopolymer mortars. Based on the results, the following conclusions can be drawn.

(1) The compressive strengths of BA geopolymer mortars were improved with increasing the fineness of BA.
(2) The BA geopolymer mortars were less susceptible to the attack by 5% sodium sulfate solutions compared to the Portland cement based system.
(3) The deterioration of BA geopolymer mortars immersed in 3% sulfuric acid solution also showed better performance than those of PC mortars and mortars containing 40% of FA and FBA. All BA geopolymer mortars showed weight loss less than 3.6% at 120 days.
(4) The better performance of the geopolymer mortars in the sulfate and sulfuric solutions were due to the more stable cross-linked aluminosilicate polymer structure as compared to the normal Portland cement hydration structure.

Acknowledgments

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Effect of SiO_2 and Al_2O_3 on the setting and hardening of high calcium fly ash-based geopolymer systems

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Abstract This study investigates the effect of silica and alumina contents on setting, phase development, and physical properties of high calcium fly ash (ASTM Class C) geopolymers. The characteristic rapid setting properties and, hence, limited workability range of high calcium fly ash geopolymers has restricted both development and potential application of these binder systems compared to conventional geopolymer binders derived from bituminous coal, i.e., (ASTM Class F) sources or from calcined kaolin feedstocks. For this study, control of setting and hardening properties were investigated by adjusting SiO_2/Al_2O_3 ratio of the starting mix, via series of mixes formulated with varying SiO_2 or Al_2O_3 contents to achieve SiO_2/Al_2O_3 in the range 2.87–4.79. Foremost is the observation that the effect of varying silica and alumina in high calcium fly ash systems on setting and hardening properties is markedly different from that observed for traditional Class F geopolymer systems. Overall, increases in either silica or alumina content appear to shorten the setting time of high calcium-based systems unlike conventional geopolymer systems where increasing Al_2O_3 accelerates setting. The setting process was associated primarily with CSH or CASH formation. Furthermore, there appears to be a prevailing SiO_2/Al_2O_3 ratio that prolongs setting, rather than Ca^{2+} ion content itself, while NASH primarily contributes to strength development. SiO_2/Al_2O_3 ratios in the range of 3.20–3.70 resulted in products with highest strengths and longest setting times. These results suggest that initial predominance of Ca^{2+} ions and its reactions effectively help maintaining a SiO_2/Al_2O_3 ratio at which amorphous geopolymer phase is stable to influence setting and initial strength development.

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Introduction

Fly ash is the fine portion of coal combustion by-products produced at power generating stations and collected from flue gases by electrostatic precipitators [1]. In Thailand, the annual output of lignite fly ash from Mae Moh Power Station is around 3.0 million tons. Around 1.2 million tons are left over and discarded at landfill sites as a waste material [2]. Nevertheless, the chemical composition and reactivity of fly ash makes it suitable for many new product development applications, especially as a cementitious material. Since the major components of fly ash are silica (SiO_2, 60–65 wt%) and alumina (Al_2O_3, 25–30 wt%) [3], it is being considered as the main raw material for inorganic polymer (geopolymer) synthesis.

Geopolymers are obtained by alkaline activation of alumino-silicate materials. A vast number of researches have been published on fly ash-based geopolymer systems. The effect of parameters such as particle size [4–6], reactive SiO_2, and Al_2O_3 content of fly ash [7–9], concentration and type of alkaline activator [8, 10, 11, 13], curing conditions

[10–12, 14] on the physical and chemical properties of fly ash-based geopolymers has been studied in detail.

Depending on the composition of original coal, fly ash can sometimes contain considerable high amount calcium oxide (>20 wt%) and is categorized as Class C fly ash from lignite coal sources. Calcium oxide gives fly ash pozzolanic properties and, relatively shorter setting times. A few studies have been reported on geopolymer systems based on Class C fly ash [15, 16]. It has been shown that the activator (NaOH) concentration, mixing procedure, and mixing time change the leaching characteristics of fly ash [13]. In addition to the alumino-silicate geopolymer phase, the microstructure of the resulting product of alkali activated Class C fly ash included a calcium silicate hydrate (CSH) phase, similar to that obtained during hydration of Portland cement [5, 17, 18] as well as traces of gismondine (calcium alumino silicate zeolite) [15]. Ettringite was also identified as a hydration product when a mixture of Class C fly ash and Portland cement was subjected to alkaline activation [16].

The main concern when Class C fly ash is used in geopolymer synthesis is its rapid setting property and hence low workability. In general, at room temperature, final setting can be achieved within 1–2 h. The setting is believed to be due to the rapid formation of CSH phase [17]. The incorporation of admixtures such as $CaCl_2$ to geopolymer systems was found to accelerate setting with the formation of CSH and $CaCO_3$ phases while Na_2SO_4 acts as a set retarder [17]. The addition of extra water has been also reported to improve workability more than conventional superplasticizers [16].

Calcium sources are generally used to accelerate the setting of low calcium fly ash-based geopolymers [19] and metakaolin-based geopolymer systems [20, 21]. The coexistence of CSH phase with the geopolymeric gel has been shown to improve the mechanical properties of the final product [19]. The role of calcium sources such as ground granulated blast furnace slag (GGBFS), cement, wollastonite ($CaSiO_3$), and $Ca(OH)_2$ on mechanical properties of metakaolin geopolymer is reported elsewhere [20]. Specifically, the effects of different calcium silicate sources on geopolymerization seem to be highly dependent on the crystallinity and thermal history of the calcium silicate sources, as well as the alkalinity of the alkaline activator.

The effect of alumina and silica on conventional geopolymer systems has also been reported. Increases in Al_2O_3, tend to accelerate the setting of geopolymers while addition of SiO_2 inhibits the setting [22]. Nevertheless, increased SiO_2 content tends to produce microstructures with low porosity and hence enhance the strength of geopolymers [22, 23]. The effect of nano-scale silica in improving physical properties of cementitious systems has also been reported with Portland cement systems [24].

This study specifically examines the effects of silica derived from two separate sources i.e., nano-silica and rice husk ash (RHA), and alumina (nano-alumina) on the setting, microstructure, phase development, and physical properties of high calcium fly ash-based geopolymer systems.

Materials and methods

Materials

Lignite-based high calcium fly ash (mean particle size of 13.67 μm) supplied from the Mae Moh Power station in Northern of Thailand was used as the main silicate and aluminate source. The nano-silica (12 nm), RHA (125 μm), and nano-alumina (13 nm) were used as additional SiO_2 and Al_2O_3 sources, respectively. The chemical compositions of the materials used are shown in Table 1. Sodium silicate with 28.70% SiO_2, 8.90% Na_2O, and 62.50% H_2O by weight and NaOH were used as the alkaline activators.

Geopolymer synthesis

Mix formulation $Na_2O.1.17Al_2O_3.4.80SiO_2.11.45H_2O$ was used as the control mix. (This formulation provides the accepted molar ratios for ordinary geopolymers, especially $SiO_2/Al_2O_3 = 4$, with the lowest possible amount of H_2O to get the maximum consistency of paste). The control mix was prepared using fly ash, sodium silicate, and NaOH in required quantities. The other mixtures were prepared by keeping the fly ash and water content constant, but changing the silica and alumina contents, by adding nano-silica, RHA, or nano-alumina as shown in Table 2. The molar quantities of silica and alumina additions were in the range of 4.80–5.60 and 1.17–1.87, respectively.

In the preparation of mixtures, fly ash and other solids (RHA, nano silica, or alumina) were first mixed for 5 min and then mixed with required amount of 10 M NaOH solution until a homogeneous mixture was obtained. Finally,

Table 1 Chemical composition of starting materials

Chemical composition (wt%)	Fly ash	Nano-silica	RHA	Nano-alumina
SiO_2	35.21	99.00	95.92	–
Al_2O_3	16.57	–	0.13	99.00
Fe_2O_3	13.66	–	0.30	–
CaO	25.52	–	0.72	–
Na_2O	2.73	–	0.21	–
K_2O	1.99	–	2.07	–
MgO	3.28	–	0.08	–
Other oxide	1.04	1.00	0.57	1.00

Table 2 Mixture formulations of fly ash geopolymer pastes

Added SiO_2 or Al_2O_3 amount (moles)	Molar composition	SiO_2/Al_2O_3	Na_2O/SiO_2	Na_2O/Al_2O_3	CaO/SiO_2	CaO/Al_2O_3
Control mix	$Na_2O.1.17Al_2O_3.4.80\ SiO_2.11.45H_2O$	4.00	0.21	0.85	0.69	2.81
0.14SiO_2 (nano-SiO_2)	$Na_2O.1.17Al_2O_3.4.94\ SiO_2.11.45H_2O$	4.22	0.20	0.85	0.67	2.81
0.18SiO_2 (nano-SiO_2)	$Na_2O.1.17Al_2O_3.4.98\ SiO_2.11.45H_2O$	4.26	0.20	0.85	0.66	2.81
0.25SiO_2 (nano-SiO_2)	$Na_2O.1.17Al_2O_3.5.05\ SiO_2.11.45H_2O$	4.32	0.20	0.85	0.65	2.81
0.14SiO_2 (RHA)	$Na_2O.1.17Al_2O_3.4.94\ SiO_2.11.45H_2O$	4.22	0.20	0.85	0.67	2.81
0.18SiO_2 (RHA)	$Na_2O.1.17Al_2O_3.4.98\ SiO_2.11.45H_2O$	4.26	0.20	0.85	0.66	2.81
0.25SiO_2 (RHA)	$Na_2O.1.17Al_2O_3.5.05\ SiO_2.11.45H_2O$	4.32	0.20	0.85	0.65	2.81
0.50 SiO_2 (RHA)	$Na_2O.1.17Al_2O_3.5.30\ SiO_2.11.45H_2O$	4.53	0.19	0.85	0.62	2.81
0.80 SiO_2 (RHA)	$Na_2O.1.17Al_2O_3.5.60\ SiO_2.11.45H_2O$	4.79	0.18	0.85	0.59	2.81
0.20 Al_2O_3	$Na_2O.1.37Al_2O_3.4.80\ SiO_2.11.45H_2O$	3.50	0.21	0.78	0.69	2.40
0.30 Al_2O_3	$Na_2O.1.47Al_2O_3.4.80\ SiO_2.11.45H_2O$	3.27	0.21	0.68	0.69	2.24
0.33 Al_2O_3	$Na_2O.1.50Al_2O_3.4.80\ SiO_2.11.45H_2O$	3.20	0.21	0.67	0.69	2.19
0.50 Al_2O_3	$Na_2O.1.67Al_2O_3.4.80\ SiO_2.11.45H_2O$	2.87	0.21	0.60	0.69	1.97
0.70 Al_2O_3	$Na_2O.1.87Al_2O_3.4.80\ SiO_2.11.45H_2O$	2.57	0.21	0.53	0.69	1.76

sodium silicate solution was added to the mixture and mixed for further 5 min. Alkali-activated fly ash paste was then cast into 2.5 × 2.5 × 2.5 cm^3 cube molds and cured at 60 °C, 95% RH for 24 h. The X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDXA), and compressive strength analyses were studied on the hardened geopolymer paste.

A separate set of mixtures of the same mix formulation were prepared for setting time measurements. Setting time trials were performed at room temperature, i.e., 22 °C, using standard Vicat needle apparatus. At final setting time, the reaction was stopped by mixing the ground paste with acetone. XRD and SEM analyses were conducted on the dried paste samples.

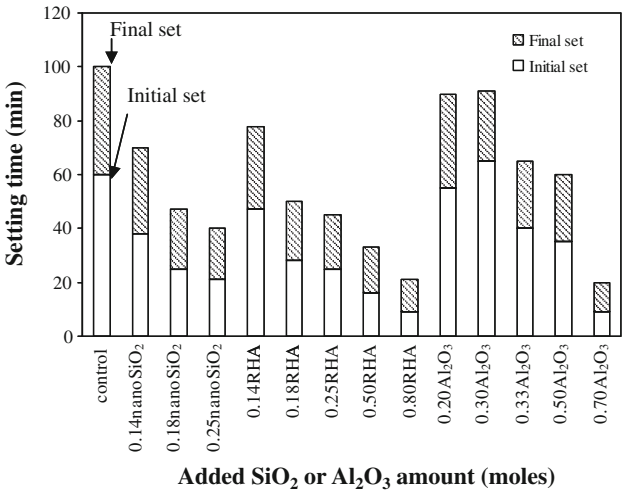


Fig. 1 Setting time of mix formulations at 22 °C

Results

Setting time

The setting time results of mix formulations investigated are shown in Fig. 1. The initial and final setting times of the control mix ($SiO_2/Al_2O_3 = 4.00$) were 60 and 100 min, respectively. These results are in line with the previously published data [17]. Irrespective of the source of silica, i.e., either nano-silica or RHA, increases of SiO_2 content of the original mix accelerated both initial and final setting. The trend is also very similar for both silica sources. Correspondingly, increasing Al_2O_3 content of the original mix also led to a decrease in both initial and final setting times of mixes with the fastest setting of less than 20 min recorded for the mix with 0.7 Al_2O_3 addition ($SiO_2/Al_2O_3 = 2.57$).

Increasing both SiO_2 and Al_2O_3 tend to accelerate setting in high calcium fly ash systems and there exists a maximum SiO_2/Al_2O_3 ratio (Fig. 4), at which the system display longest setting times. The most favorable SiO_2/Al_2O_3 ratio for setting falls within the range of 3.20–3.70.

Solid phase development by XRD

The XRD patterns of raw fly ash, fly ash geopolymer pastes with 0.80 SiO_2 addition ($SiO_2/Al_2O_3 = 4.79$) and 0.50 Al_2O_3 addition ($SiO_2/Al_2O_3 = 2.87$) at the final setting time (22 °C) and after 24 h curing at 60 °C are shown in Figs. 2a–d, 3a–d, respectively.

Solid phase development by XRD of pastes at final setting time

The XRD pattern of raw fly ash comprises mainly of amorphous phase with traces of crystalline anhydrite

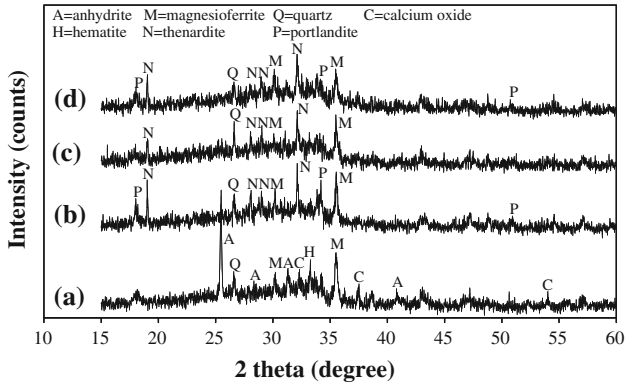


Fig. 2 XRD patterns of raw fly ash and geopolymer paste with different additives at final setting under ambient conditions. *a* fly ash, *b* control, *c* 0.80 mol of RHA, and *d* 0.50 mol of Al_2O_3

($CaSO_4$), quartz (SiO_2), magnesioferrite ($MgFe_2O_4$), calcium oxide (CaO), and hematite (Fe_2O_3). The phase distributions of samples at final setting time of activated fly ash samples are shown in Fig. 2b–d. As shown by the XRD pattern of control sample (Fig. 2b), the main changes occurring during alkali activation are the disappearance of $CaSO_4$ and CaO (originally present in fly ash) suggesting initial involvement of Ca^{+2} ions in the setting process. Trace amounts of Na_2SO_4 and $Ca(OH)_2$ are also detectable at this stage. The XRD patterns of SiO_2 rich sample (Fig. 2c) showed the presence of Na_2SO_4 only, with no sign of $Ca(OH)_2$. This suggests greater consumption of Ca^{+2} ions in the setting process when extra silica is present in the system. As with the control sample, the XRD pattern of alumina-added sample also showed the formation of new phases Na_2SO_4 and $Ca(OH)_2$. There is no unreacted Al_2O_3 present in the alumina-added sample (Fig. 2d) indicating involvement of the added alumina in the reactions during the setting period.

Calcium silicate hydrate (CSH), calcium aluminate silicate hydrate (CASH), and sodium aluminate silicate hydrate (NASH, geopolymer gel phase) are the possible phases expected to form at the setting time of these systems [25]. The presence of CSH (and or CASH) and NASH gel phases in the XRD patterns are usually associated with a broad peak around 28–30° (2θ) for the geopolymer phase and main peak at 30° (2θ) for CSH, CASH phases [21, 25–27]. There is a weak indication of the presence of humps around 28–30° (2θ) in the XRD patterns of all three samples studied, though this evidence is not firm and would require further investigation. The amorphous nature of the gel phases and the interference between peaks of other phases makes it difficult to fully identify trace reaction products. However, the involvement of Ca^{+2} ions in the setting time process can be corroborated by the disappearance of calcium containing phases in the fly ash and conversion into hydration products.

In all three mix formulations investigated, the continuous presence of quartz and magnesioferrite phases (originally present in fly ash) prevailing throughout the setting period indicates no involvement of these phases in the reactions.

Solid phase development by XRD of pastes cured at 60 °C

The XRD patterns of raw fly ash and fly ash geopolymer pastes at 60 °C with or without additives are shown in Fig. 3a–d. In all three samples examined (control, SiO_2-added, and Al_2O_3-added) the formation of geopolymer phase is strongly evident by the presence of the broad peak around 28° (2θ) and the presence of CSH phase can be confirmed by the presence of peaks at 29.35° and 32.05° (2θ). In addition, the control and Al_2O_3-added samples (Fig. 3b, d) also contain traces of unreacted $Ca(OH)_2$. However, there is no indication of the presence of $Ca(OH)_2$ in SiO_2-added sample (Fig. 3c). This further supports the argument that more Ca^{+2} ions are consumed during setting and hardening process of high calcium-based systems when extra silica is present in the system, possibly via reacting with silica.

In addition, in all three samples, there is no presence of Na_2SO_4 which had been previously detected at the setting time analysis of these samples (Fig. 2b–d). This indicates the involvement of SO_4^{-2} ions in the reaction process during curing stage. As there was no presence of ettringite-like phases detected in these samples, it is conceivable that SO_4^{-2} ions could also be involved in the geopolymer reaction. Possible incorporation of SO_4^{-2} ions in the geopolymer reaction and hence in the polymeric network structure has also been suggested in previous studies [28].

Compressive strength

The compressive strength results of paste after curing at 60 °C for 24 h are shown in Table 3.

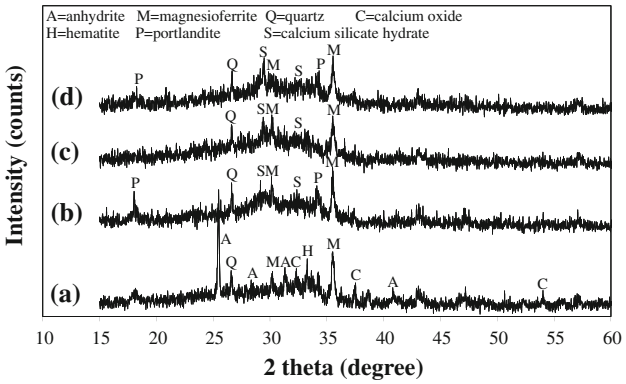


Fig. 3 XRD patterns of raw fly ash and geopolymer paste with different additives after curing at 60 °C. *a* fly ash, *b* control, *c* 0.80 mol of RHA, and *d* 0.50 mol of Al_2O_3

Table 3 Compressive strength of mix formulations

Added SiO_2 or Al_2O_3 amount (moles)	Molar composition	Compressive strength (MPa)
Control mix	$Na_2O.\ 1.17Al_2O_3.\ 4.80\ SiO_2.\ 11.45H_2O$	62.6
0.14 SiO_2 (nano-SiO_2)	$Na_2O.\ 1.17Al_2O_3.\ 4.94\ SiO_2.\ 11.45H_2O$	60.4
0.14 SiO_2 (RHA)	$Na_2O.\ 1.17Al_2O_3.\ 4.94\ SiO_2.\ 11.45H_2O$	58.3
0.50 SiO_2 (RHA)	$Na_2O.\ 1.17Al_2O_3.\ 5.30\ SiO_2.\ 11.45H_2O$	34.6
0.80 SiO_2 (RHA)	$Na_2O.\ 1.17Al_2O_3.\ 5.60\ SiO_2.\ 11.45H_2O$	30.9
0.20 Al_2O_3	$Na_2O.\ 1.37Al_2O_3.\ 4.80\ SiO_2.\ 11.45H_2O$	64.0
0.30 Al_2O_3	$Na_2O.\ 1.47Al_2O_3.\ 4.80\ SiO_2.\ 11.45H_2O$	60.0
0.50 Al_2O_3	$Na_2O.\ 1.67Al_2O_3.\ 4.80\ SiO_2.\ 11.45H_2O$	63.2

The control sample with $SiO_2/Al_2O_3 = 4.00$ had strength of 62.6 MPa. Compared to the control, 0.14 mol of SiO_2 addition ($SiO_2/Al_2O_3 = 4.22$) shows a decrease in strength with both types of silica. However, the effect of decreasing strength is also higher with increasing SiO_2 content; increase in total SiO_2 content from 4.8 to 5.8 (SiO_2/Al_2O_3 from 4.00 to 4.79) decreased the strength by about 50% (from 62.6 to 30.9 MPa) and the trend is similar with both the sources of silica.

It was particularly interesting to note that increasing Al_2O_3 content did not show any significant effect on the compressive strength, both the control ($SiO_2/Al_2O_3 = 4.00$) and 0.50 Al_2O_3 addition ($SiO_2/Al_2O_3 = 2.87$) had comparable strengths, around 63 MPa. In conventional geopolymer systems, however, increasing Al_2O_3 content ($SiO_2/Al_2O_3 < 4.00$) decreases the strength while the effect of silica appears to be similar in two systems.

Final setting times and compressive strength with respect to SiO_2/Al_2O_3 ratio

Combined final setting times and compressive strength with respect to SiO_2/Al_2O_3 molar ratio of the mixes studied are shown in Fig. 4. It is evident that setting time characteristics and strength development do not follow the same trend. Decreasing of the SiO_2/Al_2O_3 ratio (or increasing Al_2O_3) favors higher strengths reaching a maximum at around SiO_2/Al_2O_3 ratio 3.50 and remains constant thereafter. There is an optimum SiO_2/Al_2O_3 ratio (3.20–3.70) which leads to products with longest setting time with reasonably high strengths. Likewise for conventional geopolymer systems, SiO_2/Al_2O_3 ratios around 3.50–4.00 are regarded as the most suitable for optimal strength characteristics although a somewhat linear relationship between SiO_2/Al_2O_3 ratio and setting time has been suggested [29].

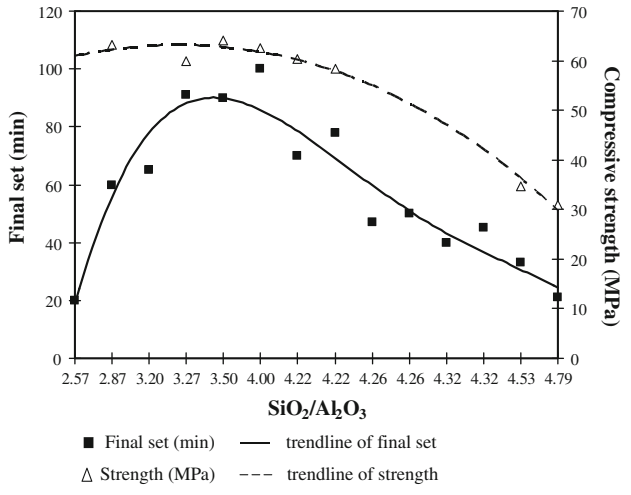


Fig. 4 Final setting times and compressive strength with respect to SiO_2/Al_2O_3 ratio

SEM/EDAX analysis of geopolymer pastes cured at 60 °C

The hardened geopolymer paste of the control sample, and samples with 0.80 mol SiO_2 (RHA) and 0.50 mol Al_2O_3 are given in Fig. 5a–c, respectively.

The control mix (Fig. 5a) consists of many unreacted fly ash particles embedded in a continuous matrix. It also contains white globules of CSH or CASH (as analyzed by EDXA) in the matrix. CSH appears to be more abundant in the silica rich sample (Fig. 5b) and this sample also consists of more developed cracks. This perhaps is responsible for the low strengths observed with this sample. Figure 5d shows a higher magnification of a fly ash particle surface with CSH formations.

The microstructure of samples containing excess alumina (Fig. 5c) appears to be somewhat different from that of the excess silica sample. In this microstructure, the white globules of CSH or CASH are concentrated in the matrix rather than on fly ash surfaces. The matrix also looks somewhat homogeneous and continuous with embedded fly ash particles and has minimal cracks. This sample produced higher strengths.

Figure 5e, f show the microstructure of hardened samples of 0.14 mol SiO_2-added samples in the form of nano-silica (Fig. 5e) and RHA (Fig. 5f). There appears to be no difference in the microstructure of these samples implying minimal effect due to arising from the source of added silica in the reaction process. These samples also had comparable strength and setting times.

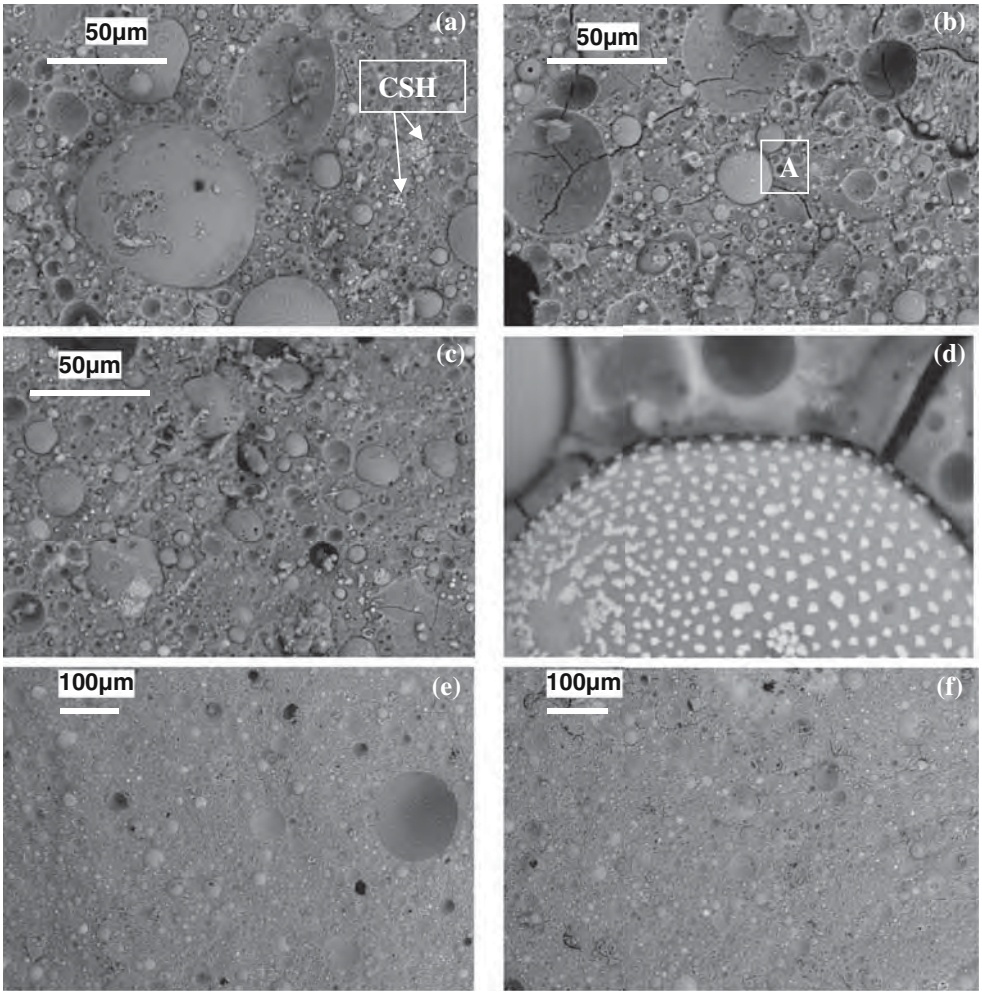


Fig. 5 SEM of fly geopolymer pastes with different additives. **a** control, **b** 0.80 mol RHA, **c** 0.50 mol Al_2O_3, **d** CSH in 0.80 mol RHA (enlarged area A), **e** 0.14 mol nano SiO_2, and **f** 0.14 mol RHA

The EDXA spot analyses on the dense matrix area of the control, 0.14 SiO_2 and 0.80 SiO_2-added and 0.5 Al_2O_3-added samples are shown in Table 4. The results are the averages of 3–4 analyses and they show the variation of elemental oxide composition of Al_2O_3, SiO_2, CaO, and SO_3. It is understood that EDXA provides semi-qualitative analysis of compositions and not a reliable indicator of exact compositions but instead represents elemental distribution of the matrix.

Table 4 The oxide content (%wt) from EDXA results

Formula	Control	0.14 SiO_2 (nano-silica)	0.14 SiO_2 (RHA)	0.80 SiO_2 (RHA)	0.50 Al_2O_3
Na_2O	15.47	14.14	14.40	22.35	14.54
MgO	3.89	2.35	1.98	1.61	1.81
Al_2O_3	9.86	10.05	10.03	7.46	18.35
SiO_2	26.34	33.11	30.33	32.59	24.46
SO_3	12.00	8.83	9.06	6.05	12.23
K_2O	1.29	1.59	1.73	1.59	1.57
CaO	21.76	20.80	22.02	22.62	19.20
FeO	9.39	9.05	8.86	5.99	7.83

In all four mix compositions investigated, a considerable amount of (6–12%) SO_3 is present in the matrix. The trend further confirms that $CaSO_4$, originally present in the fly ash, dissolved during reaction and SO_4^{-2} becomes a part of the matrix and is present in conjunction with other elements in the matrix. The percent of CaO is also comparatively higher and consistent (around 20%) in the matrix in all mix combinations confirming the presence of Ca^{+2} as CSH or CASH phases.

Discussion

The effect of increasing silica and alumina contents of high calcium fly ash systems appears different from that of traditional Class F fly ash geopolymer systems in many

ways. In particular, for conventional geopolymer systems, setting is typically associated with the sodium aluminate silicate hydrate gel (NASH) formation [22, 30]. As shown with metakaolin-based systems [30], when the system is high in SiO_2 more silicate species are available for condensation and reaction between silicate species, resulting oligomeric silicates, becomes dominant; further condensation between oligomeric silicates and aluminates result in a rigid 3D network. The rate of condensation between silicate species is slow and, this normally leads to longer setting times. Correspondingly, when the system has excess Al_2O_3, increased aluminate ($Al(OH)_4^-$) species become available for the reaction leading to a faster rate of condensation between $Al(OH)_4^-$ and silicate species and shorter setting times [30].

The key difference in high calcium-based systems is the availability of Ca^{+2} ions arising from dissolution of $CaSO_4$ and CaO. Hence, during the setting process, and considering the Na_2O-SiO_2-Al_2O_3-CaO-H_2O system as a whole, the dissolution-precipitation reactions and hence the stable equilibrium phase assemblages involving these oxides mainly have been shown to depend on the pH of the medium and oxide concentration [25]. This initial reaction pathway is typically governed by the CSH, CASH, or NASH gel formation process. As shown previously [25], at high pH (>12) and with CaO/SiO_2 (0.24–3.20) and SiO_2/Al_2O_3 (2.00–6.00), the presence of calcium degrades NASH in favor of CASH or (NC) ASH formation; $CaO/SiO_2 = 1.10$ with $SiO_2/Al_2O_3 = 6.00$ favoring CASH phase and $CaO/SiO_2 = 0.24$ with $SiO_2/Al_2O_3 = 2.00$ resulting (NC) ASH phase.

At the high pH (>13) during early hydration for the systems investigated in the present study, with CaO/SiO_2 (0.59–0.69) and SiO_2/Al_2O_3 (2.57–4.79), it is apparent that the setting process is governed by the formation of CSH or CASH-like phases rather than pure NASH. Fast dissolution of highly active Al_2O_3 and SiO_2 sources in high pH medium provides high initial concentrations of silicate ($SiO_2(OH)_2^{2-}$ or $SiO(OH)_3^{-1}$) and aluminate ($Al(OH)_4^{-1}$) to react with Ca^{+2} forming CASH phase resulting shorter setting times. Therefore, increase in both SiO_2 and Al_2O_3 tend to decrease the setting time giving an optimum SiO_2/Al_2O_3 ratio for the longest setting time.

The reaction between Ca^{+2} and aluminate, silicate species continues until all the available Ca^{+2} ions are exhausted and, with time, concentration of Ca^{+2} becomes the limiting factor for this reaction. The pH of the system also decreases with time, due to the consumption of OH^- during hydrolysis to further form silicate and aluminate species. The low pH and limited Ca^{+2} environments facilitate the polymerization reaction between silicate and aluminate species producing NASH gel.

Possible dissolution-precipitation reactions occurring during setting and hardening processes of high calcium-based systems can be presented as follows:

i. Dissolution of SiO_2, Al_2O_3 and calcium sources ($CaSO_4$ and CaO).

$$SiO_2 + Al_2O_3 \xrightarrow{OH^-} SiO_2(OH)_2^{2-} \text{or } SiO(OH)_3^{-1} + Al(OH)_4^-$$

$$CaSO_4,\ CaO \xrightarrow{H_2O} Ca^{+2} + SO_4^{-2} + OH^-$$

ii. Precipitation reactions

$$Ca^{+2} + SiO_2(OH)_2^{2-} \text{or } SiO(OH)_3^{-1} + Al(OH)_4^- \rightarrow \text{CASH gel} \quad (1)$$

$$Na^+ + SiO_2(OH)_2^{2-} \text{or } SiO(OH)_3^{-1} + Al(OH)_4^- \rightarrow \text{NASH gel} \quad (2)$$

As CASH gel is stable at high pH (>12) environments and reaction 1 is dominant in the setting process, whereas reaction 2 becomes feasible at lower pH (9–12) where NASH is stable. Therefore reaction 2 becomes secondary in these systems which is mainly responsible for strength development.

As shown by this study, sulfate, coming from dissolution of $CaSO_4$, first tend to form Na_2SO_4 rather than ettringite-like phase during early hydration and then disappear during higher temperature curing. It was evident from EDXA results that sulfate ions are most likely incorporated in the geopolymer network structure at later stages of the curing process.

Although increase in Al_2O_3 causes rapid setting of conventional geopolymer systems it also has a detrimental effect on strength development [29]. This effect on the strength has been attributed to the formation of crystalline sodium aluminate silicate (zeolitic) phases originated from NASH phases of with low SiO_2/Al_2O_3 (<3.8) ratios. The high calcium fly ash systems investigated in the present study disclose that increasing alumina ($SiO_2/Al_2O_3 = 2.87$) neither induced any zeolitic phase development (as evident from XRD results) nor showed any significant effect on initial strength development. The observation that increasing Al_2O_3 had minimal detrimental effect on the strength may also be attributed to the presence of high amounts of Ca^{+2} ions in these systems. Accordingly, the excess Al_2O_3 is rapidly consumed by Ca^{+2} during the setting process resulting in SiO_2/Al_2O_3 ratio at a higher level at which amorphous sodium aluminate silicate phase (geopolymer gel) is stable. In other words, the presence of Ca^{+2} may hinder the formation of sodium-based zeolitic phases

possibly reducing potential detrimental effect on the strength. However, further investigations are needed to confirm this hypothesis.

As with conventional geopolymer systems, increase in silica ($SiO_2/Al_2O_3 > 4$) decreased the strength of high calcium-based geopolymers irrespective of silica source with no significant differences in strength trends between the two silica sources investigated.

Conclusion

Following conclusions on high calcium-based geopolymer systems can be derived from this study:

1. Increase in both alumina or silica, accelerate the setting with an optimal SiO_2/Al_2O_3 ratio in the range 3.20–3.70 controlling setting rather than Ca^{+2} ions itself.
2. The setting process is conceivably regulated by initial CASH formation.
3. Formation of NASH at later stages of curing is mainly responsible for strength development.
4. Increasing alumina (SiO_2/Al_2O_3 up to 2.87) neither induced any zeolitic phase development nor showed significant influence on strength development contrary to ordinary geopolymers systems. Furthermore, the presence of Ca^{+2} appears to hinder the formation of sodium-based zeolitic phases thereby reducing its detrimental effect on the strength.
5. As with ordinary geopolymer systems, increase in silica ($SiO_2/Al_2O_3 > 4.3$) delivers a corresponding strength reduction for high calcium-based geopolymers. This trend is independent on silica source for the two silica sources investigated.

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Very Low Loss Tangent and High Dielectric Permittivity in Pure-$CaCu_3Ti_4O_{12}$ Ceramics Prepared by a Modified Sol-Gel Process

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We present a simple strategy to achieve excellent dielectric and nonlinear current–voltage properties for pure–$CaCu_3Ti_4O_{12}$ ceramics prepared by a modified sol–gel method with different calcining conditions. At 1 kHz and room temperature, the best CCTO ceramic can exhibit a high dielectric constant (ε') of 9516 with a very low dielectric loss, tan δ ~0.020. The minimum value of tan δ is 0.018 at 2.5 kHz with ε' ~9433. High breakdown field of 4032 V/cm and nonlinear coefficient of 7.05 were obtained.

I. Introduction

Development of novel functional materials for electronic applications has recently been motivated by device miniaturization. $CaCu_3Ti_4O_{12}$ (CCTO) gained considerable attention due to its high and nearly temperature independent dielectric constant (ε' ~10^3–10^5) over the range of 100–600 K.[1–13] Generally, the degree of electronic device miniaturization utilizing capacitive components is decided by the value of the material's ε' value. The size of such devices can be reduced by replacing dielectric layers with a relative high–dielectric material. CCTO can exhibit nonlinear current–voltage behavior,[2,8–10] resulting from Schottky barriers at grain boundaries (GBs). This is desirable for application in varistors.

Unfortunately, the loss tangent for CCTO ceramics is still too large (tan δ >0.05 at 1 kHz), making them unsuitable for many applications. Therefore, reduction of this high tan δ for CCTO ceramics is an important and urgent issue requiring investigation. Improvement of tan δ in CCTO ceramics using dopants has been extensively studied.[3,5,11] However, improvement of dielectric properties of pure–CCTO was rarely reported. Sun *et al.*,[9] reported values of ε'~2–4 × 10^4 and tan δ ~0.04 [at 1 kHz and room temperature (RT)] for CCTO ceramics prepared by a sol–gel process. Previously, we reported values of ε' ~5.1 × 10^3 and tan δ ~0.048 (at 1 kHz and RT) for a CCTO ceramic prepared by using a very simple method.[10] From these reports, we observed that sources of Ca and Cu ions used to synthesize the high–performance CCTO ceramics were obtained from Ca– and Cu–acetates whereas most investigations used Ca– and Cu–nitrates as sources.[7,13] We therefore expect that CCTO ceramics, prepared from Ca– and Cu– acetates by using suitable chemical route, may show better performance of dielectric properties.

In this work, we successfully prepared pure–CCTO ceramics with high–performance dielectric properties by using a modified sol–gel method using Ca– and Cu–acetates as sources of Ca^{2+} and Cu^{2+} ions. The best CCTO ceramic exhibited high ε' ~9516 and very low tanδ ~0.020, respectively. A high breakdown electric field (E_b) value was found, 4,032 V/cm, with a nonlinear coefficient (α) of ~ 7.05.

II. Experimental Procedure

By using a modified sol–gel method, $CaCu_3Ti_4O_{12}$ was prepared as follows. Firstly, stoichiometric amounts of Ca $(C_2H_3CO_2)_2.H_2O$ and $Cu(CH_3COO)_2.H_2O$ were dissolved in an aqueous solution of citric acid and ethylene glycol with constant stirring at RT. Secondly, $C_{16}H_{28}O_6Ti$ was dissolved slowly in the above solution. Then, several drops of ethanol were added to the mixture and heated to 250°C without stirring. After several minutes, a clean and transparent solution was obtained. This solution was further heated to 150°C until it formed a viscous gel. This gel was decomposed in air at 350°C for 1 h. The precursor was ground and calcined in air at 850°C for 2 h (P1), 850°C for 8 h (P2), and 900°C for 4 h (P3). These CCTO powders were pressed by uniaxial compression at 200 MPa into disks having 9.5 mm diameter and thickness ~1–2 mm. Finally, these disks were sintered in air at 1100°C for 6 h. CCTO ceramics sintered using the P1, P2, and P3 powders were referred to as the CCTO-1, CCTO-2, and CCTO-3 samples, respectively.

The X-ray diffraction (XRD) process (PW3040 Philips; Eindhoven, the Netherlands), scanning electron microscopy (SEM) (LEO 1450VP; Cambridge, UK), and transmission electron microscopy (TEM) (FEI Tecnai G^2, Eindhoven, the Netherlands) were used to characterize the CCTO powders and ceramics. Ceramics were polished and sputtered with Au on pellet surfaces using a Polaron SC500 (Sussex, UK) sput-

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ter coating unit. The dielectric properties were measured using an Agilent E4980A (Hayward, CA) Precision LCR Meter over the frequency range of 10^2–10^6 Hz with an oscillation voltage 1 V. Current–voltage measurements were made using a high voltage measurement unit (Keithley Model 247, Estado St Pasadena, CA). The rise rate of the source voltage is 1.3 V/s. The values of E_b and α were obtained at a current density (J) of 1 mA/cm^2 and in the range of 1–10 mA/cm^2.

III. Results and Discussion

The XRD patterns of CCTO powders that were calcined under various conditions and CCTO ceramics sintered at 1100°C for 6 h prepared from different powders are shown in Fig. 1. These XRD patterns confirm the formation of the $CaCu_3Ti_4O_{12}$ phase (JCPDS card no. 75–2188) in powders and sintered ceramics. The main phase of CCTO was detected in both powders and ceramics. However, diffraction peaks corresponding to impurity phases of CuO and TiO_2 still appeared in the XRD pattern of P1 powder (calcined at 850°C for 2 h). These impurities were greatly reduced by increasing sintering time to 8 h (P2 powder), and cannot be detected in P3 powder (calcined at 900°C for 4 h). Pure–CCTO phase was observed in all CCTO ceramics sintered from these three powders. The values of lattice parameters calculated from the XRD patterns were found to be 7.389, 7.387, 7.389, 7.393, 7.391, and 7.393 Å for P1, P2, P3, CCTO-1, CCTO-2, and CCTO-3 samples, respectively. These values are comparable to the literature value of 7.391 Å.[1]

Microstructure of CCTO ceramics is shown in Figs. 2(a)–(c), revealing grain and GB structures. The presence of impurity phases in P1 powder has a significant influence on the microstructure of sintered CCTO-1 ceramic. The microstructure of the CCTO-1 ceramic shows a large amount of pores; CCTO-2 and CCTO-3 ceramics are relatively dense. Generally, the densification and grain growth processes in polycrystalline ceramics are primarily caused by matter transport, e.g., diffusion of atoms, ions, and charged species. For CCTO ceramics, these processes are related to the liquid phase sintering mechanism.[4] In the first stage of sintering processes, particles of the CuO secondary phase melted into the liquid state due to their relatively low melting point. This leads to enhanced densification through enhanced rearrangement of CCTO particles and enhanced matter transport through the liquid. However, the second–phase particles of TiO_2 (and perhaps $CaTiO_3$) remained as solid-state particles, which were insoluble in this state. The rate of grain growth, i.e., the movement of GBs, is inhibited by TiO_2 solid particles. In the latter stage, the second phases of CuO and TiO_2 were interred into CCTO lattices, forming a solid solution. As seen in the XRD pattern of CCTO-1 ceramic, there were

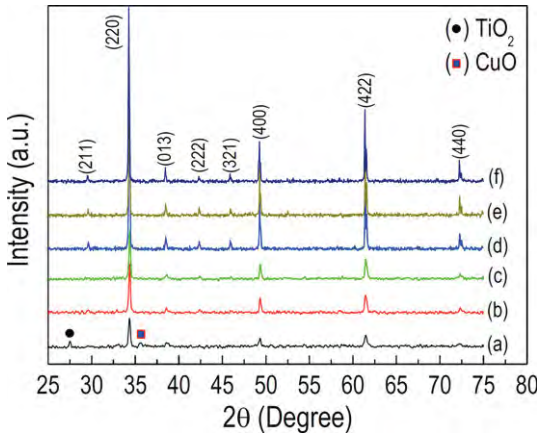


Fig. 1. XRD patterns of $CaCu_3Ti_4O_{12}$ powders calcined at (a) 850°C for 2 h, (b) 850°C for 8 h, (c) 900°C for 4 h, (d) CCTO-1, (e) CCTO-2, and (f) CCTO-3 ceramic samples.

no observed CuO and TiO_2 secondary phases. Generally, densification process is slow in the final stage due to the long distances of diffusion.[14] During this process, the formation rate of solid solution was much higher than the densification rate, resulting in pore formation in the microstructure of CCTO-1 ceramic. Fig. 2(d) shows a TEM image of P3 CCTO particles, revealing a large distribution of particle sizes ~80–200 nm.

Figure. 3(a) shows frequency dependence of ε' at RT for CCTO ceramics synthesized from different ceramic powders. It was found that calcining conditions have significant influences on both the microstructure and ε' of CCTO ceramics. Interestingly, CCTO-2 and CCTO-3 ceramics exhibit high ε' ~8291 and 9516, respectively, with very low tan δ (0.022 and 0.020, respectively). As shown in Fig. 3(b), tan δ values of all ceramics are lower than 0.05 in the frequency range from 0.1 kHz to 30 kHz. The lowest tan δ value was found to be 0.018 at 2.5 kHz with ε' ~9433 for CCTO-3 ceramic. To our knowledge, this is the lowest tan δ for pure–CCTO ceramics that can exhibit ε' of ~10^4. As shown in the inset of Fig. 3(b), ε' of CCTO ceramic tends to be enhanced with increasing calcination time and temperature; concurrently, tan δ tends to decrease gradually.

Generally, total energy loss in dielectric materials is the sum of loss due to the dielectric relaxation process and loss due to DC conductivity.[6] The total loss tangent can be expressed as,[15]

$$\tan\delta = \frac{\omega^2\varepsilon_0\tau(\varepsilon'_s - \varepsilon'_\infty) + (1+\omega^2\tau^2)\sigma_{dc}}{\omega\varepsilon_0(\varepsilon'_s + \varepsilon'_\infty\omega^2\tau^2)}, \quad (1)$$

where ε'_s and ε'_∞ are, respectively, the static and high - frequency limits of dielectric permittivity, τ is relaxation time, ε_0 is permittivity of free space, and σ_{dc} is DC conductivity. At low frequencies, $\omega\tau \ll 1$, Eq. (1) is estimated to be

$$\tan\delta \approx \frac{\sigma_{dc}}{\omega\varepsilon_0\varepsilon'_s}. \quad (2)$$

According to the Maxwell–Wagner polarization model for CCTO ceramics,[16] σ_{dc} can be expressed as $\sigma_{dc} = 1/C_0(R_g + R_{gb})$, where R_g and R_{gb} are grain and GB resistances, respectively, and C_0 is empty cell capacitance. For CCTO ceramics, $R_g \ll R_{gb}$. Therefore, σ_{dc} is decreased by increasing R_{gb}, resulting in the reduction of tan δ. Very low tan δ values for CCTO-2 and CCTO-3 ceramics are attributed to their high R_{gb}. However, values of R_{gb} at RT cannot be calculated because the semicircle arc corresponding to the GB response does not appear in an impedance plot.

To study the physical nature of electrical transport at the GBs for CCTO ceramic samples, non - Ohmic characteristics were investigated. Fig. 4 shows the nonlinear current density–electric field (J–E) characteristics at RT for CCTO-2 and CCTO-3 ceramics. The inset of Fig. 4 shows the J–E characteristics at RT for CCTO-1 ceramics. It is now widely accepted that non - Ohmic behavior and electrical response at GBs of CCTO ceramics likely are caused by a Schottky–type potential barrier.[2,9,17,18] α values of the CCTO-1, CCTO-2, and CCTO-3 samples were found to be 1.98, 7.05, and 5.83, respectively. E_b values were found to be 1064, 4032, and 2268 V/cm, respectively. The CCTO-2 ceramic shows the best varistor properties among the three samples. To our knowledge, 4032 V/cm is a higher E_b value than any reported in literature for pure–CCTO ceramics with grain sizes less than 10 μm.[2,9,10,17,18] The values of E_b and α for the CCTO-2 ceramic are comparable to the values observed in TiO_2–rich $CaCu_3Ti_{5.5}O_{12}$ ceramic (E_b = 3910 V/cm and α = 7.9).[17]

Non–Ohmic properties of CCTO ceramics can be improved by annealing CCTO in oxygen–rich atmospheres[18] and increasing the molar ratio of Ti from the stoichiometric value of $CaCu_3Ti_4O_{12}$.[17] These are effective methods to enhance non

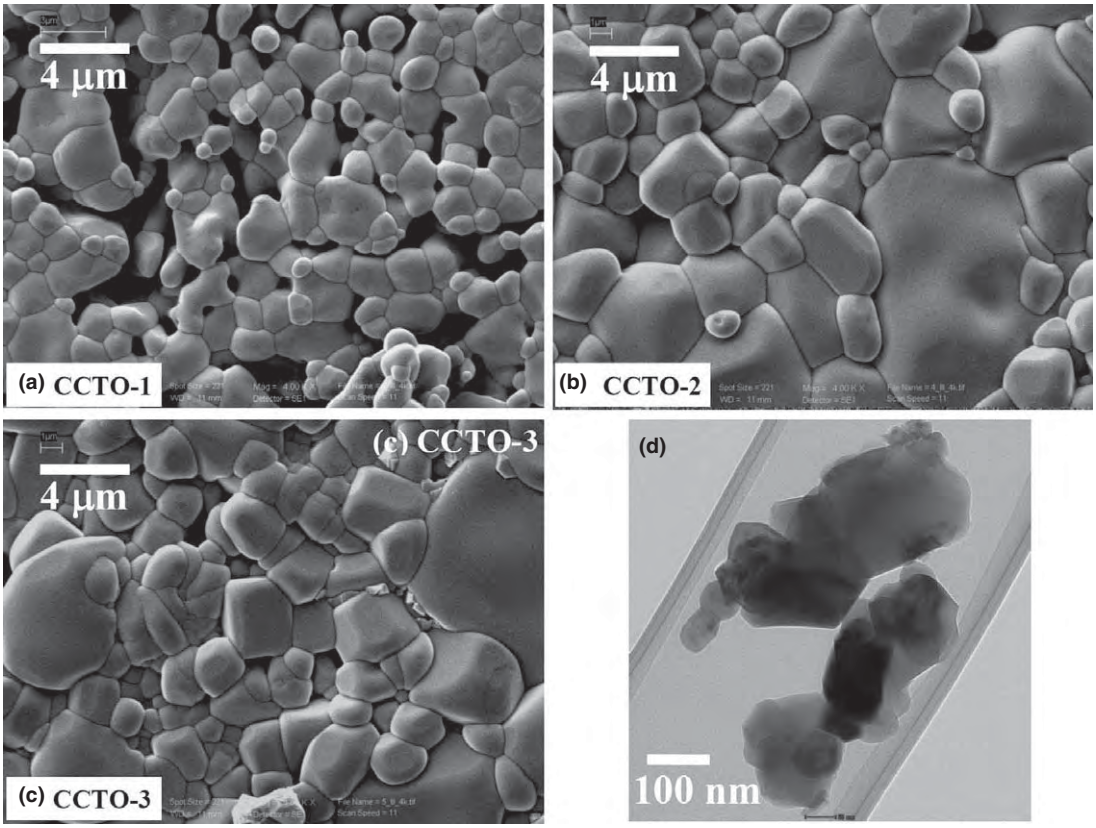


Fig. 2. SEM images of surface morphologies for (a) CCTO-1, (b) CCTO-2, (c) CCTO-3 ceramic samples, and (d) TEM image of CCTO-3 powder.

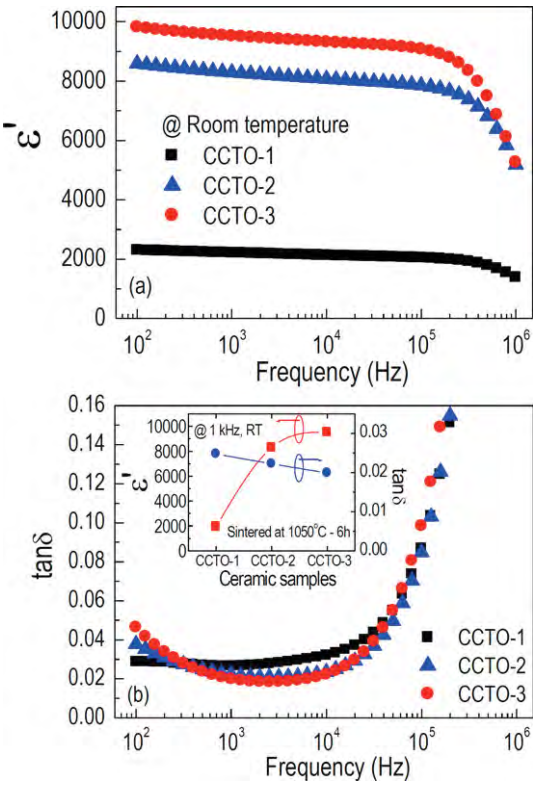


Fig. 3. Frequency dependence of (a) ε′ and (b) tan δ at RT for $CaCu_3Ti_4O_{12}$ ceramics; inset shows values of ε′ and tan δ for $CaCu_3Ti_4O_{12}$ ceramics.

–Ohmic properties of CCTO ceramics. This indicates that a Schottky–type potential barrier at GBs is related to oxygen content. Generally, high R_{gb} in electroceramics is caused by

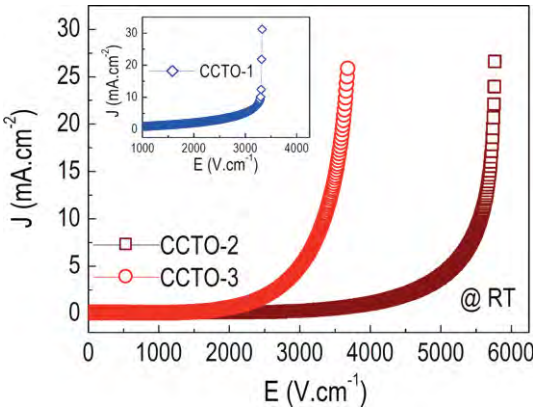


Fig. 4. Non-Ohmic characteristics (*J-E* curves) of CCTO-2 and CCTO-3 ceramic samples; inset shows *J-E* curve of CCTO-1 sample.

one of two phenomena i.e., the existence of a space charge layer at the GB with higher oxygen concentration and a second phase acting as insulating film at GBs. These may cause high R_{gb} for CCTO ceramics. It was found that tan δ decreased with increasing E_b.[9,10,17] Thus, very low tan δ values for CCTO-2 and CCTO-3 ceramics are associated with unusually high E_b values. It is difficult to explain how starting material types affect the electrical properties of GBs. It is most likely that preparation CCTO ceramics by this manner modifies the defect equilibrium at GBs. We propose that investigation of new chemical routes to synthesize CCTO ceramics using Ca– and Cu–acetates is a potential way to further improve dielectric properties of CCTO ceramics.

IV. Conclusions

In conclusion, CCTO ceramics prepared using Ca– and Cu–acetates as starting raw materials showed excellent dielectric

properties. The best pure–CCTO ceramic can exhibit an ultra low–tan δ of ~0.020 at 1 kHz; whereas ε′ is still too large at 9516. The best non–Ohmic properties with high values of E_a and α were found to be 4032 V/cm and 7.05, respectively.

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Improved geopolymerization of bottom ash by incorporating fly ash and using waste gypsum as additive

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ABSTRACT

This research studied the improvement of the geopolymerization of bottom ash (BA) by incorporating fly ash (FA) and using flue gas desulfurization gypsum (FGDG) as additive. The BA:FA ratios of 100:0, 75:25, 50:50, 25:75, and 0:100 were used as the blended source materials. The source materials were then replaced with 0%, 5%, 10%, and 15% of FGDG. NaOH, sodium silicate and temperature curing were used to activate the geopolymer. Test results indicated that the increase in FA content in the BA–FA blends improved the strengths of geopolymer mortars owing to the high glassy phase content and high reactivity of FA compared to those of BA. The use of up to 10% of FGDG as additive also significantly increased the strengths of geopolymer. In this case, the compressive strength enhancement was due to the increase in the Al^{3+} leached from BA in the presence of SO_4^{2-} and the formation of additional calcium silicate hydrate.
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1. Introduction

Geopolymer is an alkali-activated aluminosilicate cementitious material with a much smaller CO_2 footprint than traditional Portland cement [1]. Several researches have shown that it possesses good strength and mechanical properties [2]. Geopolymerization process relies on the reaction of silica and alumina with high alkali solution. The source materials can, therefore, be industrial or agricultural by-products and solid waste containing silica and/or alumina.

The use of bottom ash (BA) for making alternative cementitious material can both reduce the growth of Portland cement usage and help solve the problem of waste discard at landfill site. BA can also be used as replacement for sand in mortar and concrete [3]. Mae Moh power plant in northern Thailand produces around 0.8 million tons of pulverized coal combustion (PCC) BA per year. Ground to a proper fineness, this BA can be used as source material for making geopolymer with reasonable strength [4]. Research has also shown that the strength of BA geopolymer was lower than that of FA geopolymer [5]. The physical differences such as morphology, particle size, surface properties, and amorphous phase content affect their abilities to react in geopolymer syntheses [6]. For instance, FA is composed of spherical shape and contains high content of amorphous phase which can greatly improve the compressive strength of geopolymer. In contrast, BA comprises of large fragments with only a small amount of semi-spherical particles [7] and less glassy constituent phase [8].

FA is a good pozzolan and is widely used to replace Portland cement to improve the properties of concrete [9,10]. Both PCC class C and class F fly ashes are good source materials for producing geopolymer [11,12]. To improve the reactivity of low grade source material such as fluidized bed combustion ashes, it is blended with a good source of silica and alumina such as PCC FA and metakaolin [13,14]. The PCC FA is able to increase the workability of the blended ash mixes, contribute to the packing of the source material and thus enhances the strength of the geopolymer products [13].

In the process of burning of coal to generate electricity, many power plants need to reduce the amount of sulfur emission to the atmosphere. The method of desulfurization results in waste material called flue gas desulfurization gypsum (FGDG) in the form of calcium sulfate. Up to now, this waste gypsum has not been utilized and has been discarded at landfill site. It is known that the incorporation of gypsum alters the performances of the Portland cement concrete. Similarly in geopolymer, the addition of gypsum can enhance the degree of geopolymerization [15]. The leaching of alumina can be improved with the presence of sulfate and thus leads to the strength enhancement [16].

The present work aims to improve the strength development of BA geopolymer mortars with the addition of PCC FA and the use of FGDG as additive. This knowledge would be beneficial to the utilization of these waste materials.

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2. Materials and methods

2.1. Materials

PCC FA, PCC BA and FGDG from Mae Moh Power Plant in northern Thailand were used. BA was ground and used as the main source material for making geopolymer. The as-received FA was used to replace part of BA to improve the quality of the main source material. FGDG was oven dried at 105 °C, ground and used as additive to improve the strength of the geopolymer. The chemical and mineralogical compositions of FA, BA and FGDG are shown in Table 1. The major oxides of BA and FA were SiO_2, Al_2O_3, Fe_2O_3, and CaO with a small SO_3 content. The main compositions of FGDG were CaO and SO_3 oxides. The physical characteristics of materials are shown in Table 2. The median particle sizes of BA, FA, and FGDG were 32.2, 63.5, and 10.3 μ, the percentages retained on No. 325 sieve were 33, 50 and 3 and the specific gravity were 2.86, 2.52, and 2.39, respectively. Sodium hydroxide solution (NaOH) at 10 M concentration and sodium silicate solution (NS) with 13.8% Na_2O, 32.2% SiO_2, and 54.0% H_2O by weight were used as alkali activators. The local river sand with specific gravity of 2.62 and fineness modulus of 2.85 in saturated surface dry condition was used for making geopolymer mortars. The XRD patterns of BA and FA are shown in Fig. 1. Both of BA and FA contained glassy phase and some crystalline phases of quartz (Q: SiO_2), calcium oxide (C: CaO), and hematite (H: Fe_2O_3). The phases of mullite (M: $A_{l6}Si_2O_{13}$) and anhydrite (A: $CaSO_4$) were only found in FA, while anorthite (N: $CaAl_2Si_3O_8$) and augite (U: $(Ca(Mg,Al)(Si_2,Al)O_6$) were found in BA. The broad hump around 26° (2θ) of BA was smaller than that of FA indicating that the glassy phase of BA was lower than that of FA.

2.2. Details of mixes and tests

The NS/NaOH ratio of 1.0, liquid/ash (L/A) ratio of 0.6 and ash/sand ratio of 2.75 were used for making geopolymer. BA was replaced with FA to obtain the blended source materials with BA:FA ratios of 0:100, 25:75, 50:50, 75:25, and 100:0. The blended ashes were replaced with 0%, 5%, 10%, and 15% of FGDG by weight. Table 3 gives the details of mix proportions and molar oxide ratios. The SiO_2/Al_2O_3, Na_2O/SiO_2 and H_2O/Na_2O ratios were 4.56–4.76, 0.30–0.35 and 9.0–10.0, respectively which are comparable to the optimum values of $SiO_2/Al_2O_3 = 3.0$, $Na_2O/SiO_2 = 0.3$ and $H_2O/Na_2O = 10.0$ for metakaolin geopolymers [17].

The samples were prepared by mixing BA, FA, and FGDG until the uniform color was obtained. The NaOH was then added and mixed for 5 min. The NS solution was added and mixed for another 5 min. (For geopolymer mortar, sand was then added and mixed again for 5 more minutes). After mixing, the fresh paste or mortar was casted into plastic 5 × 5 × 5 cm cubic molds in accordance with ASTM C109 [18] and subjected to final vibration of 10 s. The molds were then wrapped with polyvinyl sheet to prevent a loss of moisture. Samples were cured in an electric oven at 40 °C for 48 h and then kept at 25 °C and 50% R.H. room. At the age of 7 days, the mortar samples were tested for compressive strengths in accordance with ASTM C109. The paste samples at 28 days were used for the investigations of microstructures. The fractured surfaces were coated with gold and scanned using JEOL scanning electron microscope (SEM). The pastes were ground to particle size less than 75 μ (passed sieve No. 200) and used for XRD analysis using PANalytical X-ray diffractometer with CuKα radiation and fourier transform infrared spectroscopy (FT-IR) at the range of 4000–400 cm^{-1}.

Table 2
Physical characteristics of BA, FA and FGDG.

Materials	Median particles size (μ)	Specific gravity	Retained on sieve #325%
BA	32.2	2.86	33
FA	63.5	2.52	50
FGDG	10.3	2.39	3

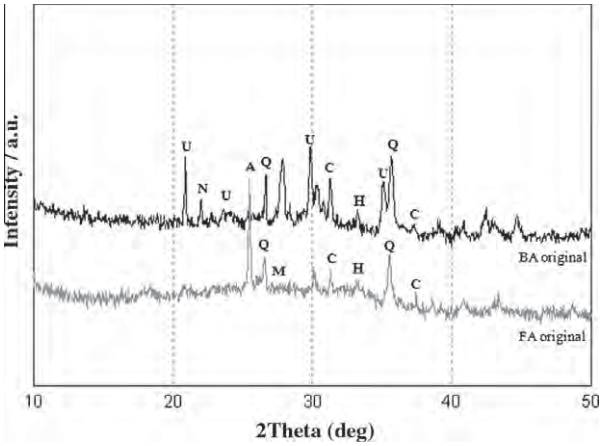


Fig. 1. XRD patterns of BA and FA original.

3. Results and discussion

3.1. Compressive strength

The compressive strengths of BA and FA geopolymer mortars with different FGDG contents are shown in Fig. 2. Without FGDG,

Table 1
Chemical and mineralogical compositions of BA, FA and FGDG.

Chemical Composition (%)	Raw materials		
	BA	FA	FGDG
CaO	13.0	24.5	37.7
SiO_2	35.5	35.2	4.0
Al_2O_3	16.8	16.5	2.0
Fe_2O_3	15.1	13.6	0.5
SO_3	0.6	1.6	54.1
Na_2O	3.8	2.7	0.0
MgO	8.4	3.2	1.6
K_2O	1.8	1.9	0.1
P_2O_5	0.2	0.2	0.0
TiO_2	0.3	0.3	0.0
Loss on ignition	4.7	0.4	14.7
Mineral composition	Quartz, anorthite, augite, magnetite, mullite	Anhydrite, quartz, magnetite, calcium oxide, mullite	Gypsum

Table 3
Mix proportions of BA and/or FA geopolymer with FGDG.

Series	BA:FA	FGDG (%)	SiO_2/Al_2O_3	Na_2O/ SiO_2	H_20/ Na_2O	Ms
A	100:0	0	4.56	0.32	9.00	3.11
		5	4.61	0.33	9.11	3.04
		10	4.65	0.34	9.23	2.97
		15	4.71	0.35	9.35	2.90
B	75:25	0	4.57	0.32	9.16	3.16
		5	4.62	0.32	9.28	3.09
		10	4.67	0.33	9.39	3.01
		15	4.72	0.34	9.51	2.94
C	50:50	0	4.59	0.31	9.34	3.22
		5	4.63	0.32	9.45	3.14
		10	4.68	0.33	9.55	3.06
		15	4.73	0.34	9.67	2.98
D	25:75	0	4.60	0.31	9.52	3.28
		5	4.64	0.31	9.62	3.19
		10	4.69	0.32	9.72	3.11
		15	4.75	0.33	9.83	3.03
E	0:100	0	4.61	0.30	9.71	3.33
		5	4.66	0.31	9.80	3.25
		10	4.71	0.32	9.90	3.16
		15	4.76	0.33	10.00	3.08

Note: water/solid = 0.30.

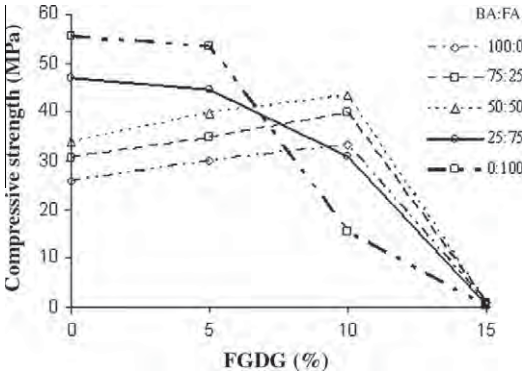


Fig. 2. Compressive strength of BA and FA geopolymer mortars with 0–15% FGDG.

the compressive strengths of pure BA and FA geopolymer mortars were 25.5 and 55.5 MPa, respectively. The degree of geopolymerization of the FA geopolymer is higher than that of the BA geopolymer [5] owing to the high glassy phase content and higher reactivity of FA compared to those of BA. Additionally, Ca^{2+} reacted with silicate from FA and formed additional calcium silicate hydrate (CSH) gel [15,19]. The strength of blended geopolymer mortars, therefore, improved with the increase in the FA content. For the low FA content of 0%, 25%, and 50%, the strengths of geopolymer mortars were reasonable at 25.5, 30.5, and 34.0 MPa, respectively. The addition of 5–10% of FGDG significantly increased the compressive strengths of mortars. For example, the strength of 75:25 (BA:FA) blend replaced with 0%, 5%, and 10% FGDG mortars were 30.5, 35.0, and 40.0 MPa. The strength enhancement was due to the increased Ca^{2+} reacted with silicate and formed additional CSH and also reacted with aluminosilicate group and strengthened the aluminosilicate network [20]. In addition, SO_4^{2-} ions in the system promoted the dissolution of Al^{3+} ions in BA [21] and led to a stronger geopolymer.

When the FGDG content was increased to 15%, the strengths of all mortar mixes were very low between 0.3 and 1.0 MPa. The high FGDG content obstructed the geopolymerzation process and drastically reduced the strength of the mortar. Also for the high FA content of 75% and 100% where the strength of mortars were already high, the incorporation of FGDG decreased the strength of mortars. The reduction was dependent on the replacement level. At low replacement level of 5% of FGDG, the strengths were slightly reduced. The strength reductions were significant when the replacement levels were 10% and 15%. For the high FA blended mixture, the dissolution of the Si and Al ions was already in a good state and hence the addition of FGDG did not enhance the dissolution of Al ions.

In normal geopolymer system, the molar SiO_2/Na_2O ratios or Ms has a significant effect on strength [22]. The Ms values and strengths of geopolymer mortars were, therefore, plotted as shown in Fig. 3. At low 0% and 5% FGDG, the compressive strengths increased with Ms as expected. At the low dosage level, the effect of FGDG on strength was not large. For 10% FGDG, the trend of compressive strength versus Ms started to change. This was probably due to the increase in effect of FGDG. The mortars with high BA content still exhibited the normal increase in strength with the increase in Ms. For mortars with high FA content, however, the strengths reduced with the increase in Ms indicating the negative effect of FGDG. For high FGDG addition of 15%, the negative effect of FGDG became dominant and the compressive strengths of all mixes were adversely affected.

3.2. Scanning electron microscope

The SEM-photomicrographs of BA and FA geopolymer pastes with different FGDG contents as shown in Fig. 4 indicated that

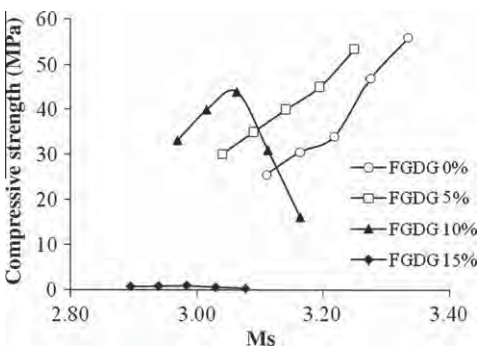


Fig. 3. Compressive strength and Ms of BA and FA geopolymer mortars with 0–15% FGDG.

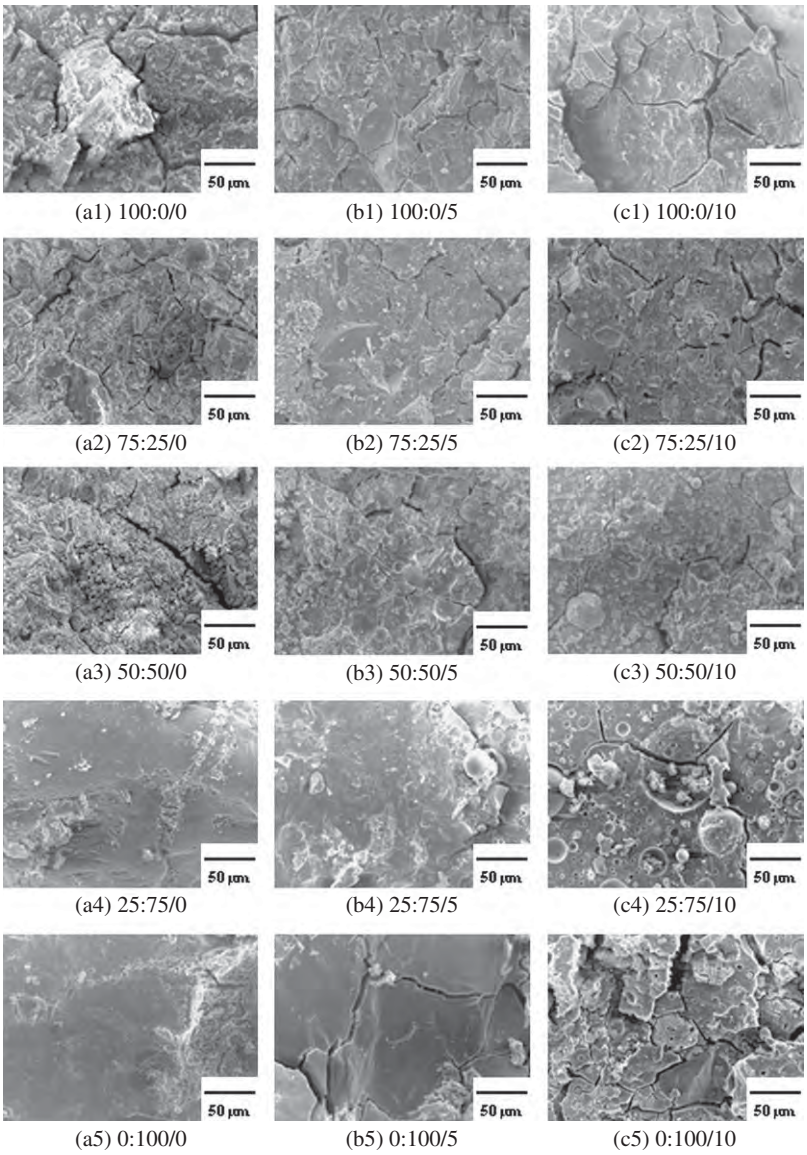


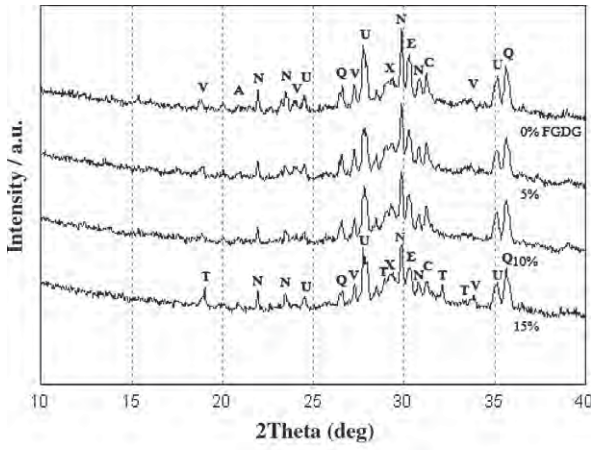
Fig. 4. SEM photography of fractured BA and FA geopolymer pastes (BA:FA/FGDG).

the polymerization products were well-connected structures consisting of glassy phase structures with no definite grain boundary. Without FGDG, the matrices of high FA content geopolymer (mixes with 75% and 100% FA) appeared very dense as shown in Fig. 4a4 and a5. For the mixes with 0%, 25%, and 50% FA, the matrices were less dense and less homogenous as shown in Fig. 4a1–a3. For the low FA mixes (mixes with 0% and 25% FA), the incorporation of 5% and 10% FGDG appeared to improve the homogeneity and the denseness of the matrices as shown in Fig. 4a1–c1 and a2–c2. The principle of activation by FGDG is based on the ability of the sulfate ions to react with alumina in ashes led to the dense alumino-silicate network [23]. For high FA mixes, the incorporation of 10% FGDG appeared to lower the homogeneity and the denseness of the matrices as shown in Fig. 4c4 and c5. The samples with good homogeneity and dense matrix corresponded to mixes with high compressive strengths.

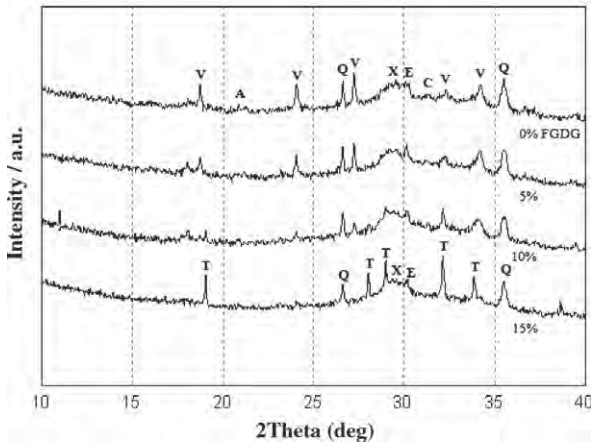
In order to check the Si/Al ratios of the geopolymer products, the EDX study was performed on the FA and BA geopolymer pastes. The results are shown in Table 4. With no FGDG, the geopolymer products of 100% FA and 100% BA mixes contained average Si/Al ratios of 2.93 and 5.41, respectively. The high Si/Al ratio gave geopolymer with low strength but good elasticity properties [24]. The dissolution of Al ions from aluminosilicate glassy phases of FA was much easier than that of BA even though the Al_2O_3 contents of both FA and BA were similar. Furthermore, the Si/Al ratios of FA geopolymer increased, while those of BA geopolymer reduced with the addition of FGDG as shown in Table 4. The dissolution of Al from FA was obstructed, while the dissolution of Al from BA geopolymer was enhanced with the presence of sulfate ions.

Table 4
The Si/Al ratios of BA and/or FA geopolymer pastes with FGDG calculated from EDX.

Series	BA:FA	FGDG (%)	Si/Al ratios
A	100:0	0	5.41
		5	4.43
		10	3.76
E	0:100	0	2.93
		5	3.09
		10	3.33



(a) BA



(b) FA

Fig. 5. XRD patterns of BA and FA geopolymer pastes with 0–15% FGDG.

3.3. X-ray diffraction

The XRD patterns of BA and FA geopolymer pastes are shown in Fig. 5. In general, the XRD patterns of the source materials and those of the BA and FA geopolymers were not very different. For BA and FA geopolymer pastes, the intensity peaks of SiO_2 (Q) and CaO (C) reduced, while CSH (X), amorphous phase, and aluminosilicate gel around 30° (2θ) increased as compared to those of the source materials. Additionally, gehlenite (E: $Ca_2Al_2SiO_7$) phase and the new zeolite phases named vishnevite (V: $Na_8Al_6Si_6O_{24}(SO_4)\cdot 2H_2O$) and thenardite (T: $NaSO_4$) were presented in both geopolymers.

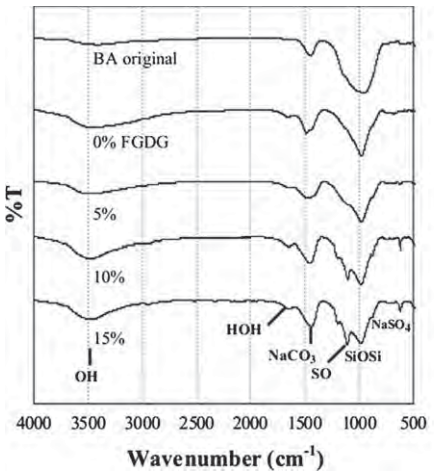
For BA geopolymer, the phases were transformed into more stable known as anorthite and augite aluminum. The addition of 5–10% FGDG in BA produced the additional increases in CSH, gehlenite, and vishnevite phases. The strength enhancement was due to the presence of some of these crystalline phases [25,26]. The increase of FGDG to 15% produced thenardite (Na_2SO_4) phase which did not contribute to the strength of geopolymer.

For FA geopolymer, the results showed the increases in CSH, vishnevite, and glassy phase compared to BA geopolymer. The incorporation of 5–15% FGDG resulted in an increase in the thenardite phase but a decrease in the vishnevite phase. The large percentage of thenardite phase existed as an impurity in the system [27] and thus weakened the geopolymer.

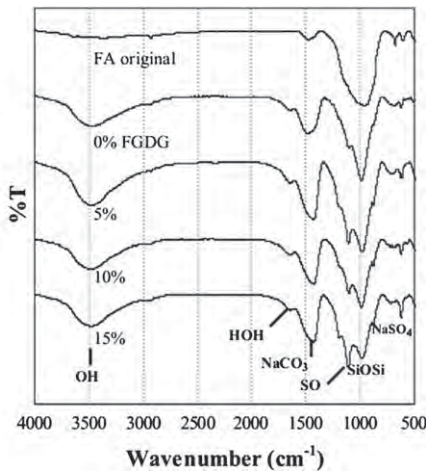
3.4. IR spectra

The results of the IR spectra of BA and FA source materials and BA and FA geopolymer pastes are shown in Fig. 6. The considerable broad bands located at 3700–2200 cm^{-1} and 1700–1600 cm^{-1} were assigned to O—H stretching and H—O—H bending, respectively. These characterized the spectrum of stretching and deformation vibration of O—H and H—O—H groups from the weakly bound water molecules which were adsorbed on the surface or trapped in large cavities between the rings of geopolymer products [28]. The increase in H_2O/Na_2O mole ratios (Table 3) raised the intensity of peaks at 3500 and 1650 cm^{-1}. The Si—O—Si and Al—O—Si stretching vibrations related to the degree of geopolymerization were detected at the wave number of 950 cm^{-1}. The increases in FA and FGDG provided high intensity Si—O—Si and Al—O—Si bands. The spectra at 1460 cm^{-1} represented the sodium carbonate from carbonation process which resulted from the unreacted Na_2O [17].

The addition of FGDG resulted in a noticeable change in the spectra of BA and FA geopolymer pastes. The SO_4^{2-} bonding was detected at wave numbers of 1200 and 636 cm^{-1} for S=O stretching and Na_2SO_4, respectively [29]. This demonstrated that SO_4^{2-} ion reacted with alkaline solution and formed SO_4 compound. For BA geopolymer, SO_4 compound could not be detected with the



(a) BA and BA pastes



(b) FA and FA pastes

Fig. 6. FTIR of BA, FA and BA and FA geopolymer pastes with 0–15% FGDG.

addition of low FGDG content of 5%. The presences of SO_4 compound were noticeable at 10% and 15% FGDG addition. At high FGDG content of 15%, the SO_4 compounds were clearly observed. The presence of SO_4 compounds in large quantity was related to the very low strength of geopolymer mortars. For FA geopolymer, the presence of SO_4 compound was noticeable with the addition of only 5% FGDG. At the high 10 and 15% FGDG, the peaks at 1200 and 636 cm^{-1} were quite distinctive. This caused the low strengths of FA geopolymer mortars containing FGDG.

4. Conclusions

The results demonstrated that the geopolymerization of BA was enhanced with the blending with FA and the addition of 5% FGDG. The strength of BA geopolymer mortar was lower than that of FA mortar. FA contained a higher amount of glassy phase and was more reactive than BA. The blending of BA with FA, therefore, increased the strength of the BA geopolymer mortars. The incorporation of 5% FGDG also resulted in the strength improvement of BA geopolymer mortar. The presence of sulfate ions increased the dissolution of Al ions from the BA and thus enhanced the geopolymerization and strength of the BA geopolymer. The incorporation of 10 and 15% of FGDG resulted in the thenardite phase which existed as an impurity in the system and weakened the geopolymer.

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Leaching of heavy metals from solidified waste using Portland cement and zeolite as a binder

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ABSTRACT

This study investigated the properties of solidified waste using ordinary Portland cement (OPC) containing synthesized zeolite (SZ) and natural zeolite (NZ) as a binder. Natural and synthesized zeolites were used to partially replace the OPC at rates of 0%, 20%, and 40% by weight of the binder. Plating sludge was used as contaminated waste to replace the binder at rates of 40%, 50% and 60% by weight. A water to binder (w/b) ratio of 0.40 was used for all of the mixtures. The setting time and compressive strength of the solidified waste were investigated, while the leachability of the heavy metals was determined by TCLP. Additionally, XRD, XRF, and SEM were performed to investigate the fracture surface, while the pore size distribution was analyzed with MIP.

The results indicated that the setting time of the binders marginally increased as the amount of SZ and NZ increased in the mix. The compressive strengths of the pastes containing 20 and 40 wt.% of NZ were higher than those containing SZ. The compressive strengths at 28 days of the SZ solidified waste mixes were 1.2–31.1 MPa and those of NZ solidified waste mixes were 26.0–62.4 MPa as compared to 72.9 MPa of the control mix at the same age. The quality of the solidified waste containing zeolites was better than that with OPC alone in terms of the effectiveness in reducing the leachability. The concentrations of heavy metals in the leachates were within the limits specified by the US EPA. SEM and MIP revealed that the replacement of Portland cement by zeolites increased the total porosity but decreased the average pore size and resulted in the better containment of heavy ions from the solidified waste.

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1. Introduction

Currently, over 80% of the hazardous wastes are from industrial processes. The sludge, heavy metals, oils and infectious waste are the most abundant hazardous wastes. The amount of industrial waste and hazardous waste from industrial plants increases every year. The toxic wastes containing heavy metals are, therefore, causing serious environmental problems in the contamination of water, air and soil. It is an issue that deserves attention to find ways to properly and appropriately capture the waste.

The hazardous waste water from industries is released from industrial facilities and is also causing critical environmental problems. The treatment processes could reduce the concentrations of the toxic waste depending on the condition of the sediment's dry residue. However, the final disposal of the waste sediment is still not safe in terms of storage and transportation because some heavy metals remain unstable and may leak into the environment. To solve the problem, the method of reducing or storing hazardous toxic waste is required to stop the leaching of toxic substances to the environment.

Solidification is a process used to treat hazardous waste from industrial plants, particularly hazardous substances or inorganic substances contaminated by heavy metals. The hazardous substances are stored in the structure by chemical bonding which neutralizes them and reduces the chance of spreading. The placeholder used in this process is normally Portland cement blended with pozzolanic materials such as fly ash, rice husk ash and silica fume. Solidification eases the safe transport of the solid cast mass and allows disposal in a landfill.

Zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4. The alumino-silicate structure is negatively charged and attracts the positive ions that reside within the zeolites. This results in large vacant spaces or cages in their structures that allow space for large cations such as sodium, potassium, barium, calcium and even relatively large molecules as well as cation groups of water, ammonia, carbonate ions and nitrate ions (Feng et al., 2000). The spaces are interconnected and form long and wide channels of various sizes depending on the minerals. These channels allow easy movement of the resident ions and molecules into and

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Table 1
Sample mix proportions (by weight).

Binder			S (%)	*w*/*b*	Symbol
OPC (%)	SZ (%)	NZ (%)			
100	–	–	–	0.4	OPC100
			40	0.4	OPC40S
			50	0.4	OPC50S
			60	0.4	OPC60S
80	20	–	–	0.4	OPC20SZ
			40	0.4	OPC20SZ40S
			50	0.4	OPC20SZ50S
			60	0.4	OPC20SZ60S
60	40	–	–	0.4	OPC40SZ
			40	0.4	OPC40SZ40S
			50	0.4	OPC40SZ50S
			60	0.4	OPC40SZ60S
80	–	20	–	0.4	OPC20NZ
			40	0.4	OPC20NZ40S
			50	0.4	OPC20NZ50S
			60	0.4	OPC20NZ60S
60	–	40	–	0.4	OPC40NZ
			40	0.4	OPC40NZ40S
			50	0.4	OPC40NZ50S
			60	0.4	OPC40NZ60S

out of the structure. The zeolites are thus characterized by their ability to lose and absorb water without damaging their crystal structures (Quanlin and Naiqian, 2005).

Clinoptilolite is a naturally occurring zeolite that forms through the devitrification (the conversion of glassy material to crystalline material) of volcanic ash in lake and marine waters. It is the most studied of all zeolites and is widely regarded as the most useful. Clinoptilolite has a particularly high cation exchange capacity which provides many useful properties (Poon et al., 2000). Clinoptilolite is used in many applications such as chemical sieves, gas absorbers, feed additives, food additives, odor control agents and water filters for municipality, residential drinking water and aquariums (Feng and Peng, 2005). Clinoptilolite is well suited for these applications because of its large amount of pore space, high resistance to extreme temperatures and chemically neutral basic structure.

Sludge produced by the metal plating industry is generally considered to be "hazardous waste" because of its toxic heavy metal content. Solidification techniques applied prior to the deposition of this waste in landfills provide good results allowing the safe disposal of inorganic sludge. The use of materials such as zeolite with its pozzolanic property and the ability to bind metal ions generally gives a good performance. The solidification can store a large amount of sludge and help protecting the environment. This study, therefore, aims to investigate an effective solidification technique for sludge from a metal plating factory using both natural and synthesized zeolites in corporation with Portland cement.

2. Experimental investigation

2.1. Materials

The materials used were ordinary Portland cement (OPC) per ASTM C150, sodium aluminum silicate ($Na_{96}Al_{96}Si_{96}O_{384}$) as synthesized zeolite (SZ), clinoptilolite ($(Na,K,Ca)_6(Si{\cdot}Al)_{36}O_{72}20H_2O$) as natural zeolite (NZ), sludge (S) from the treatment of wastewater from a nickel plating plant and tap water. The S contained 35% water and 65% solid. It was dried and then sieved through a No. 100 sieve.

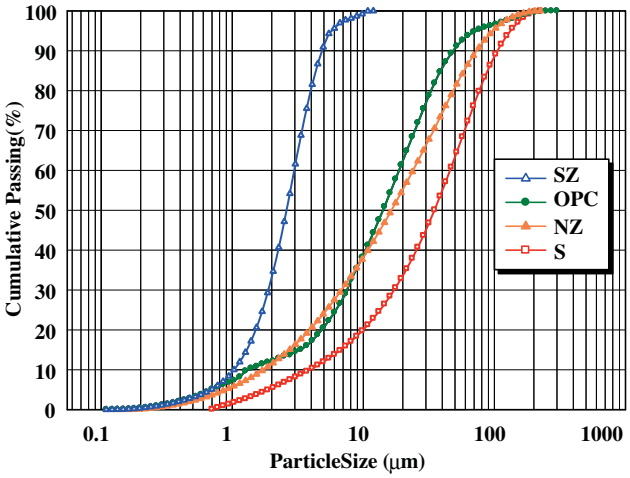


Fig. 1. Particle size distribution of OPC, SZ, NZ and S.

2.2. Mixture proportions

The sludge waste was solidified using OPC containing SZ and NZ as a binder. Zeolites were used to partially replace OPC at rates of 0%, 20%, and 40% by weight of the binder. The plating sludge was used to replace the binders at the rates of 40%, 50% and 60% by weight. A constant water to binder (*w*/*b*) ratio of 0.40 was used. The pastes were mixed in a mechanical mixer, and the specimens were cast in 50-mm cube molds. The fresh samples were covered with a plastic sheet to prevent water evaporation. After casting for 24 h, the samples were removed from the molds and cured in saturated lime water (Table 1).

3. Test programs

3.1. Specific gravity and particle size

The specific gravity of OPC, SZ, NZ and S was measured in accordance with ASTM C188, and their particle sizes were measured using laser particle size analysis.

3.2. Normal consistency

The normal consistency of the pastes was measured in accordance with ASTM C187 using Vicat apparatus.

3.3. Compressive strength

The compressive strength of the solidified waste was tested in accordance with ASTM C109 at ages of 7, 28, and 90 days. Five samples were tested for each age group.

Table 2
Specific gravity, median particle size and surface area of OPC, SZ, NZ and S.

Sample	Specific gravity	Mean particle size d_{50} (μm)	Surface area[a] (cm^2/g)
OPC	3.15	14.12	2600
SZ	1.87	2.51	32,500
NZ	2.09	16.17	5400
S	2.14	34.81	1900

[a] BET analysis.

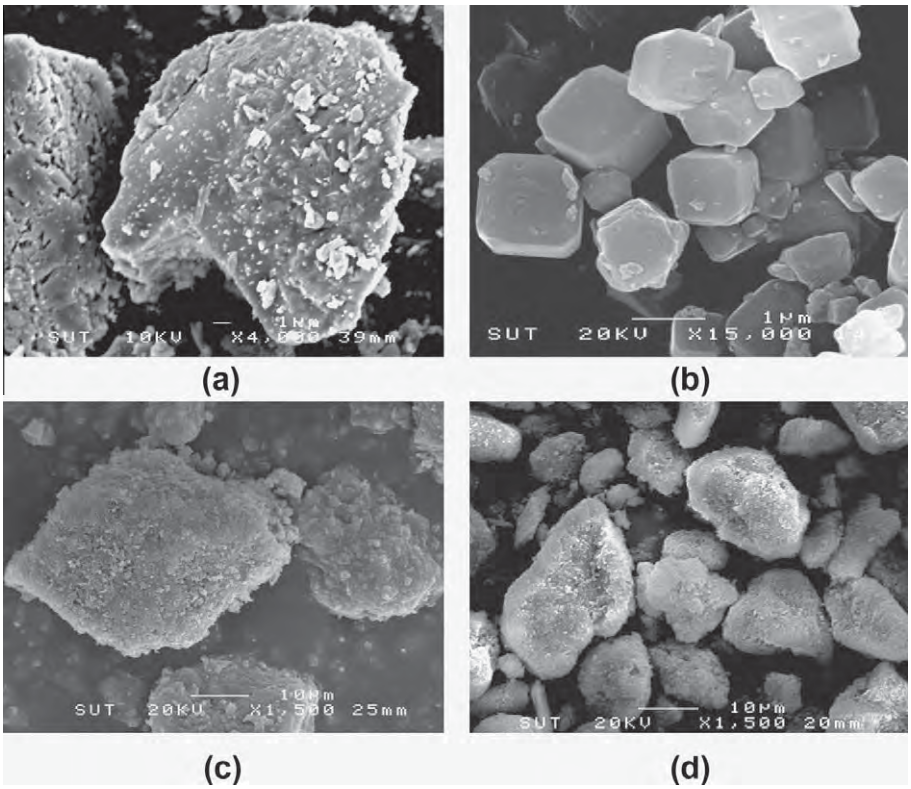


Fig. 2. SEM micrographs of (a) OPC at 4000 time, (b) SZ at 15,000 time, (c) NZ at 1500 time and (d) S at 1500 times.

Table 3
Chemical composition of materials.

Chemical composition (%)	OPC	SZ	NZ	S
SiO_2	19.85	65.3	75.32	5.53
Al_2O_3	4.49	26.18	10.28	3.78
Fe_2O_3	3.56	0.03	2.66	–
CaO	66.96	0.12	3.95	25.32
MgO	1.36	0.08	1.2	–
K_2O	0.34	2.64	4.29	–
Na_2O	–	1.87	0.89	–
NiO	–	–	–	40.88
CuO	–	–	–	13.08
ZnO	–	–	–	10.33
CrO	–	–	–	0.64
LOI	0.98	5.65	2.3	0.44

3.4. Scanning electron microscopy (SEM)

A JEOL scanning electron microscope (model JSM6400) was used to examine the phase development and microstructure of the solidified plating waste. The paste cubes at the ages of 7 and 28 days were broken and the fractions in the middle part of the specimens were used for the analyses. The solid was placed on a brass stub sample holder with double stick carbon tape. Then, the sample was dried using infrared light for 5 min. Subsequently, the sample was coated with a layer of gold approximately 20–25 Å thick using a blazer sputtering coater. Micrographs were recorded at 12 kV and 500–10,000× magnifications (Chindaprasirt et al., 2005).

3.5. X-ray diffractometer (XRD) and X-ray fluorescence (XRF) analyses

The XRD scans were performed for $2\theta^\circ$ between 10° and 70°, with an increment of 0.03°/step and a scan speed of 0.5 s/step. XRD analysis using Bruker's TOPAS software and using wavelength dispersive XRF (WDXRF). The positions of the diffraction peaks were identified by comparison to reference database compounds (Chindaprasirt et al., 2005).

3.6. Mercury intrusion porosimetry procedure (MIP)

The pore diameter distribution in the hardened cement pastes was measured by mercury intrusion porosimetry (MIP) at a pressure capacity of 228 MPa. After curing for 7, 28 and 90 days, the samples were split from the middle portion of the hardened blended cement paste. To stop the hydration reaction, the samples were submerged directly into liquid nitrogen for 5 min and were then evacuated at a pressure of 0.5 Pa at −40 °C for 48 h. This method has been used previously to stop the hydration reaction of cement paste (Chindaprasirt et al., 2007).

3.7. Toxicity characteristic leaching procedure (TCLP)

The metal leaching from the solidified plating waste cured for 7, 28 and 90 days and was assessed using the TCLP as defined by the US EPA (Li et al., 2001). The samples were crushed to reduce the particle size to less than 9.5 mm. The crushed sample was extracted using an acetic acid solution (pH 2.88) in a volume with a weight equal to 20 times the weight of the sample. The extraction vessels were rotated in an end-over-end manner at 30 rpm for 18 h. The leachate was filtered through a 0.45-μm membrane filter to remove suspended solids and was then divided into two portions. One portion was used for a pH measurement, and the other was used for the determination of the metals present in the leachate by ICP-AES. Each extraction was performed in triplicate, and the average value was reported to ensure the reproducibility of the data (Asavapisit et al., 2005).

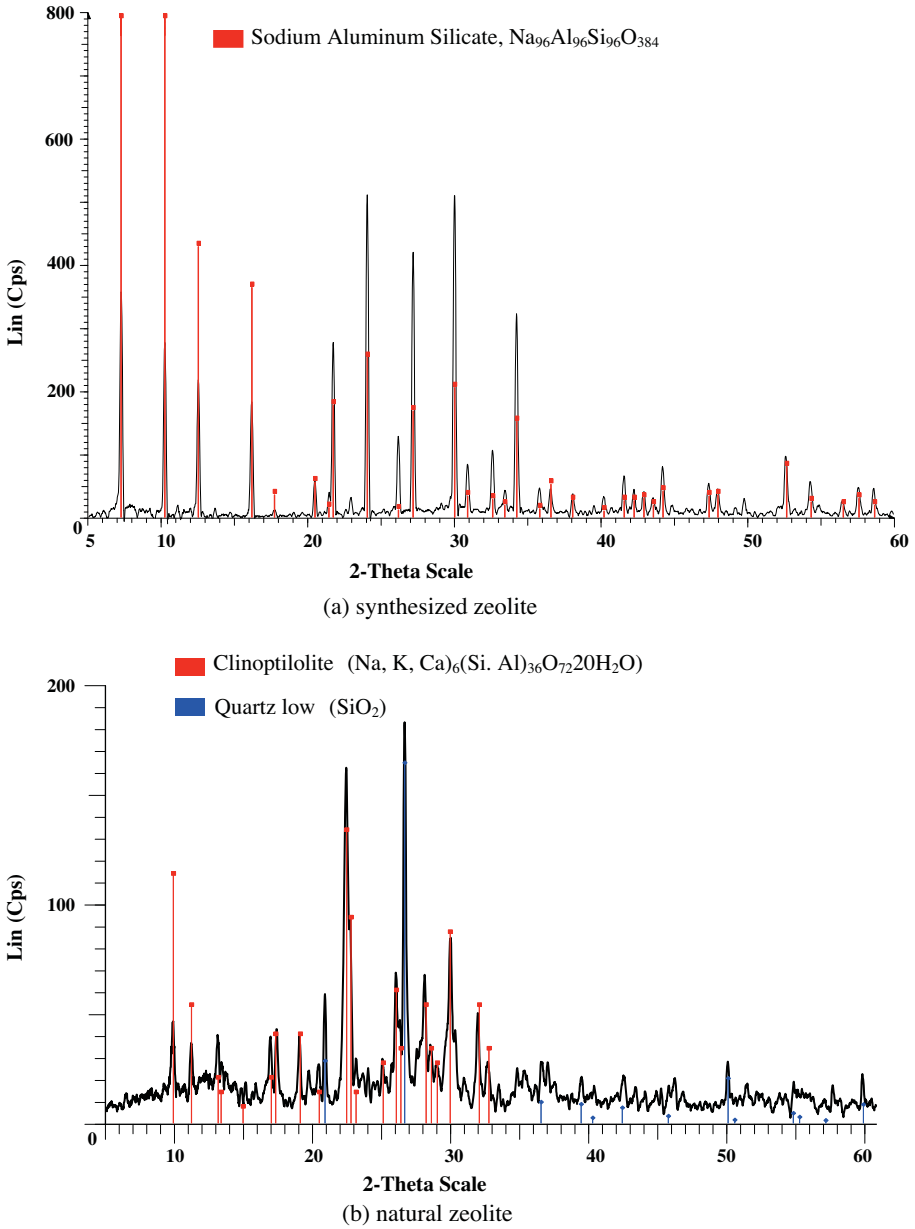


Fig. 3. XRD patterns of synthesized zeolite and natural zeolites.

4. Results and discussion

4.1. Properties of materials

4.1.1. Physical results for OPC, SZ, NZ and S

The specific gravity and median particle size (d_{50}) of the OPC, SZ, NZ and S are shown in Table 2. The median particle size (d_{50}) of the OPC was approximately 14.1 μm, while those of SZ, NZ and S were 2.5, 16.2 and 34.8 μm, respectively. The surface areas of the OPC, SZ, NZ and S were 2600, 32,500, 5400 and 1900 cm^2/g, respectively. The particle size distribution for the OPC, SZ, NZ and S was measured with a Mastersizer and is graphically shown in Fig. 1. For the OPC, NZ and S, the particle shape was solid and angular, whereas the surface of the SZ was smooth and exhibited a hexagonal character (Fig. 2).

4.1.2. Chemical composition and material patterns

Table 3 shows the chemical composition of the OPC, SZ, NZ and S, which was analyzed by XRF. SZ and NZ were found to be mainly SiO_2 and Al_2O_3. As can be seen, these two components were 90% for SZ and 85% for NZ. Additionally, the main elements of S were NiO (40.88%), CaO (25.32%), CuO (13.08%) and ZnO (10.33%).

Fig. 3 shows the XRD patterns for the SZ and NZ. The figure indicates that the intensity peak of sodium aluminum silicate ($Na_{96}Al_{96}Si_{96}O_{384}$) and (Na,K,Ca)$_6$(Si·Al)$_{36}O_{72}20H_2O$ appeared at 0–60° (2θ).

4.2. Properties of pastes

4.2.1. Normal consistency of pastes

The normal consistency of OPC100 was found to be 25.5%. Higher replacement of SZ and NZ resulted in a higher normal consistency. For example, the normal consistencies of pastes OPC20SZ, OPC40SZ, OPC20NZ and OPC40NZ were 32.4%, 34.4%, 31.2% and 32.0%, respectively. The normal consistency of pastes containing SZ and NZ, which have a higher fine content, was higher than those containing coarser zeolites. This occurs because the particles of SZ and NZ have a higher fine content and a higher porosity; thus, they absorb more water, which results in greater water consumption.

Table 4
Setting time and compressive strength of the solidified wastes.

Sample	Time (min)		Compressive Strength (MPa)		
	Initial setting time	Final setting time	7-day	28-day	90-day
OPC100	132	181	53.8	72.9	79.4
OPC40S	148	192	0.9	1.3	1.5
OPC50S	151	195	0.6	1.0	1.2
OPC60S	154	197	0.5	0.8	1.1
OPC20SZ	141	185	21.6	31.1	38.2
OPC20SZ40S	149	186	2.1	13.5	16.1
OPC20SZ50S	152	186	1.3	4.9	10.7
OPC20SZ60S	156	185	0.8	1.4	2.0
OPC40SZ	143	187	10.2	23.4	26.9
OPC40SZ40S	149	188	0.3	6.0	17.4
OPC40SZ50S	151	189	0.3	4.2	13.6
OPC40SZ60S	152	190	0.1	1.2	3.2
OPC20NZ	133	183	52.0	62.4	71.1
OPC20NZ40S	135	184	43.4	57.3	65.2
OPC20NZ50S	135	185	35.7	49.1	58.4
OPC20NZ60S	136	186	30.5	41.3	50.3
OPC40NZ	134	184	40.5	50.7	61.3
OPC40NZ40S	135	184	19.5	36.2	43.4
OPC40NZ50S	136	185	15.2	31.5	39.3
OPC40NZ60S	136	187	12.1	26.0	33.8

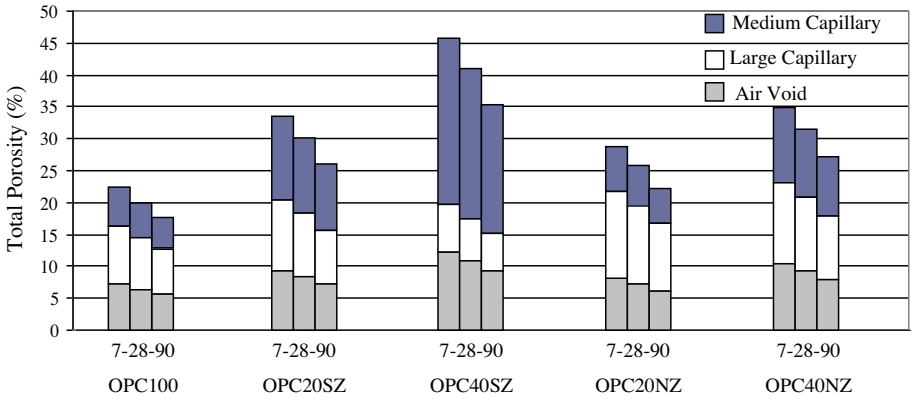


Fig. 4. Total porosity of cement paste and blended cement pastes at 7, 28 and 90 days.

4.2.2. Setting time of blended cement pastes and pastes containing solidified plating waste

The setting times of the blended cement pastes containing SZ and NZ were similar to those of the Portland cement paste. For example, the final setting times of OPC paste, was 181 min. The initial setting time of mixes with SZ was 185 and 187 min and those with NZ were 183 and 184 min. For the incorporation of S, the initial setting time was increased to 148–154 min and the final setting times to 191–192 min. The similar or slightly increase in the setting time were probably due to the pastes mixed with zeolites have higher water contents at normal consistency than Portland cement paste. Moreover, the use of zeolite to replace Portland cement resulted in a smaller amount of cement and thus caused a longer setting time to be observed. For the use of S, the reductions in the amount of cement and pozzolan resulted in an even smaller amount of cementing material and hence the setting times increased.

4.2.3. Compressive strength of the blended cement pastes

Table 4 shows the development of compressive strength in the cement paste in relation to the cement replacement level for the case of synthesized zeolites and natural zeolites. Concerning the use of SZ and NZ, replacement of 20% and 40% zeolites led to lower compressive strengths at all ages. It was observed that the compressive strengths of the cement pastes containing NZ were higher than those with SZ for the same replacement conditions and age, because more silica dioxide (the main component of nat-

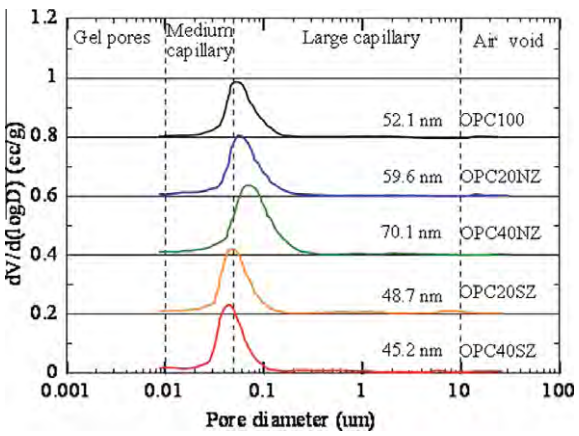


Fig. 5. Relationship between pore diameter and volume intruded of the blended cement pastes at 28 days.

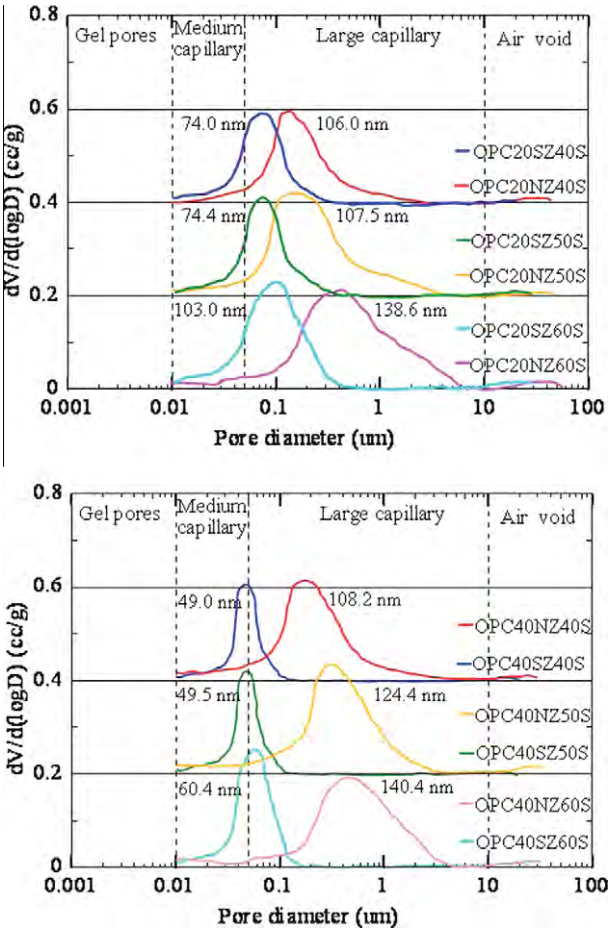


Fig. 6. Relationship between pore diameter and volume intruded of the solidified plating wastes using OPC, NZ and SZ as binders at 28 days.

ural zeolite) is contained than in the synthesized zeolites and cement. The pozzolanic activity of zeolite normally depends on the amount of the active amorphous phases of silica and alumina. As indicated in the XRD patterns in Fig. 3, the amount of the active amorphous phases of NZ is higher than that of SZ. The results of the compressive strengths of pastes OPC20SZ, OPC40SZ, OPC20NZ and OPC40NZ at 28 days of 31.1, 23.4, 62.4 and 50.7 MPa, respectively confirms the observation.

4.2.4. Compressive strength of pastes containing solidified plating waste

The experimental results showed that the rates of strength development in the solidified waste using SZ and NZ as solidification binders were higher than that with OPC. The composition of OPC hydration product is dominated by calcium silicate hydrate (C–S–H) which typically comprises 70–80% of the product (Deja, 2002). The metals may react with calcium hydroxide to produce insoluble compounds as a form of metal hydroxide; this mechanism inhibited the hydration and decreased the strength of the wastes, especially when the concentration of metal in the solidified waste was more than 0.3% by weight (Li et al., 2001; Asavapisit et al., 2001; Qin et al., 2003). The strength of these solidified wastes could be very low due to the inhibition of the cement reactions by the metal ions in the waste. Additionally, the strength of the solidified waste decreased when the amount of waste increased. For example, the strengths of pastes OPC20NZ40S, OPC20NZ50S, and OPC20NZ60S at 28 days were 57.3, 49.1 and 41.3 MPa, respectively. The results indicated that the plating sludge can be loaded in a proportion as high as 60 wt.% of the cement blended with 40 wt.% SZ and NZ at a 28-day compressive strength that meets the minimum requirement for disposal in a secure landfill (0.34 MPa).

4.2.5. Porosity and average pore diameter of blended cement pastes

The total porosity, capillary porosity and average pore diameter of the pastes at 7, 28 and 90 days are shown in Fig. 4. The incorporation of SZ and NZ increased the total porosity of the blended cement pastes as compared with the OPC paste at all ages. The total porosity increased with an increase in replacement by SZ and NZ. The increase in total porosity as a result of the utilization of zeolite was mainly due to the decrease in capillary porosity. Note that the compressive strength decreased, while the porosity of the blended cement paste increased (Poon et al., 2000; Isaia et al., 2003). The capillary porosity of the cement paste blended with NZ at all replacement levels decreased in comparison to that with SZ.

Fig. 4 shows the effect of the percent replacement of SZ and NZ on the average pore size in the cement pastes at age 7, 28 and 90 days. It can be observed that the average pore size of the additives decreased at the respective period of hydration because of the gradual filling of large pores by hydration products of cementitious materials; however, the extent of the decrease was variable. A greater decrease was observed for replacement by SZ, whereas the decrease was comparatively less for replacement by NZ. The average pore size tends to decrease as the percent replacement increases. The relationship between the pore diameter and incremental pore volume of the blended cement paste at 28 days is shown in Fig. 5. The critical pores sizes of the OPC100, OPC20NZ and OPC40NZ pastes were 52.1, 59.6 and 70.1 nm, respectively, and the pores were distributed as large capillary pores. The critical pores sizes of the OPC20SZ and OPC40SZ pastes were 48.7 and 45.2 nm, respectively, and these were distributed as medium capillary pores. These values were lower than that of the OPC100 paste. This suggests that the greater fineness of the zeolite was more effective in reducing the pore diameter of the paste. The results also showed that the blended cement paste containing zeolite presented a smaller pore size than the Portland cement paste. The pore size decreased with an increase in zeolite replacement. Similar results have also been reported in other studies (Poon et al., 1997, 1999a,b).

The relationship between the pore diameter and incremental pore volume of the solidified waste using OPC, SZ and NZ as binders at 28 days is shown in Fig. 6. The critical pore sizes of OPC20SZ40S, OPC20SZ50S and OPC20SZ60S were 74.0, 74.4 and 103.0 nm, respectively, and these pores were distributed as large capillary pores. Additionally, the critical pore sizes of the OPC40SZ40S, OPC40SZ50S and OPC40SZ60S pastes were 49.0, 49.5 and 60.4 nm, respectively. These results suggested that the increase in the amount of the plating waste resulted in increase in pore diameter of the paste. In contrast, the increase in the amount of SZ resulted in the decrease in the pore diameter of the paste.

As shown in Fig. 6, the critical pore sizes of OPC20NZ40S, OPC20NZ50S, OPC20NZ60S, OPC40NZ40S, OPC40NZ50S and OPC40NZ60S were 106.0, 107.5, 138.6, 108.2, 124.4 and 140.4 nm, respectively. These results suggested that as the amount of plating sludge increased, the pore diameter of the paste increased.

4.2.6. Fracture surface analysis by scanning electron microscopy (SEM)

The microstructure morphology of the fractured surface was determined by SEM for OPC100, OPC20SZ, OPC40SZ, OPC20NZ and OPC40NZ pastes at 28 days (see Fig. 7). The microstructure of OPC100 was porous and exhibited many voids, while OPC20SZ, OPC40SZ, OPC20NZ and OPC40NZ showed uniform and dense pastes. The incorporation of zeolites resulted in the increased hydration and pozzolanic reaction and thus reduced the pore sizes.

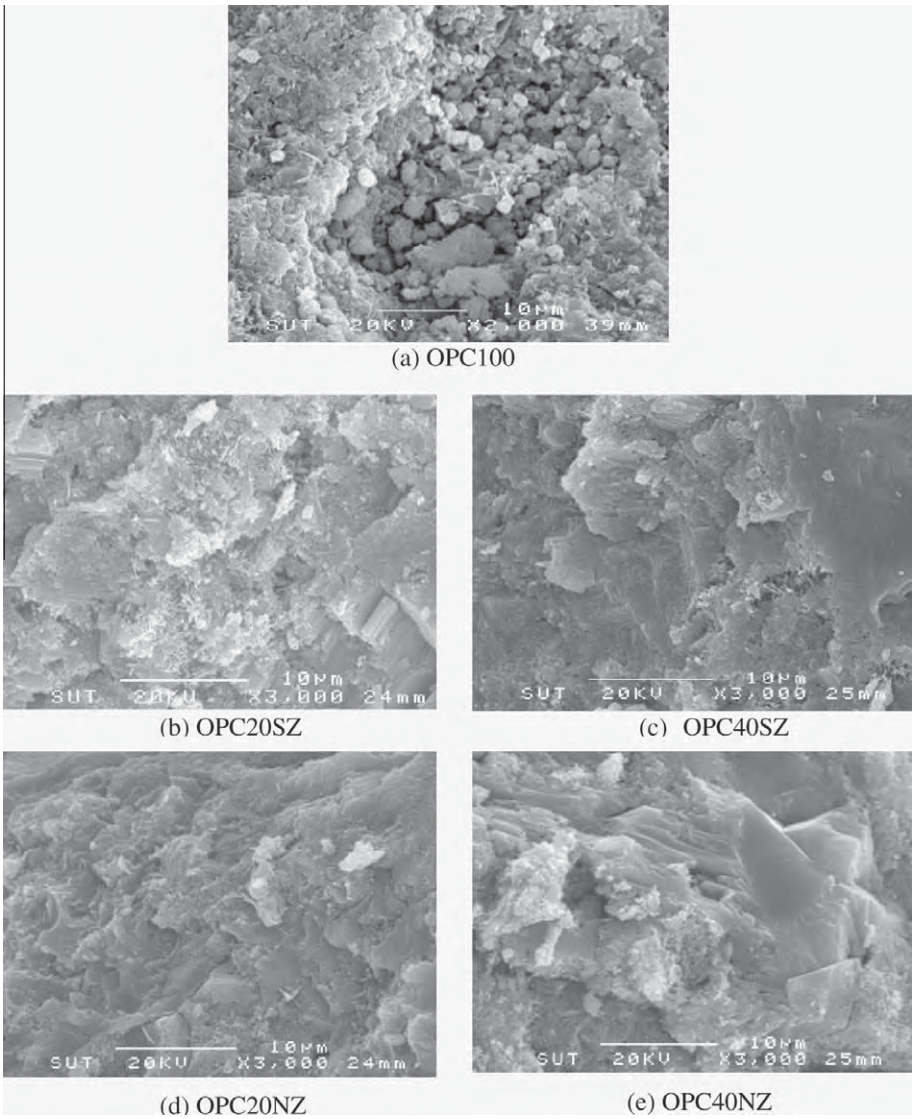


Fig. 7. Fracture surface of the blended cement pastes at 28 days.

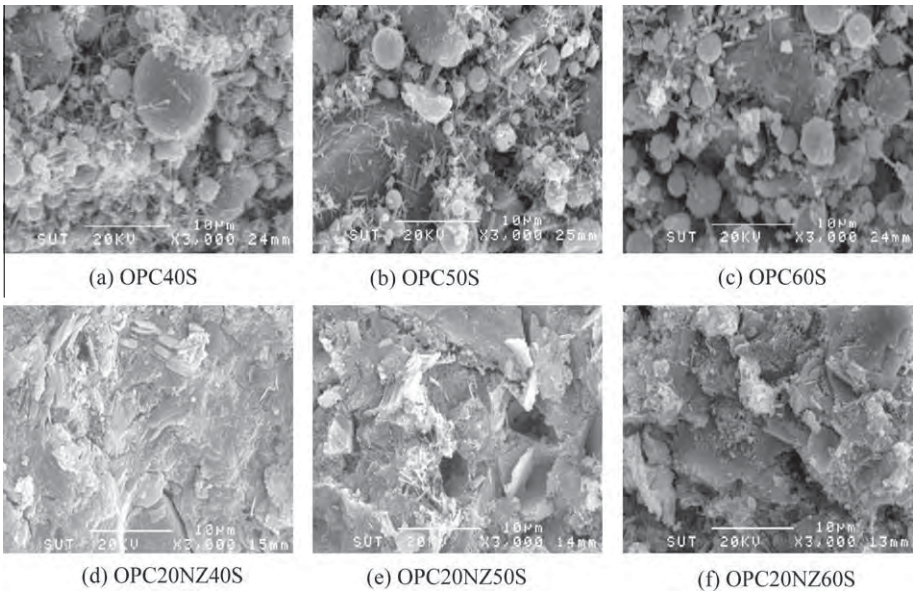


Fig. 8. Fracture surfaces of the solidified plating wastes at 28 days.

Table 5
Leachate pHs in TCLP leachates.

Sample	pH		
	Age 7 days	Age 28 days	Age 90 days
OPC100	6.3	6.5	6.6
OPC40S	6.4	6.6	6.7
OPC50S	7.1	7.2	7.2
OPC60S	7.7	7.7	7.7
OPC20SZ40S	7.6	7.5	7.4
OPC20SZ50S	7.9	7.9	7.8
OPC20SZ60S	7.8	7.9	7.9
OPC40SZ40S	9.8	9.5	9.5
OPC40SZ50S	8.8	8.8	8.7
OPC40SZ60S	8.5	8.5	8.6
OPC20NZ40S	11.4	11.5	11.5
OPC20NZ50S	11.2	11.2	11.2
OPC20NZ60S	11.1	11.1	11.1
OPC40NZ40S	11.2	11.1	11.1
OPC40NZ50S	10.8	10.8	10.9
OPC40NZ60S	9.7	9.6	9.6

Thus, replacing the Portland cement with some zeolites resulted in a dense paste.

Fig. 8 shows the fractured surfaces of the solidified plating waste at 28 days, as determined by SEM. The paste with more plating sludge showed a lower density because the proportion of binder in the mixture decreased. Because heavy metals inhibit hydration, the cement reaction was not completed, and some heavy metals did not react (Bishop et al., 2003). The replacement of Portland cement by zeolites showed a higher density than used Portland cement alone. The consequences of this are that the solidified waste was more porous, and the compressive strength of the solidified waste decreased significantly compared with those with the absence of plating sludge in the mixture.

4.2.7. Leaching analysis

Table 5 shows the leachate pH values in the TCLP leachates at 7, 28 and 90 days. The pH of the solution extracted from the solidified waste is increased from the initial pH. For example, the pH of pastes OPC100, OPC40S, OPC20SZ40S and OPC20NS40S pastes at 28 days were 6.5, 6.6, 7.5 and 11.5, respectively. The pH values increased because calcium hydroxide in the pores dissolved into the acid. Fig. 9 shows the metal concentrations in TCLP leachates, the results showed that the concentration of Cr in the leachate for all solidified waste samples was lower than the limit specified by the standards of the US EPA (<5.0 mg/l). It should be noted here that the untreated sludge also meets US EPA criteria for Cr. For example, the concentrations of Cr in the leachate of pastes

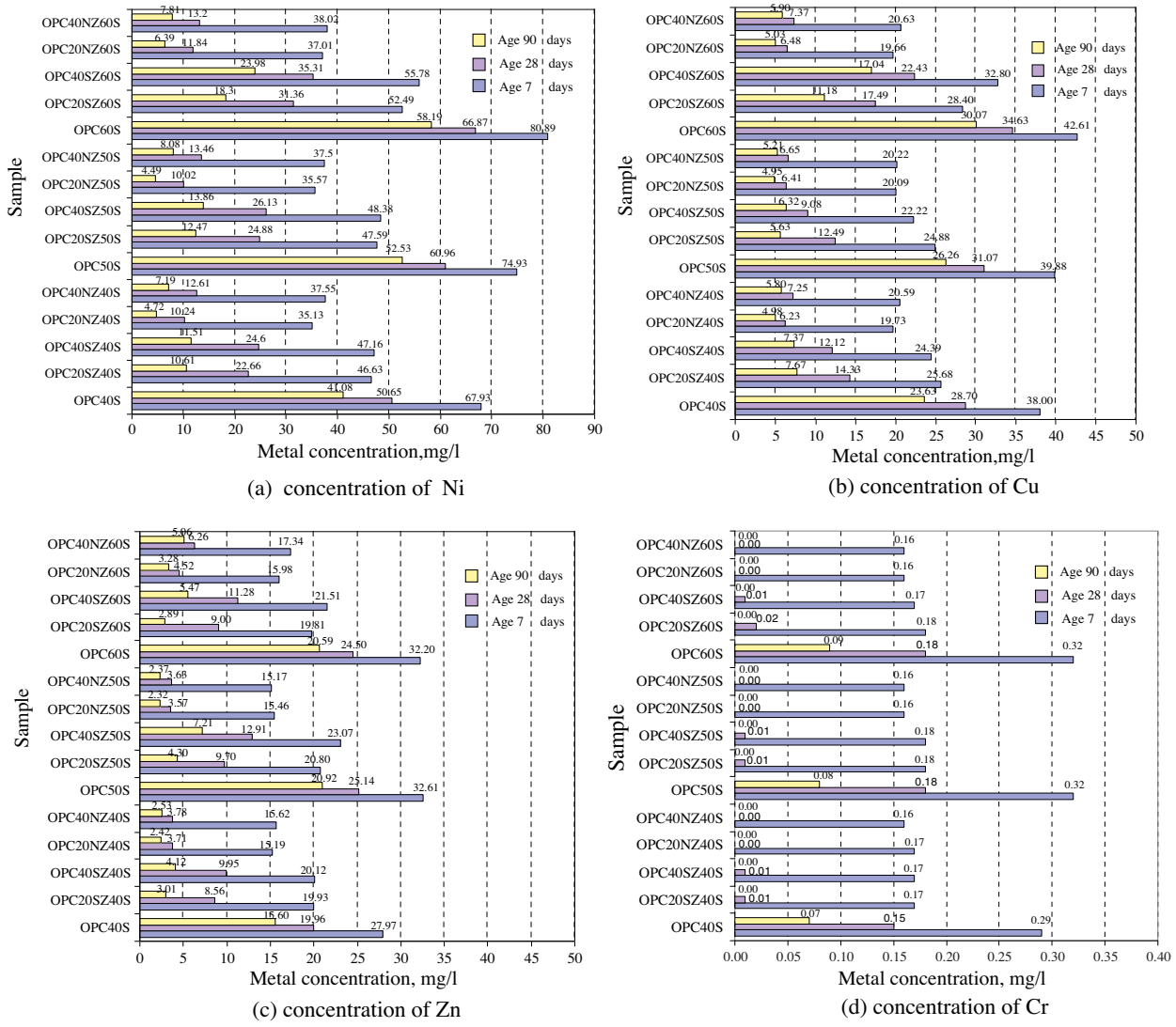


Fig. 9. Metal concentrations in TCLP leachates.

OPC20SZ40S, OPC20SZ50S, OPC20NZ40S and OPC20SZ50S at 7 days were 0.17, 0.18, 0.17 and 0.16 mg/l respectively. The Ni, Cu and Zn have no regulatory standards because these three metals are not classified as hazardous waste by the US EPA. The results showed that when sample age increased the effectiveness in reducing the leachability increased, For example, it was detected that OPC20NZ40S contained Ni of 35.13 mg/l at 7 days and this decreased to only 10.24 mg/l at 90 days. Using NZ as a binder effectively reduced leaching more than using SZ. For example, the concentrations of Ni in the leachate of pastes OPC40NZ40S and OPC40SZ40S at 28 days were 12.61 and 24.60 mg/l respectively. Additionally, the metal concentrations in the TCLP leachates that were extracted from the cement-based solidified plating waste were much lower than that extracted from the plating sludge. Effectiveness in reducing the leachability of solidified waste using SZ and NZ to replace OPC as a binder was higher than 80.0% at all ratios. This was because SZ and NZ mainly composed of SiO_2, Al_2O_3 and Fe_2O_3; and the structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (Cheng and Bishop, 1992; Peralta et al., 1992). Thus, the effectiveness in reducing the leachability was higher using SZ and NZ than that with OPC alone. These results indicated that during the ion-exchange process, the metal ions had to move through the pores of zeolite mass and through channels of the lattice, and they had to replace exchangeable cations. The diffusion was fast through the pores, but was retarded when the ions moved through the smaller diameter channels. In this case, the metal ions uptake could mainly be attributed to the ion-exchange reactions in the microporous minerals of zeolite (Erdem et al., 2004).

5. Conclusions

On the basis of the results of this study, the following conclusions can be drawn.

1. The blended cement pastes containing synthesized zeolite and natural zeolite exhibited higher total porosity and capillary porosity than those containing Portland cement alone. This resulted in the lower compressive strengths of blended cement pastes compared to that of the control Portland cement paste.
2. The pore size distribution and the average pore diameter of the blended cement paste containing zeolites decreased with an increase in zeolite content which resulted in the dense structure of the paste. This effect was caused by the hydration reaction and the pozzolanic reaction.
3. The use of zeolites to partially replace Portland cement as a solidification binder produced solidified waste with lower strength. However, it is more effectiveness in terms of leachablity than the use of Portland cement alone.
4. The application of natural zeolite as a binder with Portland cement to reduce the leaching of heavy metals resulted in a better outcome than using synthetic zeolites with cement, or cement alone. The use of natural zeolite with Portland cement as a binder to solidify waste sludge is appropriate as the leachablity was reduced and the compressive strength complied with the US EPA standard.

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Microstructure and strength of blended FBC-PCC fly ash geopolymer containing gypsum as an additive

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ABSTRACT: This study focused on the microstructure and strength of blended fluidized bed coal combustion fly ash (FBC-FA) and pulverized coal combustion fly ash (PCC-FA) geopolymers containing gypsum as an additive. The source materials consisted of 100% FBC-FA and a blend of 75% FBC-FA and 25% PCC-FA. Gypsum was used as an additive at the dosage levels of 0, 5, and 10%wt of the source materials. NaOH and Na_2SiO_3 were used to activate aluminosilicate sources and temperature curing to accelerate the geopolymer reaction. The microstructures of the geopolymer pastes were examined using XRD, FTIR, MIP and SEM tests. The compressive strengths of the geopolymer mortars were also tested. Test results showed that the blending of FBC-FA and PCC-FA improved the geopolymerization and resulted in a dense matrix with reduced porosity and increased compressive strength as compared to those of the FBC-FA geopolymer. The improvement is due primarily to the high glassy phase content of PCC-FA. In addition, the use of 5% gypsum as an additive further improved the geopolymerization. The sulphate ions enhanced the leaching of alumina from the source materials forming additional aluminosilicate and increased calcium in the system which resulted in the formation of additional CSH.

KEYWORDS: fluidized bed coal combustion, pulverized coal combustion, porosity, paste, mortar

INTRODUCTION

The pulverized coal combustion (PCC) process has been used to burn coal for almost a century. This technology requires less excess air whilst uses high firing temperature to improve thermal efficiency creating a spherical shape, highly amorphous phase contents, and reactive by-product materials such as fly ash. Fly ash from pulverized coal combustion (PCC-FA) is commonly used as a pozzolanic material for partial replacement of Portland cement in concrete work[1,2]. The recently developed fluidized bed coal combustion (FBC) technology for power plant supersedes PCC. The FBC process operates at lower burning temperatures and emits lower CO_2, sulphur, and nitrogen oxide. The process can use burnable material such as grubby coal, municipal waste, and all types of biomass, including wood, rice husks, sugarcane bagasse, olive/palm oil residues, fruit residues, or even wet coffee as fuel materials. Even though the FBC method is a clean coal technology, it provides poorer grade of by-product materials.

In Thailand, the fluidized bed power plant normally uses two types of fuel, viz., coal and coal plus biomass. Biomass burning can use biological waste material derived from plants and animal wastes. The composition of biomass ashes is, therefore, quite variable. For example, wood contains low silica and high CaO, while agricultural residues contains high silica and low calcium. The use of biomass to partially replace coal reduces the overall emission of greenhouse gas[3]. However, the FBC fly ash (FBC-FA) is irregular in shape, less reactive, and contains smaller proportion of glassy phase compare to the PCC-FA. It cannot replace cement replacement[4], but it can be used as a source material for making geopolymer[5]. Geopolymer is an alkali-activated aluminosilicate material. The source material, therefore, contains high amorphous silica and alumina contents. It offers good strength, improved mechanical properties, and reduced CO_2 emission[6,7]. Although FBC-FA can be used to produce geopolymer, the strength is low compared to that of the PCC-FA geopolymer[8,9]. The blending of FBC-FA with a high glassy phase material such as PCC-FA is recommended to improve the strength of FBC-FA geopolymer[5].

The degree of geopolymerization can be increased by incorporating additives such as $CaCl_2$, $CaSO_4$, or Na_2SO_4[10]. Sulphate additives give slightly better performance than the chloride additive. $CaSO_4$ or

Table 1 Chemical compositions of FBC-C, FBC-Bi, PCC-FA, and G.

Chemical composition	Materials			
	FBC-C	FBC-Bi	PCC-FA	G
CaO	15.8	40.0	24.5	58.8
SiO_2	38.8	22.6	35.2	–
Al_2O_3	17.6	10.0	16.5	–
Fe_2O_3	11.9	7.6	13.6	–
SO_3	8.1	12.7	1.6	41.2
Na_2O	0	0	2.7	–
MgO	4.0	3.4	3.2	–
K_2O	2.3	1.5	1.9	–
P_2O_5	0.5	1.1	0.2	–
TiO_2	0.7	0.7	0.3	–
LOI	0.5	0.5	0.4	–

gypsum is a good choice as it available in the market at very reasonable cost.

This study, therefore, attempted to improve the compressive strength of geopolymer from FBC-FA. Gypsum was used to improve the FBC-FA and PCC-FA blend reaction. This knowledge would be instrumental to understand and use FBC-FA to produce geopolymeric material.

MATERIALS AND METHODS

Materials

The source materials for making geopolymer were fly ashes from FBC and PCC power plants. Two types of FBC-FA, viz., 100% coal burning (FBC-C) and 70% coal with 30% biomass burning (FBC-Bi) from central area and PCC-FA from Mae Moh Power Plant in northern Thailand were the source materials. Commercial graded gypsum (G) was selected as an additive to improve the geopolymer properties. The chemical compositions of FBC-C, FBC-Bi, PCC-FA, and G were determined by XRF analysis and shown in Table 1. The FBC-C, FBC-Bi, and PCC-FA consisted of SiO_2, Al_2O_3, Fe_2O_3, and CaO as the main oxides. SO_3 was also present in a substantial quantity in FBC ashes. The main components of G were CaO and SO_3 oxides. The physical characteristics of materials are examined by analysing particle sizes, specific gravity, and percentages retained on No. 325 sieve and tabulated in Table 2. The median particle sizes of FBC-C, FBC-Bi, PCC-FA, and G were 22.6, 28.9, 63.5, and 6.4 μm, respectively, with the corresponding specific gravity of 2.69, 2.78, 2.52, and 2.31, respectively. Sodium silicate was a commercially available solution with 13.8% Na_2O, 32.2% SiO_2, and 54.0% H_2O by weight and sodium hydroxide (NH) solution at 10 M concentration was prepared one day before mixing to ensure equilibrium. The NH and NS (Na_2SiO_3) were used as alkali activators. Local river sand with specific gravity of 2.62 and fineness modulus of 2.85 was used to make geopolymer mortar.

Table 2 Physical characteristics of FBC-C, FBC-Bi, PCC-FA, and G.

Materials	Median particles size (μm)	Specific gravity	Retained on sieve #325 (%)
FBC-C	22.6	2.69	15.1
FBC-Bi	28.9	2.78	21.7
PCC-FA	63.5	2.52	50.0
G	6.4	2.31	3.0

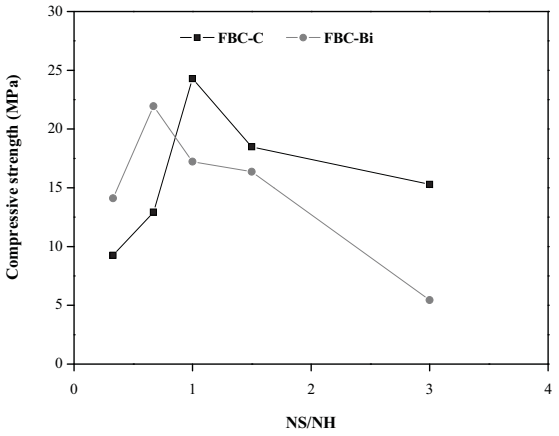


Fig. 1 Compressive strength of FBC-C and FBC-Bi geopolymers based on NS/NH ratios.

Details of mixing and testing

The source materials were the FBC-FA and the blend of 75%wt FBC-FA and 25%wt PCC-FA. Three levels of gypsum additive of 0, 5, and 10% by weight of solid binder content were used. The liquid/ash (L/A) ratio of 1.0 and sand/ash ratio of 2.75 were used for both FBC-C and FBC-Bi mixes. The NS/NH ratios of 1.0 and 0.67 for FBC-C and FBC-Bi geopolymers were selected from the optimum compressive strengths from the trial mixes (Fig. 1). The details proportion details are tabulated in Table 3. SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios were calculated from the source materials and alkaline solution in the reaction.

The FBC-FA and PCC-FA were blended thoroughly to obtain a uniform blended source material. Gypsum was added to the source material and mixed in a container. NH solution was added and mixed for 5 min. After that, NS solution was added and

Table 3 Mix proportions and oxide molar ratio of blended FBC-FA and PCC-FA containing G as an additive.

Mixes	FBC-FA: PCC-FA	G (%)	SiO_2/ Al_2O_3	Na_2O/ Al_2O_3
FBC-C100-G0†	100:0	0	5.29	1.74
FBC-C100-G5		5	5.38	1.83
FBC-C100-G10		10	5.47	1.93
FBC-C75-G0	75:25	0	5.29	1.83
FBC-C75-G5		5	5.37	1.93
FBC-C75-G10		10	5.46	2.03
FBC-Bi100-G0†	100:0	0	6.02	3.22
FBC-Bi100-G5		5	6.14	3.39
FBC-Bi100-G10		10	6.26	3.58
FBC-Bi75-G0	75:25	0	5.64	2.87
FBC-Bi75-G5		5	5.74	3.01
FBC-Bi75-G10		10	5.85	3.18

† Control mix.

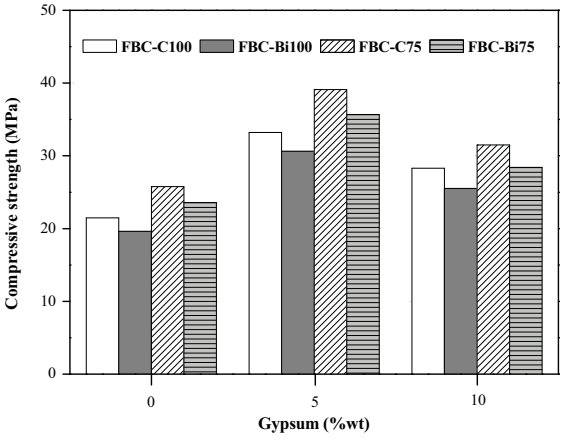


Fig. 2 Compressive strength of FBC-C and FBC-Bi based geopolymer mortars.

mixed for another 5 min. After mixing, the fresh paste was casted in $5 \times 5 \times 5$ cm cubic plastic moulds in accordance with ASTM C109 and compacted in a vibrating table for 10 s. The mould was then wrapped with polyvinyl sheet to prevent a loss of moisture. Samples were cured in an electric oven at 40 °C for 48 h and then kept at 25 °C and 50% R.H. room until testing. The paste samples were used for the XRD, FTIR, MIP, and SEM analyses. For the geopolymer mortar, sand was added at the final stage and mixed again for 5 min. The curing regime was the same as the paste samples. The compressive strength of mortar was tested at the age of 7 days in accordance with ASTM C109.

RESULTS AND DISCUSSION

Compressive strength

The results of compressive strength of mortars are shown in Fig. 2. The strength of FBC-C mortar was slightly higher than that of FBC-Bi mortar. The compressive strengths of FBC-C100-G0 and FBC-Bi100-G0 control mortar mixes were 21.5 and 19.6 MPa, respectively. The FBC-C contained a higher percentage of silica and alumina than those of FBC-Bi (Table 1). Although the reactivity of both FBC-C and FBC-Bi were low, the high silica and alumina of FBC-C was responsible for its slightly better performance than that of FBC-Bi. Blends of FBC-FA and PCC-FA significantly improved the strengths of mortars compared to the control mortars with no PCC-FA. The compressive strengths of blended FBC-C and PCC-FA, and FBC-Bi and PCC-FA mortars increased to 25.8 and 23.4 MPa, respectively. In addition, calcium silicate hydrate (CSH) gel from the reaction between Ca^{2+} from ashes and silicate group could increase the strength of the matrix [10]. The increase in strength in this case was due to the increased reactive amorphous phase of the mixture resulted from the blending of FBC-FA with PCC-FA [11].

The incorporation of 5% G as an additive further improved the compressive strengths of the mortars (Fig. 2). Addition 5% G increases the compressive strengths of FBC-C100-G5 and FBC-Bi100-G5 mortars to 33.2 and 30.6 MPa, respectively. The additions of 10% G also produced geopolymer mortars with high strength but were slightly lower than those with the addition of 5% G. The high amount of G hindered the geopolymer reaction and slightly decreased the strength of the geopolymer mortars [10]. The compressive strengths of FBC-C100-G10 and FBC-Bi100-G10 were 28.3 and 25.5 MPa, respectively.

For the blended fly ash mortars, the addition of G also showed the same trend of results as that of the FBC-FA mortars. The optimum increase in strength was obtained with the addition of 5% G. For the blended FBC-C and PCC-FA, the maximum compressive strength was 39.1 MPa with the addition of 5% G. For the blended FBC-Bi and PCC-FA, the maximum compressive strength was 35.7 MPa also with the addition of 5% G. The increase in the strength is due to the Ca^{2+} ions from G entering the Si−O−Al−O framework and balancing the charge on Al ions [12]. This played an important role to form the CSH and the stronger aluminosilicate structure and contributed to strength improvement. Furthermore, the SO_4^{2-} ions from G attacked the Al ions from ashes [13, 14] and form

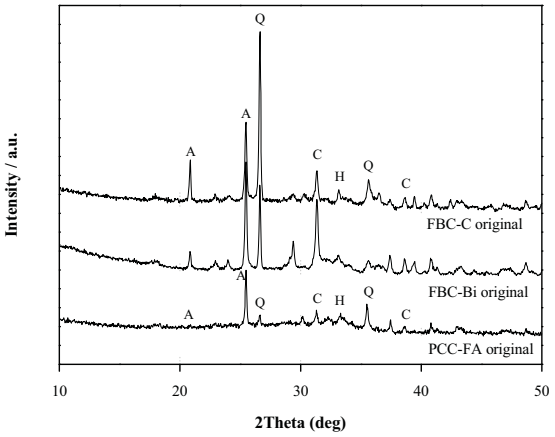


Fig. 3 XRD patterns of FBC-C, FBC-Bi, and PCC-FA originals (A = anhydrite, C = calcium oxide, H = haematite, Q = quartz).

aluminosilicate hydrate and geopolymer framework which help the strength development. However, the increase of G to 10%wt gave lower compressive strength than that of G 5%wt. There was an optimum SO_4^{2-} ions content which produced the highest compressive strength, with higher SO_4^{2-} ions content hindering the process of geopolymerization.

X-ray diffraction

The X-ray diffraction (XRD) patterns of the source materials are shown in Fig. 3. The crystalline phases of quartz (Q: SiO_2), anhydrite (A: $CaSO_4$), calcium oxide (C: CaO), and haematite (H: Fe_2O_3) were found in all FBC-Bi, FBC-C, and PCC-FA. The amount of CaO in FBC-Bi and quartz content were higher than those of FBC-C and PCC-FA. The FBC-C and FBC-Bi clearly showed lower content of amorphous phase than that of PCC-FA evident by a broad hump around 16–38° (2θ). This was due to the low combustion temperature of coal in the FBC system.

The XRD patterns of geopolymer paste are shown in Fig. 4. The XRD patterns of the source materials and those of geopolymer pastes differed in the amount of crystalline and amorphous phases. For the FBC-C and FBC-Bi pastes, the intensities of SiO_2 (Q) and CaO (C) peak decreased, while CSH (X), aluminosilicate (U), Magnesioferrite (F) and amorphous phase increased compared to those of the source materials. The broad humps of aluminosilicate gel around 30° (2θ) of the FBC-C pastes (Fig. 4a) were more pronounce than those of the FBC-Bi pastes (Fig. 4b). This suggested that the geopolymerizations of the FBC-C pastes were more advanced and agreed with

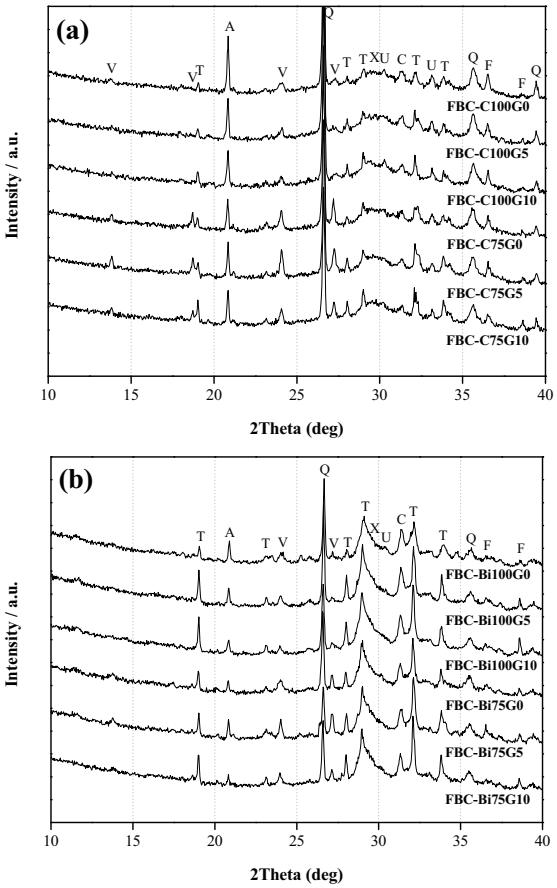


Fig. 4 XRD patterns of geopolymer pastes, (a) FBC-C and (b) FBC-Bi (A = anhydrite, C = calcium oxide, F = magnesioferrite, Q = quartz, T = thenardite, U = aluminosilicate, V = vishnevite, X = calcium silicate hydrate).

the higher compressive strength of the FBC-C pastes compared to those of the FBC-Bi pastes. Moreover, two new compounds, viz., zeolite named vishnevite (V: $Na_8Al_6Si_6O_{24}(SO_4)\cdot 2\,H_2O$) and thenardite (T: $NaSO_4$) were detected.

The blending of PCC-FA with FBC-C and FBC-Bi resulted in a reduction in the anhydrite content and an increase in the CSH, aluminosilicate, and vishnevite phases. The existence of some crystalline phase improved the strength of geopolymer paste[15]. Adding 5%wt G in FBC-C and FBC-Bi showed similar trend to those of the blending with PCC-FA with additional increases in, aluminosilicate, CSH, vishnevite, and thenardite phases. The addition of 10%wt G resulted in an increase in thenardite phase but decrease in vishnevite phase compared to the addition of

5%wt G. The reduction in the strength of geopolymer with the high amount of G was due to the reduction of vishnevite phase and the increase in the thenardite phase. It was suggested that the high percentage of Na_2SO_4 (T) existed as an impurity in the matrix [16]. Comparing the XRDs of Fig. 4a and Fig. 4b revealed that the phases of aluminosilicate and vishnevite of the mixes in FBC-C series were more pronounced than those of the mixes in FBC-Bi series. This confirmed that the higher strengths of FBC-C series compared to those of FBC-Bi series were probably due to the presence of the aluminosilicate and zeolite phase of vishnevite [17].

IR spectra

The Fourier Transform Infrared Spectroscopy (FTIR) was used to study the reaction of original materials and geopolymer pastes. The chemical bonding of IR spectra and results are shown in Fig. 5. The vibration of CO_3^{2-} at about 1500 cm^{-1} indicated the Na_2CO_3 from carbonation process [18]. The vibrations at 3700–3200 cm^{-1} of O−H stretching and 1700–1600 cm^{-1} of H−O−H bending showed the weak bond of water molecules which were easily adsorbed on the surface or trapped in large cavities between the rings of geopolymer materials. The Si−O−Si and Al−O−Si stretching of geopolymer pastes at the wavenumber of 1200–950 cm^{-1} were more prominent than in original materials. The blending with PCC-FA also showed all the common features of carbonation, O−H stretching and H−O−H bending, and Si−O−Si and Al−O−Si stretching. The noticeable difference was the larger Si−O−Si and Al−O−Si stretching band of the paste made from blending of FBC-FA with PCC-FA compared to that of the FBC-FA pastes. The increase in the Si−O−Si and Al−O−Si stretching band indicated the increase in the geopolymerization [5].

The addition of 5%wt G resulted in the increase of the intensity of Al−O−Si and S=O stretching at the wavenumber around 950–1200 cm^{-1} and vibration of Na_2SO_4 at the wavenumber of 636 cm^{-1}. The increase of G content to 10%wt resulted in the high calcium and SO_4^{2-} content. This provided the high band of Na_2SO_4 at the wavenumber of 636 cm^{-1}. The strength started to decline as Na_2SO_4 did not contribute to the strength of geopolymer.

Porosity

The total porosity of geopolymer pastes were measured by mercury intrusion porosimetry analysis (Fig. 6). For the control mixes, FBC-C100-G0 and FBC-Bi100-G0 contained the total porosity of 20.4% and 21.7%, respectively. The use of the blends of

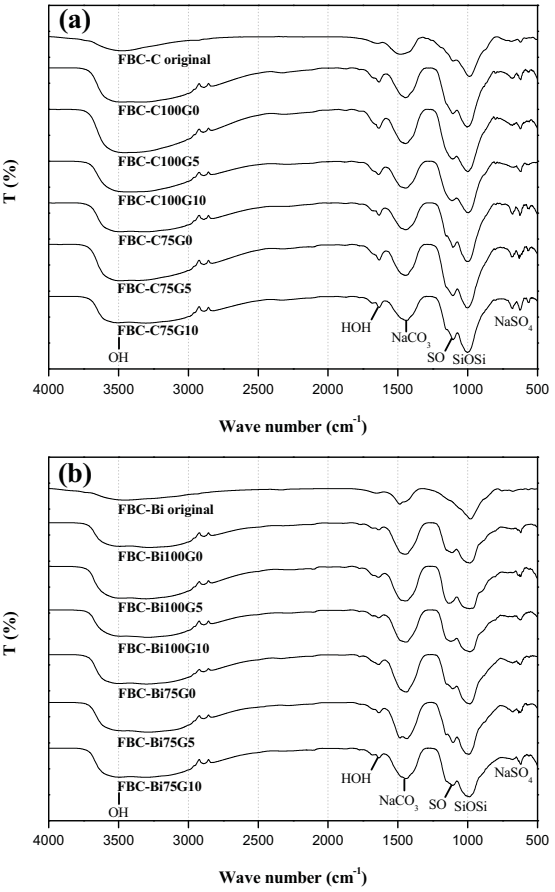


Fig. 5 FTIR spectra of original materials and geopolymer pastes, (a) FBC-C and (b) FBC-Bi.

FBC-FA and PCC-FA significantly reduced the total porosity of the pastes compared to the control mixes. The total porosity of blended FBC-C and PCC-FA; and FBC-Bi and PCC-FA decreased to 14.3 and 16.2%, respectively. The spherical shape and smooth surface of PCC-FA particle offered better distribution than that of FBC fly ash which comprised with irregular shape and high porosity particle. Additionally, PCC-FA was more effective in adjusting pores and decreasing the porosity of paste [19].

The addition of G as an additive could reduce the total porosity. For the incorporation of 5% G, the total porosity of FBC-C100-G5 and FBC-Bi100-G5 pastes were decreased to 16.5 and 17.1%, respectively. Although the additions of 10% G reduced the total porosity of geopolymer pastes compared with that of the control 0% G, they were higher than those with the addition of 5% G. This confirmed that the addition of 5% G produced a dense matrix with low porosity and

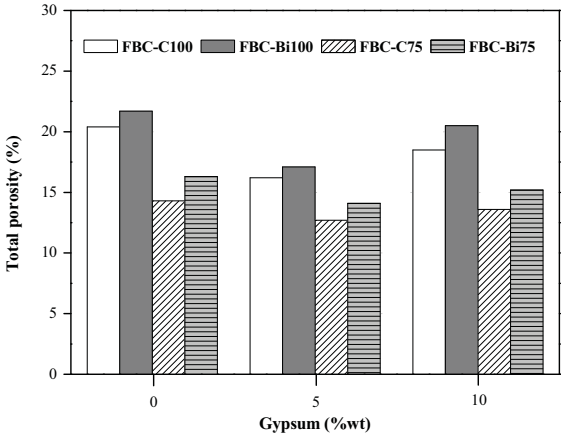


Fig. 6 Total porosity of geopolymer pastes from FBC-C and FBC-Bi.

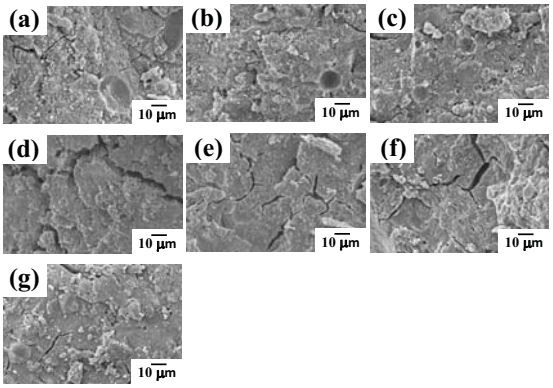


Fig. 7 SEM photography of geopolymer pastes, (a) FBC-C75G0, (b) FBC-C75G5, (c) FBC-C75G10, (d) FBC-Bi100G0, (e) FBC-Bi100G5, (f) FBC-Bi75G0, and (g) FBC-Bi75G5.

the increase in G content to 10% started to hinder the reaction. The total porosity of FBC-C100-G10 and FBC-Bi100-G10 were 18.5 and 20.5%, respectively.

For the blended fly ash pastes, the addition of G also showed a similar trend of results as that of the FBC-FA pastes. The optimum decreased in total porosity occurred with the addition of 5% G. For the blended FBC-C and PCC-FA, the total porosity was 12.7% with the addition of 5% G. For the blended FBC-Bi and PCC-FA, the minimum total porosity was 14.1% also with the addition of 5% G. The Ca^{2+} ions from G were interconnected with Si−O−Al−O chains thus provided the stronger structure and also decreased of the total porosity[20]. The incorporation of 10% G also produced geopolymer pastes with low total porosity but was slightly higher than those with the addition of 5% G. For the blended FBC-C and PCC-FA, the total porosity was 13.6% with the addition of 10% G. For the blended FBC-Bi and PCC-FA, the minimum total porosity was 15.2% with the addition of 5% G.

Scanning electron microscopy

The scanning electron microscopy (SEM) of geopolymer pastes are shown in Fig. 7. The matrix of FBC-C75 with 5% G was denser than that of FBC-C75 with 0 and 10% G as shown in Fig. 7a. This reflected an enhancement of geopolymerization by the addition of 5% G. With regard to the effect of PCC-FA, the results shown in Fig. 7b indicate that the replacement of 25% PCC-FA resulted in homogeneous and dense matrices in comparison to those without PCC-FA (FBC-Bi100) for both 0 and 5% G series. This confirmed that the PCC-FA was more reactive and contained a higher amount of amorphous phase than the FBC-FA[11].

CONCLUSIONS

The FBC-C and FBC-Bi could be used as source materials for the production of geopolymer. The blending with 25%wt PCC-FA improved the geopolymerization and resulted in geopolymer pastes with increased compressive strengths and reduced porosity. The improvement was due to the blending with the more reactive PCC-FA. The addition of G further improved the geopolymerization of the paste and resulted in additional increase in strength and reduction in porosity. The incorporation of 5%wt G was optimum. The increase in Ca^{2+} ions from G formed additional CSH and improved the strength and reduced the total porosity of geopolymer.

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Thermal treatment and utilization of Al-rich waste in high calcium fly ash geopolymeric materials

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Abstract: The Al-rich waste with aluminium and hydrocarbon as the major contaminant is generated at the wastewater treatment unit of a polymer processing plant. In this research, the heat treatment of this Al-rich waste and its use to adjust the silica/alumina ratio of the high calcium fly ash geopolymer were studied. To recycle the raw Al-rich waste, the waste was dried at 110°C and calcined at 400 to 1000°C. Mineralogical analyses were conducted using X-ray diffraction (XRD) to study the phase change. The increase in calcination temperature to 600, 800, and 1000°C resulted in the phase transformation. The more active alumina phase of active θ-Al_2O_3 was obtained with the increase in calcination temperature. The calcined Al-rich waste was then used as an additive to the fly ash geopolymer by mixing with high calcium fly ash, water glass, 10 M sodium hydroxide (NaOH), and sand. Test results indicated that the calcined Al-rich waste could be used as an aluminium source to adjust the silica/alumina ratio and the strength of geopolymeric materials. The fly ash geopolymer mortar with 2.5wt% of the Al-rich waste calcined at 1000°C possessed the 7-d compressive strength of 34.2 MPa.

Keywords: waste utilization; calcination; geopolymers; fly ash

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1. Introduction

The Al-rich waste is generated at the wastewater treatment unit of a polymer processing plant. In this process, aluminium chloride ($AlCl_3$) is used as a catalyst for the polymerization of hydrocarbon resin [1]. Neutralization with sodium hydroxide (NaOH) solution is performed on the polymer product. The resulting sewage contains aluminium hydroxide ($Al(OH)_3$) gel and is discharged into the wastewater treatment unit. The sewage is then treated with sulphuric acid (H_2SO_4) solution in order to adjust the pH value and to coagulate the Al-rich waste. The solid waste is finally separated from the wastewater and disposed off in landfill. The leaching of aluminium ions and other contaminants into groundwater is the main concern. The flowchart of the waste generation and treatment process is shown in Fig. 1.

The aluminium waste contains many forms of aluminium compounds. $Al(OH)_3$ is the major compound, and aluminium and sodium sulphate are the minor ones. The high annual output of Al-rich sludge leads to the problems of waste management and increases the treatment costs. A number of researches [2-4] have been conducted to utilize this Al-rich industrial sludge as a filler in cement and ceramic products. Due to the high water content up to 85wt% and the impurity of this sludge, treatment is needed to improve its properties before it can be effectively used. After the filter pressing

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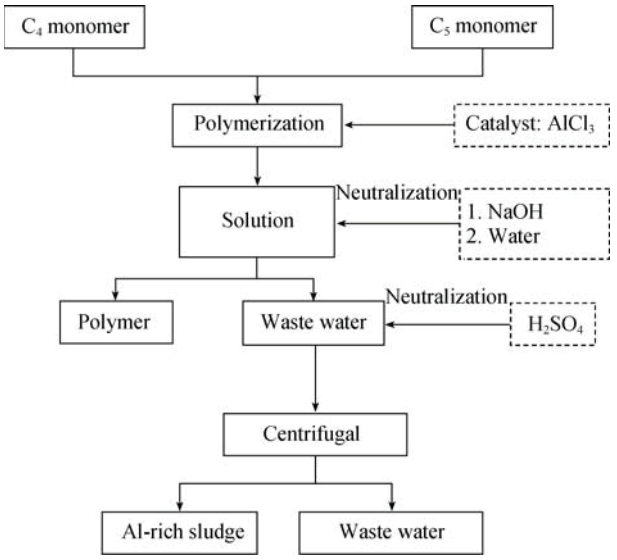


Fig. 1. Flow diagram of waste generation.

process, this sludge is basically the colloidal aluminium hydroxides with some soluble salts such as aluminium sulphate [2].

The high water content and the gel-like consistency of the sludge make it difficult to form the homogeneous mixture with other raw materials. This is the main reason for an increase in the drying shrinkage of ceramic bodies obtained from this sludge [3]. The pre-drying of Al-rich sludge at 100°C gives a strong agglomerated structure and also makes it difficult to obtain the proper mixing with other materials. Due to its high alumina content, calcination provides the opportunity for the application of this waste in the alumina-based materials such as mullite or mullite-alumina products.

In Thailand, the transportation cost for disposal is rather high at US$ 25-30/t and keeps rising. The amount of this waste increases every year and thus prompts the industry to find ways to utilize it. Therefore, this work aims to reuse the Al-rich waste by improving its properties with calcination. The calcined product should then be ready as an aluminium source material to produce the aluminosilicate binder or the geopolymeric material using low temperature curing [5-7]. Geopolymeric material is the aluminosilicate compound prepared at 40-90°C [6-7]. This material possesses high early compressive strength compared to the normal concrete at the same curing age.

Fly ash is widely used as an aluminosilicate source material for making geopolymer. It has been shown that high calcium fly ash is a suitable source material for making geopolymer [7-8]. The properties of the fly ash geopolymer can be further adjusted with the addition of chemical additives and mineral compounds such as rice husk ash [9-10]. In many instances, the source material contains low aluminium content, and the strength and other properties of the geopolymeric materials are impaired [11]. The utilization of the Al waste as an additional source material to increase the aluminium content of the geopolymer was therefore proposed.

2. Materials and methods

2.1. Materials

The Al-rich waste was obtained from a local polymer plant in Thailand. This waste contained high water content (ca. 80wt%); therefore, it was oven dried at 110±5°C for 24 h and the whitish yellow solid was obtained. The dry sample was then ground for 1 h using Rapid Mill 1105 (Compound Clay Ltd., Thailand) at 500 r/min. The median particle size of 15 μm measured by the particle size analyzer (Malvern Mastersizer S) was obtained. Grinding apparently reduced the grain size and promoted an amorphization, resulting in the enhancement of reactivity and structural changes of materials [12-13]. The chemical composition of this waste is presented in Table 1. The loss on ignition (LOI) was determined according to ASTM D7348. Differential scanning calorimetry (DSC) analysis was performed on the ground sample and on the commercial $Al(OH)_3$ sample using Pyris Diamond DSC (Perkin-Elmer) at a heating rate of 10°C/min, nitrogen purging at 20.0 mL/min, and the operation range from 50 to 400°C.

For the preparation of geopolymeric materials, the high calcium fly ash from the pulverized coal combustion process (PCC), sodium silicate solution (9wt% Na_2O, 30wt% SiO_2,

Table 1. Chemical composition of as-received Al-rich waste and fly ash **wt%**

Composition	Al-rich waste	Fly ash
$Al(OH)_3$	82.5	—
Na_2SO_4	4.7	—
NaCl	4.6	—
SiO_2	—	39.4
Al_2O_3	—	21.6
CaO	—	12.0
Fe_3O_4	—	11.4
SO_3	—	2.8
MgO	—	10.9
K_2O	—	2.1
LOI	8.2	0.8

and 61wt% H_2O), 10 M NaOH, and graded river sand with the fineness modulus of 2.8 were used [8].

2.2. Calcination of the ground sample

Since the Al-rich waste could not be used directly because of the high organic contents as indicated by the high LOI of 8.2%, the calcination was therefore employed. The LOI indicated the amount of organic compounds decomposed at 400-500°C since this waste was from a polymer plant. The ground samples were subjected to the thermal treatment at 400, 600, 800, and 1000°C for 1 h. The preliminary test indicated that 1-h calcination was sufficient. Although the cost of preparing this waste could be slightly higher than the normally used raw material, the method provides a new recycling opportunity for this kind of sludge. Mineralogical analysis was conducted using X-ray diffraction (XRD, PANalytical/Expert). Functional characterization of the calcined wastes was also performed by Fourier transform-infrared spectroscopy (FT-IR, Perkin-Elmer System 2000).

2.3. Preparation of geopolymeric materials

The Al-fly ash geopolymeric material was prepared by mixing the aluminosilicate source materials with sodium silicate solution (water glass), 10 M NaOH, and sand. The source materials were the blend of the calcined wastes (at 800 and 1000°C) and fly ash. The fly ash was replaced with 2.5wt% and 5.0wt% of the calcined wastes. The liquid was the mixture of water glass and 10 M NaOH with the mass ratio of 2:1. Powdery blend was then mixed with the liquid at the mass ratio of 60:40. Sand was used as a filler with a sand-to-powdery blend ratio of 2.0 [7-8]. The original pre-dried waste was also used to prepare the geopolymeric materials for comparison. Mix proportions are tabulated in Table 2.

Table 2. Mix proportion of geopolymeric materials g

Sample	Fly ash	Al waste	Water glass	10 M NaOH	Sand	Remark
Control	60	—	27	13	120	Control sample
2.5Al (PD)	58.5	1.5	27	13	120	Pre-dried waste
5Al (PD)	57	3	27	13	120	
2.5Al (800)	58.5	1.5	27	13	120	Calcined waste (800°C)
5Al (800)	57	3	27	13	120	
2.5Al (1000)	58.5	1.5	27	13	120	Calcined waste (1000°C)
5Al (1000)	57	3	27	13	120	

The pastes were cast into 5 cm cube acrylic plastic molds and cured at 60°C for 24 h to activate the reaction [7-8]. Specimens were then demolded and left in the controlled room of 23±2°C and with the relative humidity (RH) of 50%. The compressive strengths of specimens were measured at the age of 7 d using the compression testing machine (CB-10M, CBN Co.). The specimen was placed between the two steel plates and compressed at a uniform loading rate in accordance with the ASTM C109. Compressive strength was calculated by dividing the maximum load by the cross-sectional area of the specimen. The reported results are the averages of three samples.

The microstructural study of the hardened pastes was performed using scanning electron microscopy (SEM, Leo 1455VP SEM, Zeiss). Nonconductive specimens were coated with gold before the examination with the microscope.

3. Results and discussion

3.1. Characterization of pre-dried waste

DSC was used to study the thermal transition of the commercial pure $Al(OH)_3$ and the ground pre-dried waste. This technique observes the exothermic and endothermic events such as glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m). The temperature range of the investigation was from 50 to 400°C. The results of the DSC-thermogravimetric (TG) analysis (endothermic up) are presented in Fig. 2. The commercial $Al(OH)_3$ exhibits T_c of 240°C. At this temperature, the crystalline arrangement occurred as indicated by the drop in the heat flow. The material gave off heat when it crystallized in the exothermic transition. Endothermic transition (T_g) was also found at 345°C as heat was absorbed for phase transformation and the broad peak appeared. For the ground pre-dried waste, only the crystallization peak T_c was found at 165°C. These endothermic peaks indicated the transition of gibbsite ($Al(OH)_3$) to boehmite (AlO·OH) at ~250°C and the transition of boehmite to γ-alumina (γ-Al_2O_3) at ~350°C [14-15]. The change in location of T_c was due to contaminants in the waste. The contaminants were the unreacted hydrocarbons, polymer residue, and sodium sulphate from the polymerization and neutralization processes. These impurities of

Al-rich sludge hindered the homogeneous formation; therefore, the removal was needed to increase its efficiency. Calcination was consequently applied to this waste.

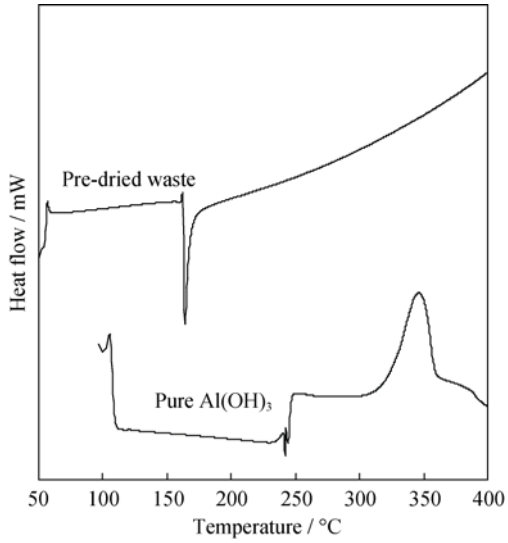


Fig. 2. DSC-TG curves of commercial pure $Al(OH)_3$ and pre-dried waste.

3.2. Characterization of the calcined waste

3.2.1. XRD analysis

The XRD results of the waste after calcination are shown in Fig. 3. The calcination duration and the temperature are significant factors for the phase change and removal of impurities. The calcination resulted in the amorphous phase with some crystalline phases [16]. The compounds detected in the pre-dried sample were gibbsite ($Al(OH)_3$), sodium sulphate ($NaSO_4$), and sodium chloride (NaCl) as shown in Table 1. At the calcination temperature of 400°C, γ-Al_2O_3 was formed. For the calcination temperatures of 600, 800, and 1000°C, two distinct peaks at 37° and 46° indicated the incipient phase of active θ-Al_2O_3. The glassy phase was increased due to the increase in calcination temperature as indicated by the appearance of broad peaks. The θ-Al_2O_3 was formed in large quantity with some impurities of NaCl and Na_2SO_4 at 600 and 800°C. The decomposition temperatures of NaCl and Na_2SO_4 were 780 and 880°C, respectively. At 1000°C, NaCl disappeared and the sample contained a higher amount of the amorphous phase. The calcination of gibbsite produced a series of transitions of alumina as shown in the following equation [14, 17]:

$$\text{Gibbsite} \xrightarrow{200^\circ\text{C}} \gamma\text{-boehmite} \xrightarrow{400^\circ\text{C}}$$

$$\gamma\text{-}Al_2O_3 \xrightarrow{750^\circ\text{C}} \delta \xrightarrow{900^\circ\text{C}} \theta \xrightarrow{1200^\circ\text{C}} \alpha\text{-}Al_2O_3.$$

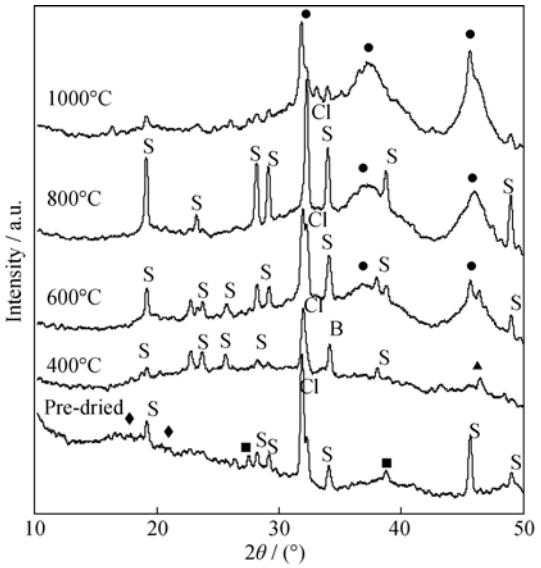


Fig. 3. XRD patterns of the Al-rich waste. Cl—NaCl; S—Na_2SO_4; ♦—gibbsite; ■—boehmite; ▲—γ-Al_2O_3; ●—θ-Al_2O_3.

All transition phases are stable at room temperature. It has been pointed out that the transformation temperatures are somewhat variable depending on the impurities of the starting materials [3, 17]. Practically, various substances can be produced with mixed crystalline forms of $Al(OH)_3$, AlO·OH, and aluminium oxide (Al_2O_3) with water molecules. These are known as hydrated alumina. Calcination of the hydrated hydroxide resulted in the loss of water and produces various kinds of active alumina. They differ in porosity, number of remaining –OH groups, and particle size. They can be used as catalyst supports and in chromatography.

3.2.2. IR spectra

Fig. 4 shows the FT-IR spectra of the pre-dried and the calcined samples at 800 and 1000°C. Spectrum characterization of the products is based on the analysis of the absorption bands, which are due to the vibrations of –OH groups in the ranges of 800 to 1300 cm^{-1} (bending vibrations) and 3000 to 3800 cm^{-1} (stretching vibrations). Despite the significant similarity of the structures, the arrangements of the layers in some hydroxides were different in the O–H···O–H distances (predetermining the length of the hydrogen bond), which led to a change in the arrangement of the IR bands [18]. The vibration stretching of S=O of the sulfonate group of Na_2SO_4 was located at ~1100 cm^{-1}. The absorption peaks in the region of 700 to 400 cm^{-1} corresponded to the existence of $Al(OH)_3$ and Al_2O_3. The IR spectra of the calcined samples were slightly different from that of the pre-dried

sample. In the region of 1000 to 400 cm^{-1}, the calcined samples showed a noticeable change with peak shift compared to that of the pre-dried sample and a broader peak at 1000 to 800 cm^{-1} resulting from the phase transformation of gibbsite to active θ-Al_2O_3. At high calcination temperature, $Al(OH)_3$ dehydrated to Al_2O_3, resulting in the absorption band shift. The change of the crystal structure could also be responsible for the differences. In addition, the band of gibbsite could partially overlap with that of boehmite at 1070 cm^{-1} as in the pre-dried sample. From the results of XRD and IR spectra, the waste samples with the calcination temperatures of 800 and 1000°C were selected to blend with fly ash for making the geopolymeric materials.

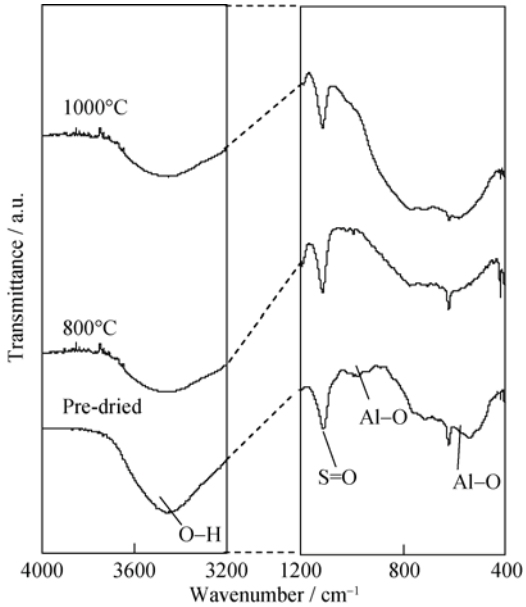


Fig. 4. IR spectra of the pre-dried and calcined samples.

3.2.3. Compressive strength

The pre-dried sample and calcined samples (if applicable) were mixed with fly ash, water glass, 10 M NaOH, and sand to form geopolymeric materials. The compressive strengths of the specimens are presented in Fig. 5. The control geopolymeric specimen had the compressive strength of 27.6 MPa. Blending of the fly ash with the pre-dried waste gave slightly lower strengths of 27.4 and 24.8 MPa for 2.5wt% and 5.0wt% replacements, respectively. The pre-died waste contained impurities and the low strength geopolymers were thus obtained. The low replacement level of 2.5wt% pre-dried waste resulted in a small decrease in strength. However, at the 5wt% replacement level, the strength was significantly reduced. In contrast, the calcined waste at 800 and 1000°C gave higher strengths than that of the control. For the calcined waste at 800°C, the 7-d compressive strengths of the mixes with 2.5wt% and 5wt% replacements were 31.2 and 29.9 MPa, respectively. At a high calcination temperature of 1000°C, the compressive strengths of the 2.5wt% and 5wt% replacements were significantly increased to 34.2 and 31.6 MPa, respectively. The higher strength was obtained as a result of the increase in amorphous phase of the calcined waste at high temperature. The amorphous phase was relatively active and enhanced a chemical bonding between the Al-compound and sodium silicate. The Al dissolved in sodium silicate solution and replaced the four-coordinate Si in the silicate network leading to a strong chemical bonding [13, 19]. The presence of gibbsite ($Al(OH)_3$) increased the strength of geopolymer compared with that containing both boehmite and gibbsite. The gibbsite readily dissolves at moderate hydroxide concentrations and temperatures. The dissolution of θ-Al_2O_3 and other Al forms, however, requires more rigorous conditions and generally is kinetically slow [20]. As a result, NaOH in the mixture helped the dissolution of gibbsite, resulting in the strength enhancement of geopolymeric materials. In addition, calcination removed impurities and promoted the phase transformation.

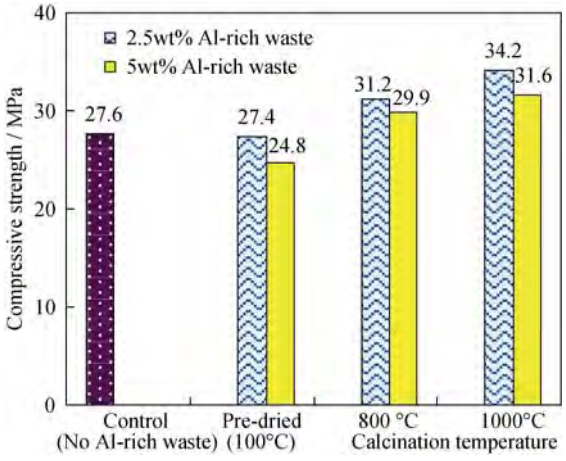


Fig. 5. Compressive strength of Al-fly ash geopolymeric materials at the 7-d curing.

However, the increase in Al content could adversely affect the strength. The surplus aluminium acted as the filler because of the insufficient amount of Si for geopolymerization reaction. However, for the source material with high silica content such as rice husk ash, the high Al dosage is beneficial for the strength development of the geopolymer [21]. The mechanical strength of the material is known to be enhanced by a high initial silica-to-alumina (SiO_2/Al_2O_3) ratio, which increases the number of strong Si–O–Si bonds in the final product [22]. The Al_2O_3 content in the system also plays an important role in the controlling process kinetics

[23-24]. The SiO_2/Al_2O_3 ratios of the specimens are shown in Table 3.

Table 3. SiO_2-to-Al_2O_3 ratio in geopolymer mixtures

Geopolymer sample	SiO_2-to-Al_2O_3 molar ratio
Control	4.32
2.5wt% Al-rich waste	3.88
5wt% Al-rich waste	3.51

It was reported that the optimum SiO_2/Al_2O_3 ratio was between 3.5 and 4.0 for good strength geopolymer. The use of low SiO_2/Al_2O_3 ratio resulted in an Al-rich aluminosilicate gel and a low strength geopolymer. The mechanical strength rose during the transformation of the Al-rich into a Si-rich aluminosilicate gel [23]. In addition, some calcium silicate hydrate (C–S–H) was also formed and coexisted with the class C fly ash geopolymeric products [24]. The formation of C–S–H contributed partly to the strength development and resulted in less silica available for the geopolymerization reaction. The aluminosilicate phase with a low Si/Al ratio was therefore obtained [25]. A decrease in Si/Al ratio could lead to the aluminosilicate compound of lower strength accompanied by the increase in crystalline phase [26]. Therefore, the increase in the fly ash replacement level of the Al-rich waste from 2.5wt% to 5wt% resulted in the geopolymer with a lower strength.

3.2.4. Microstructural study

The microstructures of Al-fly ash geopolymer pastes prepared by the pre-dried and the calcined samples (1000°C) with 2.5wt% replacement were investigated using SEM. Fig. 6 shows the geopolymer gel formation on the fly ash particles. The hardened gel prepared using the non-calcined Al-rich waste was not homogenous and agglomerations of the gel were easily detected. Partially reacted fly ash particles were easily detected as a result of the low reactivity of the waste. For the calcined Al-rich waste, the formation of the gel fully covered the fly ash particles resulting in the more homogenous matrix compared with the pre-dried Al waste sample due primarily to the increased reaction of active alumina (θ-Al_2O_3). The gel bound the fly ash particles and formed a dense geopolymer matrix, resulting in an increase in compressive strength. Therefore, calcination enhanced the reactivity of Al-rich waste, making it suitable for use as an alternative aluminium source material.

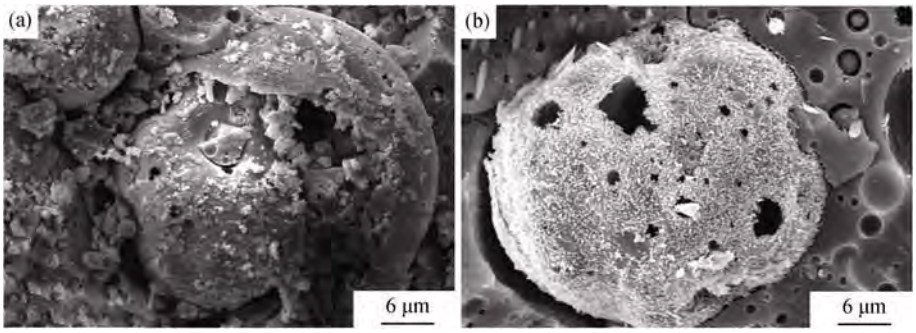


Fig. 6. SEM images of Al-fly ash geopolymer: (a) 2.5Al (PD) sample; (b) 2.5Al (1000) sample.

4. Conclusions

The improvement of the Al-rich waste from a polymer plant can be made by grinding and calcination. The calcination transformed the inactive boehmite to active alumina (θ-Al_2O_3). According to the XRD pattern, the calcination temperature of the waste needs to be higher than 800°C to obtain the phase transformation. The ground calcined waste with a median particle size of 15.0 μm can be used as an additional source material for adjusting the silica-to-alumina ratio of the fly ash geopolymeric materials. A reasonable compressive strength of 34.2 MPa was obtained at the age of 7 d for fly ash geopolymer mortar with 2.5wt% replacement of the Al-rich waste (calcined at 1000°C) compared with the strength of 27.6 MPa of the control.

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Permeability and abrasion resistance of concretes containing high volume fine fly ash and palm oil fuel ash

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Abstract. In this paper, compressive strength, water permeability and abrasion resistance of concretes containing high volume fine fly ash (FFA) and fine ground palm oil fuel ash (GPA) were studied. Portland cement type I was replaced with FFA and GPA at dosages up to 70% by weight of binder. Ground river sand (GRS) was also used to replace Portland cement in order to indicate the level of filler effect. Results indicated that FFA was slightly more reactive than GPA. The replacement of 40-70% of FFA produced concretes with compressive strength, permeability and abrasion resistance comparable to those of normal concretes. The incorporation of GPA slightly reduced the performances of concretes as compared to those of FFA concretes. The reduction of Portland cement was partly compensated by the increase in pozzolanic activity of the fine fly ash and palm oil fuel ash and thus enabled the large replacement levels.

Keywords: concrete; water permeability; abrasion resistance; fly ash; palm oil fuel ash.

1. Introduction

Strength, water permeability and abrasion resistance of concrete are recognized as important properties of concrete. They indicate the quality of concrete, its durability and service life. The most critical parameters controlling durability of concrete are governed by the transportation of liquid or fluid in concrete. Therefore, durability of concrete can be monitored as a function of water permeability. The deterioration of concrete during its service life arises primarily from its high permeability (Naik *et al.* 1996, Basheer *et al*. 2001, Khan 2003). It has been shown that incorporation of pozzolans with suitable dosage level can improve the permeability of concrete (Vedalakshmi 2003).

Abrasion resistance also indicates the durability, especially for concretes which require strong surface such as hydraulic structure, traffic pavement and parking lots. The abrasion is caused by the rolling or grinding of any element against the concrete surface. This phenomenon induces damage to concrete and can jeopardize the whole structure integrity. Abrasion resistance of concrete is

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influenced by various factors, such as mixture proportion, aggregate property and supplementary cementitious materials. Researches indicated that the abrasion resistance depended primarily on the strength of concrete (Siddique 2003, Li *et al.* 2006).

Fly ash, a well-known pozzolan, has been extensively used in concrete work. Its use increases the durability of concrete through pore refinement and reduction in calcium hydroxide of cement paste matrix (Chindaprasirt *et al.* 2007, Malhotra 2002). Properties of concrete are affected by both quality and quantity of fly ash. It is generally agreed that fine fly ash is more reactive and thus improves the properties of mortar and concrete than as-received coarse fly ash (Chindaprasirt *et al.* 2004, Chindaprasirt *et al.* 2010a, Erdogdu and Turker 1998, Sata *et al.* 2011).

Palm oil fuel ash has been recently introduced as a new pozzolanic material. It has to be properly ground to obtain satisfactory reactivity (Tangchirapat *et al.* 2009). Properties of concrete such as compressive strength, chloride penetration resistance and alkali-silica reaction can be improved when incorporated with palm oil fuel ash (Awal and Hussin 1997, Chindaprasirt *et al.* 2010b, Rukzon and Chindaprasirt 2009a, 2009b, Tay 1990). However, palm oil fuel ash is not yet being used commercially in concrete industry and almost all of it is discarded in landfills.

Because the global price of Portland cement is increasing and the production process consumes large amount of energy which leads to greenhouse effect (Malhotra 2002), many attempts are being made to utilize higher percentage of supplementary cementitious materials or pozzolans to replace conventional Portland cement. It is generally accepted that the use of supplementary material at low replacement level produced good concrete with reduced porosity, increased durability and acceptable strength (Chindaprasirt *et al.* 2005, Malhotra 2002, Ramezanianpour and Malhotra 1995). The reactivity of the pozzolanic materials increases with the increase in their finenesses (Chindaprasirt *et al.* 2004, Erdogdu and Turker 1998, Sathonsaowaphak *et al.* 2009). This should allow a higher replacement level of these pozzolanic materials in the concrete industry.

Inert materials such as ground sand are incorporated to Portland cement to produce silica cement (Neville 1995). This is to adjust some of the properties of the cement, lower the cost and reduce the use of Portland cement. It is also successful to use inert material to replace part of cement to study the filler effect on the strength development of concrete (Tangpagasit *et al.* 2005).

This work aims to investigate the water permeability and abrasion of concrete containing high volume FFA and GPA. The results will be useful and lay some ground work for utilization of high fine pozzolan replacement of Portland cement.

2. Experimental program

2.1 Materials and concrete mixtures

Ordinary Portland cement (OPC) was used for all concrete mixtures. Lignite fly ash from Mae Moh power plant in the north of Thailand was used. FFA was obtained from air classifier. GPA was obtained from ball mill grinding of palm oil fuel ash; a waste material from the palm oil extraction factory. In addition, ground river sand (GRS) with similar fineness to FFA and GPA was used to indicate the filling effect (Isaia *et al.* 2003, Nehdi 1998, Tangpagasit *et al.* 2005). Physical properties and chemical compositions of the OPC and replacement materials (R) are reported in Tables 1 and 2. FFA, GPA and GRS finenesses were similar with percentages retained on No. 325 sieve (45 μm opening) of 1.0-2.5% by weight. Natural river sand with a fineness modulus of 2.44 and specific gravity of 2.65 and crushed limestone with nominal size of 20 mm and specific gravity of 2.67

Table 1 Physical properties of cement and replacement materials

Material	Specific gravity	Retained on a sieve No. 325 (%)	Median particle size, d_{50} (μm)
Portland cement type I (OPC)	3.14	-	14.7
Classified fly ash (FFA)	2.52	2.43	5.5
Ground palm oil fuel (GPA)	2.43	1.0	8.1
Ground river sand (GRS)	2.65	2.02	6.0

Table 2 Chemical composition of cement and replacement materials

Compositions	OPC	FFA	GPA	GRS
SiO_2	20.9	41.1	57.8	92.8
Al_2O_3	4.8	22.5	4.6	3.2
Fe_2O_3	3.4	11.6	3.3	0.3
CaO	65.4	15.3	6.6	0.6
MgO	1.2	2.8	4.2	0.5
Na_2O	0.2	1.7	0.5	0.4
K_2O	0.3	2.9	8.3	0.3
SO_3	2.7	1.5	0.3	0.5
LOI	0.9	0.2	10.1	0.6

Table 3 Concretes mix proportions

Mixes	OPC (kg)	FAA (kg)	GPA (kg)	GRS (kg)	Fine (kg)	Coarse (kg)	Water (kg)	*W/C+R*	Slump (mm)
Control	300	-	-	-	915	1080	213	0.71	75
FFA20	240	60	-	-	920	1084	200	0.67	85
FFA40	180	120	-	-	933	1098	185	0.62	80
FFA55	135	165	-	-	928	1093	189	0.63	80
FFA70	90	210	-	-	902	1067	202	0.67	90
GPA20	240	-	60	-	907	1072	220	0.73	65
GPA40	180	-	120	-	900	1064	222	0.74	70
GPA55	135	-	155	-	894	1059	225	0.75	90
GPA70	90	-	210	-	889	1011	228	0.76	70
GRS20	135	-	-	60	905	1070	212	0.71	75
GRS40	180	-	-	120	896	1060	216	0.72	60
GRS55	135	-	-	165	882	1046	222	0.74	65
GRS70	90	-	-	210	886	1050	228	0.76	60

were used as fine and coarse aggregates in concrete mixtures, respectively.

Table 3 shows the concrete mixture proportions. The controlled concrete with water to cement ratio of 0.71 and slump of 75 mm was selected so that the effects of incorporating FFA and GPA can be gauged with confidence. Slumps were maintained at 75±15 mm and water to cement and replacement material ratios ($W/(C+R)$) were controlled within 0.71±0.05 except for FFA as it

improved workability and slightly lowered the *W/C+R* ratios of concretes. These were achieved without the aid of plasticizer. The concretes with Portland cement replaced with 20, 40, 55 and 70% of FFA, GPA and GRS were prepared and tested.

2.2 Testing procedure

2.2.1 Compressive strength

Concrete cylinders of 100 mm in diameter and 200 mm in height were cast, demolded at 24 hours and cured in water. The compressive strength of concretes was tested at 28 and 90 days. The report results are the average of three samples.

2.2.2 Water permeability

For permeability testing, concrete cylinder was sliced to discs of 40 mm thickness and the ends were discarded. The disc was installed in permeability cell as suggested by Khatri and Sirivivatnanon (1997). Distilled water was used as fluid to flow through concrete disc under constant pressure. The pressure of 0.5 MPa (5 bars) recommended by concrete society (1987) was employed. Report results are averages of four samples. Flow rate was monitored and the steady flow rate was used to calculate permeability using equation based on Darcy's law and equation of continuity.

$$K = \frac{\rho L g Q}{P A}$$

K - coefficient of permeability, ρ - density of water, L - thickness of concrete sample, g - gravity acceleration, Q - flow rate, P – pressure of water, A - cross sectional area of sample

2.2.3 Abrasion resistance

Abrasion resistance of concrete was evaluated according to ASTM C1138 (Underwater method). Samples of 300 mm in diameter and 100 mm in height were cast and cured in moist condition for 28 days. The samples were installed in the abrasion machine containing 70 chrome steel balls placed on the concrete upper surface. Fresh water was filled to the specified level and stirring of steel balls with blade was performed for 12 hours. This procedure was repeated 6 times. The abrasion of concrete was calculated from the weight loss of the samples.

3. Results and discussion

3.1 Properties and particle shape of materials

The chemical compositions of the materials as shown in Table 2 revealed that the classified fly ash could be assigned as class F as prescribed by ASTM C 618. For GPA, the contents of SiO_2 + Al_2O_3 + Fe_2O_3 were 65.7%, while the GRS consisted of 92.8% SiO_2.

Fig. 1 shows the particle size distribution curves of OPC, FAA, GPA and GRS and their median particle sizes (d_{50}) are 14.7, 5.5, 8.1 and 6.0 μm, respectively. The particle size distribution curves of FFA, GPA and GRS are similar. Their particle sizes are slightly finer than the OPC. As shown in Fig. 2, the FFA is spherical in shape and its surface is relatively smooth. On the other hand, OPC, GPA and GRS contain particles with angular and irregular shape as a result of crushing and milling processes.

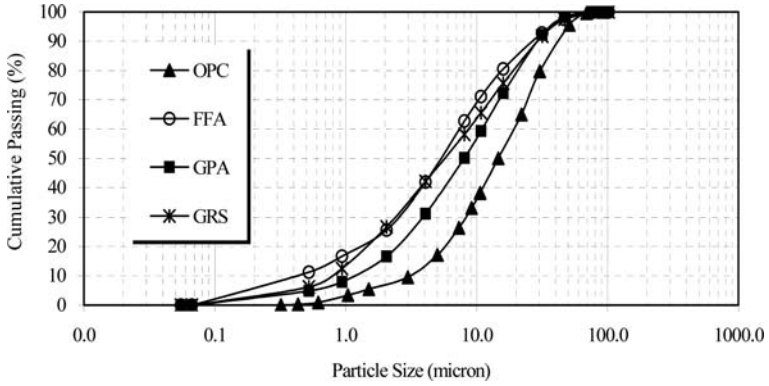


Fig. 1 Particle size distribution of cement and replacement materials

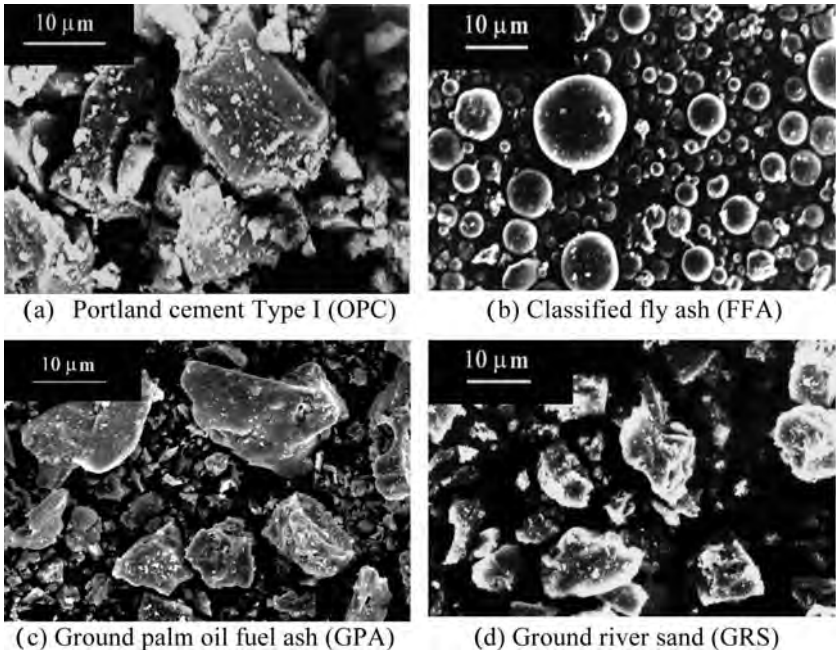


Fig. 2 Scanning electron microscopy (SEM) of cement and replacement materials

3.2 Water requirement in concrete mixes

The amounts of mixing water are shown in Table 3. The use of FFA reduced the *W*/(*C*+*R*) ratios of fly ash concrete compared to that of the control concrete. For example, the *W*/(*C*+*R*) ratios of the control concrete, FFA20 (mix with 20% FFA), FFA40, FFA55 and FFA70 concretes were 0.71, 0.67, 0.62, 0.63 and 0.67, respectively. The reduction in water requirement was the result of the ball bearing effect of the spherical FFA particles. For the GPA and GRS concretes, the opposite trend of results was obtained. The *W*/*C*+*R* ratios of both GPA and GRS concretes were slightly higher than that of control concrete and increased with the increase in the replacement level. The angular and irregular particles of GPA and GRS increased the water requirement to maintain the same workability compared to that of the control concrete.

3.3 Compressive strength

Table 4 shows compressive strengths and normalized compressive strengths of concretes containing FFA, GPA and GRS in comparison with that of control concrete. The relationship between the compressive strengths of concretes and the replacement levels are shown in Fig. 3.

The compressive strengths of FFA20 were 32.5 and 35.4 MPa or 123% and 126% of the control concrete at 28 and 90 days, respectively. The strengths of FFA concretes with the 55% replacement were still higher than that of the original concrete. When the cement replacement by FFA was 70%, the compressive strength of FFA concrete was slightly lower than that of control concrete. The

Table 4 Compressive strength, water permeability and abrasion of concretes

Mixes	Comp. Strength (MPa) –Normalized (%)		$k \times 10^{-12}$ (m/s) - k/k_{CON}		Abrasion depth
	28 days	90 days	28 days	90 days	(mm)
Control	26.1 – 100	28.2 - 100	2.89 - 1.00	2.05 - 1.00	2.55
FFA20	32.5 – 123	35.4 - 126	1.32 - 0.46	0.44 - 0.21	2.38
FFA40	31.9 – 122	34.0 - 121	0.51 - 0.18	0.32 - 0.16	2.41
FFA55	29.1 – 111	31.8 - 113	0.72 - 0.25	0.42 - 0.21	2.67
FFA70	25.5 – 98	27.1 - 96	1.85 - 0.64	1.54 - 0.90	3.45
GPA20	23.9 – 92	29.4 - 104	0.59 - 0.20	0.25 - 0.12	2.75
GPA40	20.7 – 79	23.7 - 84	0.41 - 0.14	0.26 - 0.13	3.23
GPA55	18.1 – 69	22.3 - 79	3.30 - 1.14	2.38 - 1.16	3.67
GPA70	14.9 – 57	17.5 - 62	37.30 - 12.9	23.10 - 11.27	4.34
GRS20	22.2 – 85	25.9 - 92	8.16 - 2.83	5.91 - 2.88	3.54
GRS40	16.0 – 61	17.2 - 61	22.60 - 7.83	10.20 - 4.98	4.62
GRS55	9.1 – 35	9.3 - 33	630 - 218	447 - 218	5.73
GRS70	5.1 - 20	5.2 - 18	2250 - 780	2450 - 1195	6.52

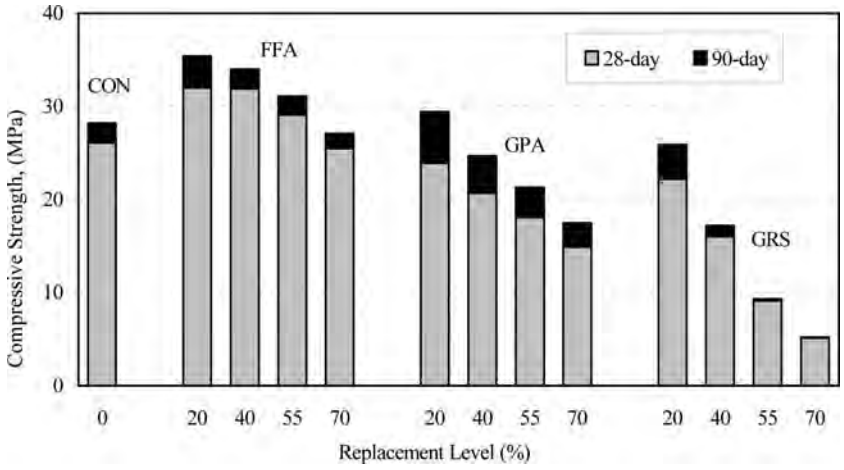


Fig. 3 Relationship between the compressive strength of concrete and the cement replacement level

results indicated better performance of high volume FFA concrete compared to that of high volume normal fly ash concrete (Jiang and Malhotra 2000, Serdar *et al.* 2007). The good performance of FFA was due to the ball bearing effect, the dispersion effect and the enhancement of the pozzolanic reaction of small particle size of FFA (Erdogdu and Turker 1998, Chindaprasirt *et al.* 2004).

The compressive strength of GPA concretes decreased with the increase in the replacement levels. The 28-day compressive strengths of GPA20, GPA40, GPA55 and GPA70 concretes were 23.9, 20.7, 18.1 and 14.9 MPa or 92, 79, 69 and 57% of the control concretes, respectively. These results were due to the less Portland cement content and the slightly larger amount of water in the concrete mixture. At 90 days, the compressive strength of GPA20 concrete was, however, improved compared to the compressive strength at 28 days. This confirmed that a substantial amount of pozzolanic reaction was obtained with the use of GPA in concrete. High volume 40-70% GPA could also be used to produce concrete with acceptable 28-day compressive strength of 15-20 MPa. It should be pointed out here that higher strength concretes could be obtained with lower water to cement ratio with the aid of superplasticizer (Jiang and Malhotra 2000, Serdar *et al.* 2007).

For GRS concretes, the 28-day and 90-day normalized compressive strengths of GRS20 concrete were 85 and 92% of control concrete. At low level of replacement, the filler effect is significant and this resulted in only slight reduction in strengths. The compressive strengths of GRS concretes, however, decreased substantially as the level of replacement was increased. The GRS produced filler effect from its small particle size without pozzolanic effect (Tangpagasit *et al.* 2005) and was thus not effective in terms of maintaining the acceptable strengths with high replacement level. At high replacement level, the pozzolanic effect played the dominant role in maintaining the acceptable level of strengths.

3.4 Permeability of concrete

The permeability of concretes and the ratios of permeability are given in Table 4. The ratio of permeability is defined as the permeability of concrete containing replacement materials divided by that of the control concrete. The values of water permeability of the control concrete at 28 and 90 days were 2.89×10^{-12} m/s and 2.05×10^{-12} m/s, respectively.

Fig. 4 shows the relationship between permeability and replacement levels of materials. The values of permeability of concretes decreased with the age of samples. This was the result of the increase in hydration and pozzolanic reaction with time (Ramezanianpour and Malhotra 1995). The permeability values of FFA concretes were lower than those of the control concretes for all replacement levels. The lowest permeability was obtained with the replacement of 40%. This result can be attributed to the pozzolanic reaction from FFA, and the less amount of mixing water influenced the reduction in volume and size of pores in cement paste (Poon *et al.* 2001). Moreover, the filler effect of the smaller particles of FFA also assisted to produce a denser cement matrix (Govindarajan and Gopalakrishnan 2009).

GPA concretes also showed the same characteristic of permeability as FFA concretes when the replacement levels were up to 40% by weight of binder. The 90-day water permeability of GPA20 and GPA40 concretes were 0.25×10^{-12} m/s and 0.26×10^{-12} m/s or 0.12 and 0.13 of those of the control concretes, respectively. For the GPA40 concrete, its water permeability was also lower than that of control concrete in spite of the slightly higher water content (0.74 for GPA40 concrete and 0.71 for control concrete). Although the pozzolanic reaction of GPA was lower than that of FFA as indicated by the strength development characteristics, the permeability values were similar at this

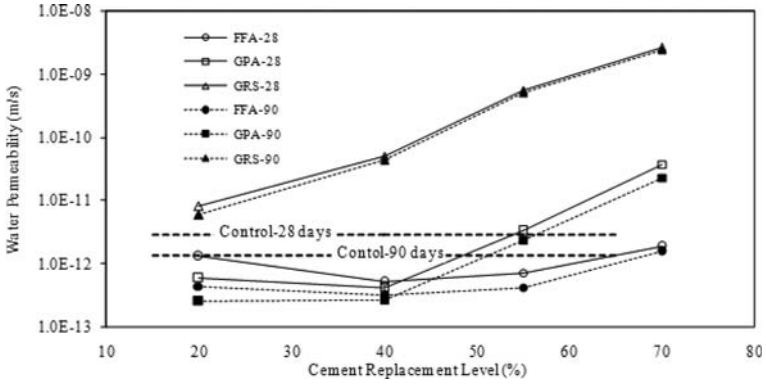


Fig. 4 Relationship between water permeability of concrete and cement replacement level

range of replacement. This suggested that filler and pozzolanic effects were comparatively high up to replacement level of 40% of GPA and contributed to the low permeability of the concretes.

At higher replacement level of 55 and 70% of GPA, the permeability increased significantly. The 90-day ratios of permeability of GPA55 and GPA70 concretes were 1.16 and 11.27, respectively. This resulted from the slightly higher water content of the mixes, the low pozzolanic reaction and the low filler effect which were not sufficient at the high level of replacement.

The ratios of water permeability of GRS20, GRS40, GRS55 and GRS70 concretes at 28 days were 2.83, 7.83, 218 and 780, respectively. Only the GRS20 concrete gave the acceptable level of permeability. For high level of replacement, the filling effect alone was not able to maintain the low level of permeability of the concretes. At high replacement level, the pozzolanic effect also played the dominant role similar to that of strength.

The relationships between water permeability and compressive strength of concrete at 90 days are presented in Fig. 5. In general, the permeability decreased when concrete compressive strengths were higher. The high volume FFA concrete showed both high strength and low permeability. The high volume GPA concrete showed slightly lower strength and higher permeability than those of

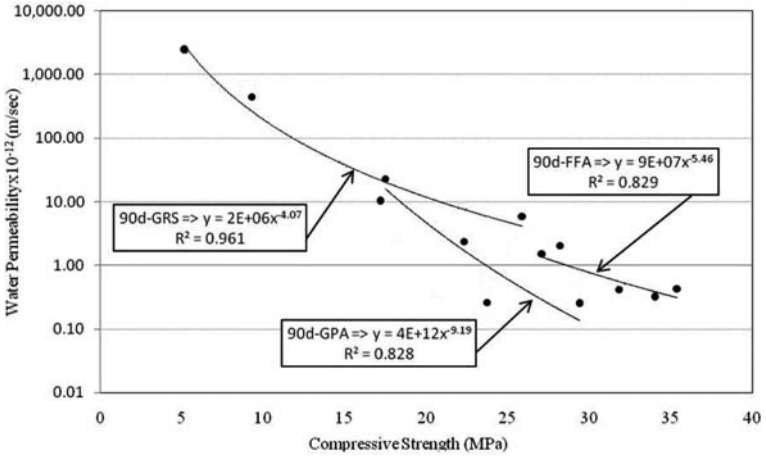


Fig. 5 Relationship between water permeability and compressive strength of concrete at 90 days

FFA concrete. At high level of replacement, the filler effect became less significant and the performances of concrete relied mainly on the pozzolanic reaction.

3.5 Abrasion resistance of concrete

The abrasion of concretes is shown in Table 4 and the relationship between abrasion and replacement levels of materials is shown in Fig. 6. The abrasion of concrete in this investigation ranged from 2.38-5.52 mm. The abrasion of FFA concrete was slightly lower than that of the OPC concrete with the replacement level up to 40% and the lowest value was 2.38 mm for FFA20 concrete compared to 2.55 mm of the OPC concrete. A similar trend of result of decreasing abrasion resistance with OPC replacement level of above 50% with class C fly ashes was reported by Naik *et al.* (2002).

For GPA concretes, the abrasion increased as the content of GPA increased. The depth of wear of GPA20 was slightly higher at 2.75 mm than those of FFA and OPC concretes. The abrasion resistance of GRS concrete significantly increased with the increase in the replacement level. This indicated that although the incorporation of GRS produced filling effect, it had an adverse effect on the abrasion resistance of concrete. The filling of GRS did not have a cementing property which helped to resist the abrasion.

Fig. 7 presents the relationships between the depth of abrasion, permeability and compressive strength of concrete at 28 days. The compressive strength of concrete with the incorporation of supplementary material is related to the abrasion resistance. The abrasion resistance increased with increasing compressive strength and could be expressed in terms of exponential equation with R^2 of 0.945. The previous researches also reported that the abrasion resistance was strongly governed by its compressive strength (Siddique 2003, Li *et al.* 2006).

The relationship between water permeability and depth of abrasion of concrete is also shown in Fig. 7. As expected, the high permeability concrete produced low abrasion resistance. The relationship could also be expressed in terms of exponential relation with R^2 of 0.899. This result agreed with

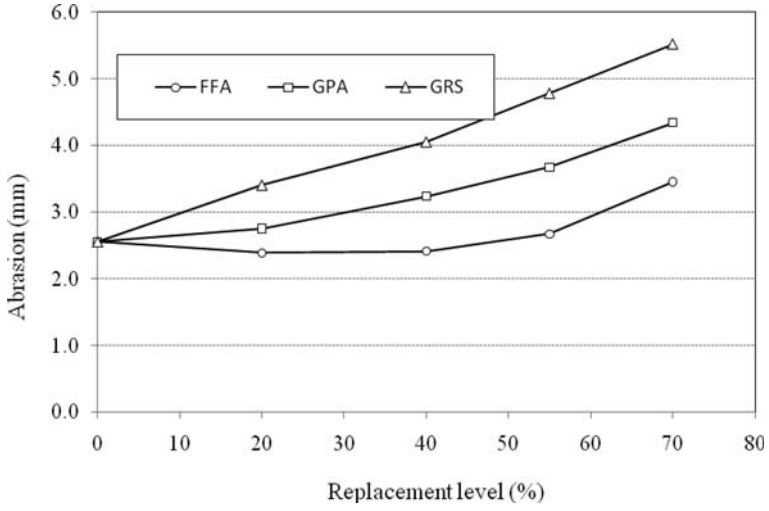


Fig. 6 Relationship between abrasion and replacement level at 28 days

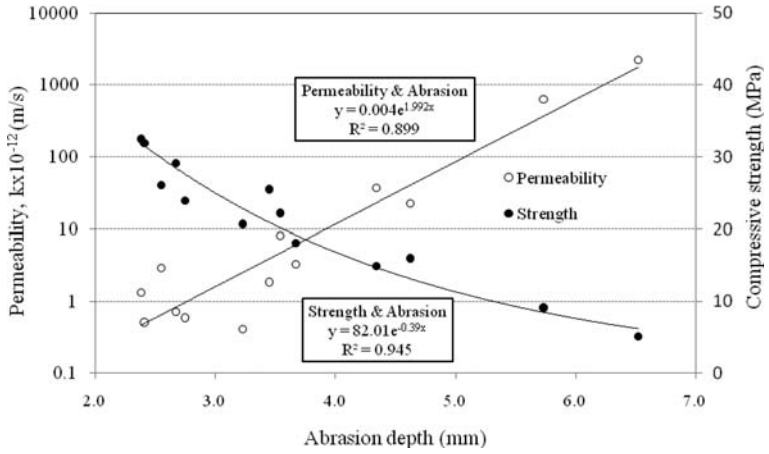


Fig.7 Relationship between abrasion, permeability and compressive strength at 28 days

that of Liu *et al.* (2006) who studied the abrasion erosion of concrete using the water-borne sand and found that the concrete with high coefficient permeability exhibited the low abrasion erosion resistance.

4. Conclusions

From this study, it can be concluded that high volume fine fly ash (FFA) and fine ground palm oil fuel ash (GPA) can produce concrete with acceptable strength, water permeability and abrasion resistance. FFA is an effective pozzolan for use in high volume as it produces good pozzolanic reaction through the small particle size and requires less water through the ball bearing effect of the spherical particles. GPA is slightly less effective pozzolan compared to FFA and its use in high volume resulted in slightly lower strength and higher water permeability.

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Dielectric Properties of 2–2 PMN-PT/Cement Composites

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Dielectric properties of 2–2 connectivity lead magnesium niobate-lead titanate (PMN-PT)/Cement composites were investigated at 0.1–20 kHz. PMN-PT of 60–80% by volume was used. The composites were fabricated using a dice and fill technique and cured in 98%RH curing chamber for 7 days before measurements. Dielectric constant (ε_r) at 1 kHz increased with PMN-PT volume, having values of 1504, 1645 and 2390 respectively. Dielectric loss (tanδ) values are 0.382, 0.185 and 0.188 at 1 kHz. In addition, the dielectric constant was found to decrease with an increase in the frequency tested having value of 1692, 1504 and 1322 for 0.1, 1 and 20 kHz respectively. The dielectric loss was found to be less with increasing frequency at 0.702, 0.382 and 0.179 for 0.1, 1 and 20 kHz respectively.

Keywords PMN-PT; cement; composites; 2–2 connectivity; dielectric properties

1. Introduction

A number of research developments have been made very recently on the composite material which consists mainly of a piezoelectric ceramic and a cement-based material [1–19]. Among those, many dielectric and piezoelectric properties of 0–3 connectivity composites were reported [1–4, 6–13, 15–19]. One of the mostly used piezoelectric ceramic materials is lead zirconate titanate (PZT) as it has very high piezoelectric coefficient (d_{33}) and dielectric constant (ε_r) [20, 21] and most of the piezoelectric-cement based composites were produced using PZT as the piezoelectric ceramic in the composite [1–14, 17–19]. Another piezoelectric material such as lead magnesium niobate-lead titanate, $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) may also be used as PMN-PT ceramic has a high dielectric constant (ε_r) and high piezoelectric coefficient [22]. For cement-based composite produced with

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piezoelectric materials other than PZT such as PMN-PT very little is know. In this research work, PMN-PT/cement composite material was produced from PMN-PT with normal Portland cement (PC) as a composite of 2–2 connectivity PMN-PT/PC composite and dielectric properties were investigated at 0.1–20 kHz.

2. Experimental

A columbite technique was first used to produce PMN powder where $MgNb_2O_6$ or MN powder was produced by calcining magnesium carbonate hydroxide pentahydrate $(MgCO_3)_4Mg(OH)_2.5(H_2O)$ and Nb_2O_5 at 1150°C. MN powder was mixed with lead oxide (PbO) in ethanol and milled together in a zirconia ball mill for 24 h, and were calcined at 800°C to produce PMN powder. Lead titanate ($PbTiO_3$) was produced in a similar manner using mixed oxide method from PbO and TiO_2. PMN and PT were then mixed together at a molar ratio of 0.67PMN – 0.33PT in ethanol and milled together for 30 minutes. PMN and PT powder were then pressed into pellets before sintering at 1250°C for 2 h to finally produce PMN-PT ceramic disc of ≈15 mm in diameter and ≈2 mm thick. The composites were fabricated using a dice and fill technique where Portland cement paste was filled in the gaps after cutting and cured in 98%RH 60°C curing chamber for 7 days before measurements. An impedance meter (Hewlett Packard 4194A) was used to obtain the capacitance and the dissipation factor (dielectric loss: tanδ) of the composites at room temperature and at frequency of 0.1, 0.5, 1, 5, 10 and 20 kHz. The relative dielectric constant (ε_r) was the calculated from the following equation:

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A}$$

where C is the sample capacitance, t is the thickness, ε_0 is the permittivity of free space constant (8.854×10^{-12} Farad per meter), and A is the electrode area.

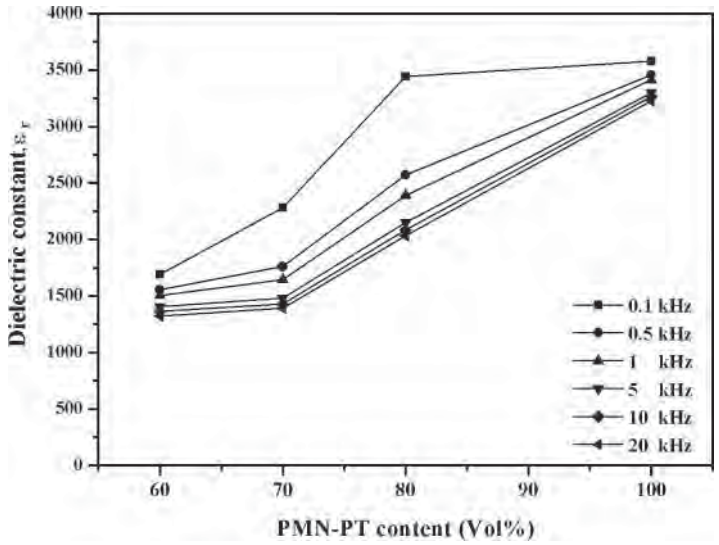


Figure 1. Dielectric constant results of 2–2 PZT-cement composites at 0.1 to 20 kHz.

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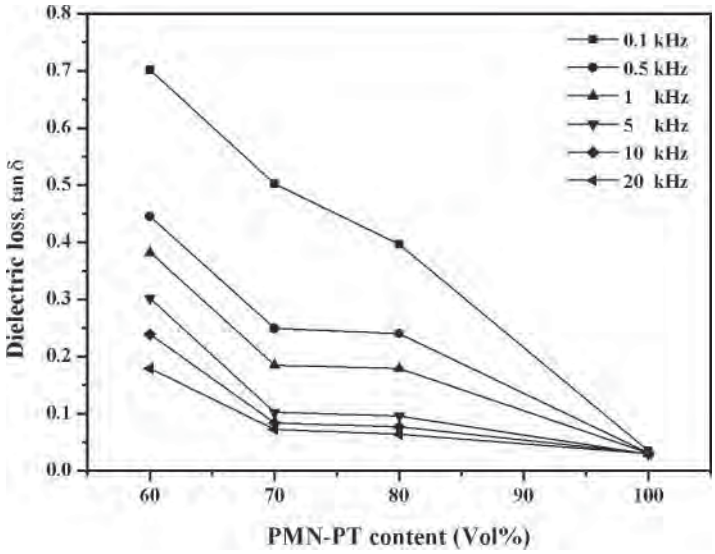


Figure 2. Dielectric loss results of 2–2 PZT-cement composites at 0.1 to 20 kHz.

3. Results and Discussion

The effect of PMN-PT on the dielectric constant at various frequencies (0.1 kHz–20 kHz) can be seen in Fig. 1 where the dielectric constant is plotted against PMN-PT content. The dielectric constant of the 2–2 composites can be seen to increase with PMN-PT content for all frequencies. Moreover, the dielectric constant can be seen to decrease with an increase in the frequency used. The dielectric constant values are 1692, 1504 and 1322 at 0.1 kHz, 1 kHz and 20 kHz for 60% PMN-PT composite respectively. At a certain frequency, i.e. at 0.1 kHz the ε_r values can be seen to increase with increasing PMN-PT vol. content which are 1692, 2283 and 3444 for composite with 60%, 70% and 80% PMN-PT respectively. At 1 kHz, the ε_r values are 1504 and 2390 for composite with 60% and 80% PMN-PT respectively. These values are noticeably higher than reported values at 1 kHz of 0–3 piezoelctric-cement composites [4–7] where the dielectric value is in the region of 200–300 for 50–70% by volume.

The effect of PMN-PT on the dielectric loss measured at the frequency from 0.1 kHz to 20 kHz can be seen in Fig. 2. In general, the dielectric loss of 2–2 PMN-PT/cement composites was found to reduce with increasing frequency, for 60% PMN-PT composite the tanδ values are 0.702, 0.38, 0.239 and 0.179 at 0.1, 1, 10 and 20 kHz respectively. The tanδ values were also found to reduce with increasing PMN-PT content at all frequency tested.

4. Conclusions

PMN-PT ceramic/ cement composites of 2–2 connectivity were produced using a dice and fill method. Dielectric constant (ε_r) of 2–2 composites at 1 kHz increased with PMN-PT volume, having values of 1504, 1645 and 2390 respectively. Dielectric loss (tanδ) values are 0.382, 0.185 and 0.188 at 1 kHz. In addition, the dielectric constant was found to decrease with an increase in the frequency tested having value of 1692, 1504 and 1322 for 0.1, 1 and

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20 kHz. The dielectric loss was found to be less with increasing frequency at 0.702, 0.382 and 0.179 for 0.1, 1 and 20 kHz respectively.

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FACTORS AFFECTING THE WORKABILITY AND STRENGTH OF ALKALI-ACTIVATED HIGH CALCIUM FLY ASH CONCRETE

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Abstract

The effects of several parameters on the workability and strength of alkali-activated high calcium fly ash (AAHCFA) concrete were investigated in this study. The AAHCFA concretes were activated with alkali sodium hydroxide solution (NaOH), sodium silicate solution (Na_2SiO_3) and heat. Three alkali liquid to fly ash (L/S) ratios of 0.55, 0.60 and 0.65, three NaOH concentrations of 10, 15 and 20 molars (M) and three Na_2SiO_3/NaOH ratios of 1.0, 1.5 and 2.0 were used. The workability was obtained by measuring the slump and the compressive strength was tested to gauge the strength of concrete. The results revealed that the workability of AAHCFA concrete was related to the molar ratio of H_2O/Na_2O in activator, the NaOH concentration, and the L/S ratio. The improvement in compressive strength was mainly related to the increase in the NaOH concentrations. The strength was, however, reduced with the increase in the Na_2SiO_3/NaOH ratio. The obtained slumps were in the range of 70 to 260 mm and the 28-day compressive strength ranged from 9.0 to 47.5 MPa. The influence of delay time (the time taken from the completion of specimen casting to the start of heat curing), curing temperature and curing duration on compressive strength were also presented.

Key words: alkali-activated material, compressive strength, concrete, high calcium fly ash, workability

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Portland cement materials in many aspects such as fire resistance, acid resistance and solidification of heavy metal wastes (Duxson et al., 2007). The binding property of alkali-activated binders depends on various factors such as source materials used, processing conditions and curing conditions. Various source materials such as blast furnace slag, clay, metakaolin and fly ash have been investigated over the past decades. A review on alkali-activated binders can be found in Pacheco-Torgal et al. (2008).

For fly ash, researchers have made intensive studies on alkali-activated low calcium or class F fly ash (FFA) mortar and concrete (Chindaprasirt et al., 2009; Hardjito and Rangan, 2005; Palomo et al., 1999). However, few papers have been published regarding the use of high calcium or class C fly ash (CFA) in making alkali-activated materials in particular alkali-activated concrete. The worldwide availability of fly ash worldwide, both FFA and CFA, has been increasing annually (Malhotra, 2002).

For the use of CFA, the presence of high amounts of calcium may have effects in the polymerization process and the microstructure. Nevertheless, the presence of calcium can greatly improve the compressive strength of alkali-activated materials and accelerates the hardening process (Yip et al., 2005). The studies on microstructures (Guo et al., 2010; Yip et al., 2005; Yip et al., 2008) have been conducted to explain this observation, however, it is still not clear why and how the presence of calcium plays such a significant role in determining the properties of an alkali-activated binder. Understanding of the use of CFA in producing alkali-activated concrete would be useful to the future applications.

This study focused on the investigation of the effects of several parameters on the mechanical properties of alkali-activated high calcium fly ash (AAHCFA) concrete. The mass ratio of alkaline liquid to fly ash (L/S), concentration of sodium hydroxide solution (NaOH), mass ratio of sodium silicate solution to sodium hydroxide solution (Na_2SiO_3/NaOH), delay time (the time taken from the completion of specimen casting to the start of heat curing), curing temperature and curing duration were the main parameters examined in the current study.

2. Materials

Fly ash from Mae Moh power station in the north of Thailand was used in this study as the source material. The loss on ignition (LOI) and chemical composition of this fly ash obtained by X-Ray Fluorescence (XRF) analysis using a Philips PW-2404 instrument is given in Table 1. The fly ash conforms to the class C, as per ASTM C 618-03 (2003), as the sum of SiO_2, Al_2O_3 and Fe_2O_3 is between 50 and 70% and the fly ash contains more than 20% of CaO. This fly ash has Blaine fineness of 3100 cm^2/g in accordance with ASTM C 204-00 (2000). The molar Si-to-Al ratio is about 1.3 which is slightly low for concrete application compared with the value of 2 suggested by Davidovits (1999). The XRD of the high calcium fly ash is shown in Fig. 1. The fly ash consisted mainly of the glassy phase which is highly disordered as indicated by the hump between 21 to 38 °2θ with some crystalline phases consisted of anhydrite, calcium oxide, magnesioferrite, hematite and quartz.

Sodium hydroxide pellets (99% purity) and sodium silicate solution (9.5 wt% Na_2O, 29.0 wt% SiO_2 and 61.5 wt% H_2O) were used for the preparation of alkaline solution. The sodium silicate solution used in this test was slightly higher in water content than the normally used one and this could affect the workability and other test results. However, it was selected as it gave a satisfactory wide range of relatively workable concretes. Local river sand with specific gravity of 2.58 and crushed stone (12.5 mm nominal size) with specific gravity of 2.65 were used as fine and coarse aggregate, respectively. Both aggregates were in saturated surface dry (SSD) condition.

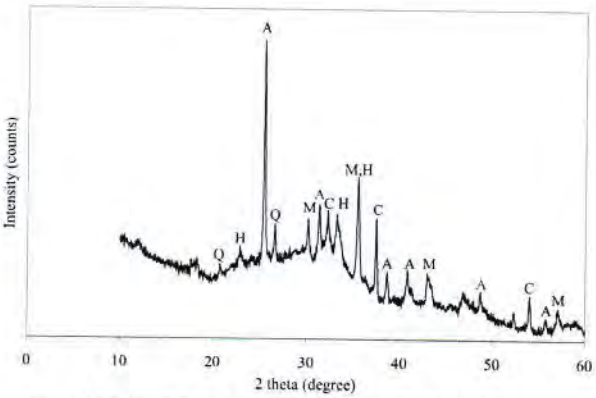


Fig. 1. XRD of fly ash: A = anhydrite ($CaSO_4$), C = calcium oxide (CaO), M = magnesioferrite ($MgFe_2O_4$), H = hematite (Fe_2O_3) and Q = quartz (SiO_2)

3. Experimental

3.1. Test on delay time, heat curing temperature and heat curing duration

For the first part, the effects of curing conditions including delay time, heat curing temperature and heat curing duration were investigated on compressive strength. The compressive strength tests were carried out at the age of 7 days.

Table 1. Chemical composition of fly ash

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	TiO_2	MgO	K_2O	P_2O_5	SO_3	LOI
Mass (%)	24.83	18.93	15.61	27.41	1.92	0.44	2.33	2.62	0.22	4.71	0.40

The mix of Na_2SiO_3/NaOH ratio of 1, NaOH concentration of 20M and L/S ratio of 0.60 were used. The mix constituents in one cubic meter are 1294 kg crushed stone, 554 kg sand, 345 kg fly ash, 103.5 kg Na_2SiO_3 and 103.5 kg NaOH.

3.1.1. Effect of delay time

The delay times of 0, 1, 8 and 24 hours were used before heat curing of the concrete specimens at 60 °C for a period of 1 day. Some delay time was found to be beneficial to strength (Hardjito and Rangan, 2005) as it allowed the dissolving of silica and alumina (Chindaprasirt et al., 2007).

3.1.2. Effect of temperature of heat curing

For this test, a constant delay time of one hour was used based on the result obtained from the test of the effect of delay time. The concrete specimens were heat cured for a period of 1 day. The curing temperatures of 25, 40, 60, 75 and 90°C were selected for this test based on the previous work. Hardjito and Rangan (2005) worked on the alkali-activated low-calcium fly ash (AALCFA) concrete and found that curing at temperatures of 60, 75 and 90°C gave AALCFA concrete with good compressive strengths. At low curing temperatures of 30 and 45 °C the strengths were rather slow. For AAHCFA pastes and mortars, the curing at moderate temperatures of 60 to 90°C was also required to obtain reasonable strength (Chindaprasirt et al., 2007; Guo et al., 2010).

3.1.3. Effect of duration of heat curing

In this test, a constant delay time of one hour and a temperature of heat curing of 60 °C were used. The heat curing durations of 0.5, 1, 2, 3 and 4 days were selected also based on the previous work. Hardjito and Rangan (2005) reported that the strength of AALCFA concrete increased with increasing curing duration of up to 4 days. Chindaprasirt et al. (2007) also reported the same trend of results with the curing duration up to 3 days.

3.2. Details of main test and mix design

In order to examine the potential influencing factors on the workability and strength of AAHCFA concrete, the effects of L/S ratio, NaOH concentration and Na_2SiO_3/NaOH ratio were investigated. Three L/S ratios of 0.55, 0.60 and 0.65, three NaOH concentrations of 10M, 15M and 20M and three Na_2SiO_3/NaOH ratios of 1.0, 1.5 and 2.0 were used. It should be pointed out that the concentrations of NaOH of 15M or 20M are high and may lead to difficulty in handling and to the increased cost. From a preliminary test, the use of low L/S ratios of 0.3 to 0.4 gave mixes with low slumps. The suitable workability range was obtained with the slightly higher values of L/S of 0.55-0.65 to avoid adding extra water in order to maintain the concentration of NaOH for better comparison of test results. The range of L/S of 0.52-0.71 was used to produce workable alkali-activated high calcium bottom ash mortar (Sathonsaowaphak et al., 2009). For reasons of cost and environmental gain, it is advisable to use slightly lower workable mix with lower L/S ratio in practice to reduce the amount of NaOH and Na_2SiO_3 usage. For example, the mix No.1 as shown in Table 2 (Na_2SiO_3/NaOH = 1, 10M NaOH and L/S = 0.55) consists of 1294 kg crushed stone, 554 kg sand, 356 kg fly ash, 98 kg Na_2SiO_3 and 98 kg NaOH. The delay time of 1 hour, the temperature of heat curing of 60 °C and the duration of heat curing of 1 day were employed based on the results obtained from the Section 3.1. The details of the mixes and their main molar ratios are given in Table 2.

The main oxide molar ratios of the mixes were varied in the following ranges: SiO_2/Al_2O_3 = 2.94-3.35, Na_2O/Al_2O_3 = 0.96-1.62 and H_2O/Na_2O = 7.06-12.20 as compared to SiO_2/Al_2O_3 = 3.5-4.5, Na_2O/Al_2O_3 = 0.8-1.2 and H_2O/Na_2O = 15-17.5 as suggested by Davidovits (1982). The 1.92 wt.% Na_2O in the fly ash was taken into account to calculate the overall ratio of H_2O/Na_2O as commonly practiced (Hardjito and Rangan, 2005; Sathonsaowaphak et al., 2009). Admittedly, it is questionable whether this Na_2O in the fly ash is present in a reactive phase and thus not all takes part in the reaction. Therefore, H_2O/Na_2O in the activator denoted by H_2O/Na_2O* and modulus of the activator (Ms) viz., molar ratio of SiO_2/Na_2O are also given in Table 2.

3.3. Specimen preparations and tests

For each mix, the alkaline solution was obtained by dissolving sodium hydroxide pellets in water and then mixed with the sodium silicate solution. The liquid was then left to cool down to the temperature of 25-28 °C prior to using. This was done to eliminate the uncontrolled temperature effect. Prior mixing of sodium hydroxide solution and sodium silicate solution in the making of alkali-activated concrete is suggested by Hardjito and Rangan (2005) for the purpose of the reduction of bleeding and segregation.

The mixing of AAHCFA concrete started with the mixing of alkaline liquid and fly ash for 5 minutes. From trial mixes using different mixing times, it was found that the use of mixing time of 5 minutes gave a consistence paste and concrete with high compressive strength. The mixing of fly ash and NaOH solution for 5 minutes was used in the previous work (Chindaprasirt et al., 2007; Sathonsaowaphak et al., 2009). Sand and crushed stone in SSD condition were mixed together for 2 minutes in a pan mixer. This was followed by the addition of the premixed alkaline liquid and fly ash and continued the mixing for another 2 minutes. Right after the mixing, the slump test was performed in accordance with ASTM C 143/C 143M-00 (2000).

Table 2. Na_2SiO_3/NaOH, NaOH concentration, L/S, SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Na_2O, H_2O/Na_2O* and Ms of the mixes

Mix No.	*Na_2SiO_3/ NaOH*	*NaOH concentraion*	*L/S*	*SiO_2/Al_2O_3*	*Na_2O/Al_2O_3*	*H_2O/Na_2O*	*H_2O/Na_2O**	*Ms*
1	1	10M	0.55	2.94	0.96	11.87	14.38	0.91
2	1	10M	0.60	3.01	1.03	12.05	14.38	0.91
3	1	10M	0.65	3.07	1.10	12.20	14.38	0.91
4	1	15M	0.55	2.94	1.18	8.97	10.44	0.71
5	1	15M	0.60	3.01	1.27	9.07	10.44	0.71
6	1	15M	0.65	3.07	1.36	9.16	10.44	0.71
7	1	20M	0.55	2.94	1.39	7.06	8.02	0.58
8	1	20M	0.60	3.01	1.51	7.13	8.02	0.58
9	1	20M	0.65	3.07	1.62	7.19	8.02	0.58
10	1.5	15M	0.55	3.08	1.07	9.82	11.64	0.95
11	1.5	15M	0.60	3.16	1.15	9.95	11.64	0.95
12	1.5	15M	0.65	3.24	1.23	10.06	11.64	0.95
13	1.5	20M	0.55	3.08	1.24	7.99	9.23	0.80
14	1.5	20M	0.60	3.16	1.34	8.08	9.23	0.80
15	1.5	20M	0.65	3.24	1.43	8.16	9.23	0.80
16	2	15M	0.55	3.18	0.99	10.49	12.61	1.15
17	2	15M	0.60	3.27	1.07	10.64	12.61	1.15
18	2	15M	0.65	3.35	1.14	10.77	12.61	1.15
19	2	20M	0.55	3.18	1.14	8.74	10.25	0.98
20	2	20M	0.60	3.27	1.22	8.85	10.25	0.98
21	2	20M	0.65	3.35	1.31	8.95	10.25	0.98

After that, specimens were cast in steel cylindrical moulds 100 mm in diameter and 200 mm in height. The fresh AAHCFA concrete was placed in three equal layers. Each layer was vibrated for 15 seconds on a vibrating table. After casting, the moulds were covered with vinyl sheet and left at 25-28 °C standing at a predetermined delay time before the temperature curing for a specified curing time in the oven. After heat curing, the specimens were put in the laboratory to cool down and then demolded. Finally, each specimen was wrapped with plastic film and left at 25-28 °C until the day of test. The compressive strength tests were conducted as per ASTM C 39/C 39M-01 (2001). The strength at the ages of 1, 3, 7 and 28 days were determined. The reported strengths are the average of three tests. The standard deviations are also plotted on the test data points as the error bar.

4. Results and discussion

4.1. Results of test for delay time, heat curing temperature and duration

4.1.1. Delay time

The results of the effect of delay time on compressive strength are shown in Fig. 2. The strength of 21.8 MPa was obtained by the sample with no delay time before the curing. When the delay time was 1 hour, the strength increased slightly to a maximum of 28.6 MPa. This is in agreement with the previous study (Chindaprasirt et al., 2007) on AAHCFA mortar, where a delay time longer than 1 hour slightly reduced the strength of mortar. For AALCFA concrete, a delay time of up to 72 hours was found to be beneficial to strength (Hardjito and Rangan, 2005). Some delay time allowed the dissolving of silica and alumina (Chindaprasirt et al., 2007) and therefore enhance the strength development of alkali-activated binder. Some delay time is highly desirable in practice especially in precast concrete industry as this gives sufficient time between casting products and preparing them for the heat curing.

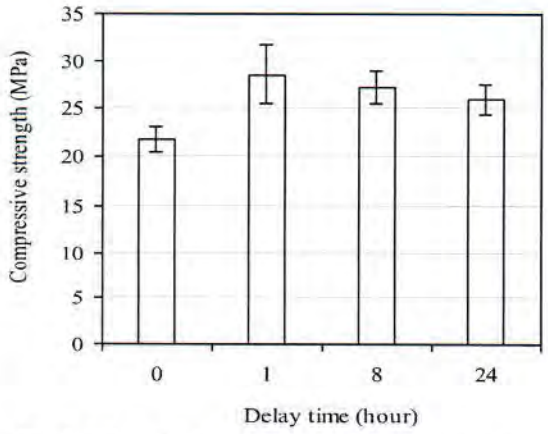


Fig. 2. Effect of delay time on the 7-day compressive strength of the Na_2SiO_3/NaOH = 1, 20M NaOH and L/S = 0.60 mixes

4.1.2. Effect of temperature of heat curing

The results of the temperature of heat curing on the strength are given in Fig. 3. The low curing temperatures of 25 and 40 °C gave the low compressive strengths of 7.5 and 10.5 MPa. The curing temperature of 60 °C gave the highest compressive strength of 28.6 MPa and when the temperature increased to 75 and 90 °C the

compressive strength slightly dropped to 25.9 and 25.7 MPa, respectively. Similar reductions in strength with high curing temperature were reported for AAHCFA paste (Guo et al., 2010) and mortar (Chindaprasirt et al., 2007). The reductions in strengths were found when the curing temperature exceeded 75 °C.

4.1.3. Effect of duration of heat curing

The relation between compressive strength and duration of heat curing is displayed in Fig. 4. The highest strength of 28.6 MPa was obtained at the curing duration for 1 day and increased curing duration resulted in a slight decrease in strength. The previous study (Chindaprasirt et al., 2007) on AAHCFA mortar indicated that the optimum curing time was 3 days. The prolonged curing at elevated temperature could weaken the microstructure of alkali-activated fly ash binders (van Jaarsveld et al., 2002).

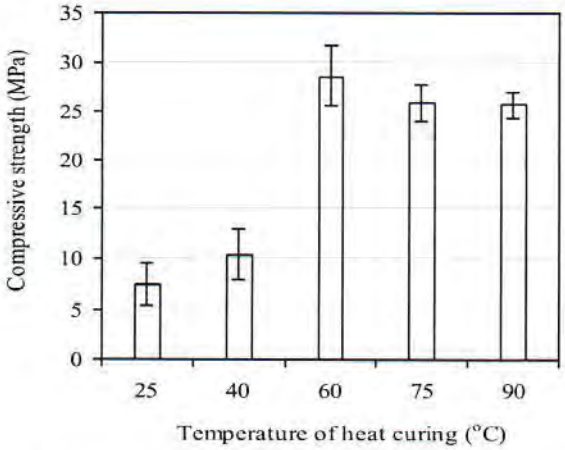


Fig. 3. Effect of temperature of heat curing on the 7-day compressive strength of the Na_2SiO_3/NaOH = 1, 20M NaOH and L/S = 0.60 mixes with heat curing duration of 1 day

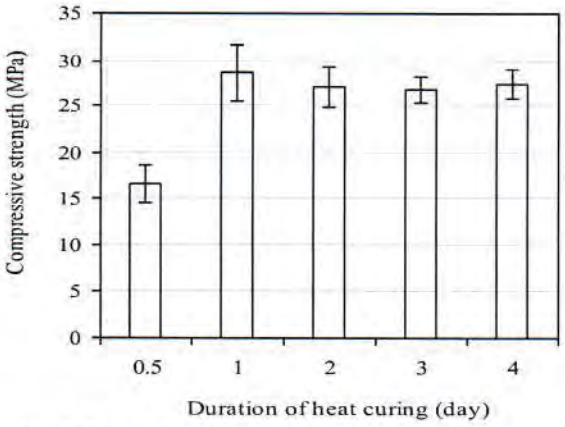


Fig. 4. Effect of duration of heat curing on the 7-day compressive strength of the Na_2SiO_3/NaOH = 1, 20M NaOH and L/S = 0.60 mixes with temperature of curing of 60 °C

4.2. Results of the main test series

4.2.1. Workability of the mixes

The details of the mixes are summarized in Table 2. For mixes with high Na_2SiO_3/NaOH ratios of 1.5 and 2.0; and NaOH concentration of 10M, the setting of AAHCFA concrete was quite fast and there were not sufficient time for proper compaction. These mixes were discarded and not used to compare with the other results. The polymeric reactions of mixes using alkaline liquid contained soluble silicate occurred at a higher rate than those using only alkaline hydroxides (Palomo et al., 1999; Xu and Van Deventer, 2000). The presence of calcium played an important role in the fast setting of concrete. It was reported that the solubility of calcium increased with decreasing pH (Phair et al., 2000). The calcium concentration in the low 10M NaOH solution should therefore be higher than those in the higher 15M and 20M NaOH solutions. The high calcium content in the fly ash led to the formation of C-S-H which co-existed with the alkali-activated products (Xiaolu et al, 2010). It was highly likely that calcium silicates precipitated and performed as nucleation sites. This caused extra precipitation of dissolved species and rapid hardening (Lee and van Deventer, 2002; van Deventer et al., 2007). The results of slumps of AAHCFA concrete are shown in Fig. 5. For Na_2SiO_3/NaOH = 1, the slump increased with increasing L/S but decreased with increasing NaOH concentration as shown in Fig. 5(a). The high liquid content naturally improved the workability of the mixes. For the high NaOH concentration, the liquid became more viscous reducing the workability of the mixes. This happened despite the fact that at high NaOH concentration there was less chance of Ca ion entered into the solution from free lime, which would prevent C-S-H type phases to be formed and therefore increased the workability. At higher Na_2SiO_3/NaOH ratios of 1.5 and 2.0 (Figs. 5(b) and 5(c)) the effect of L/S ratios was slightly less significant but the effect of NaOH concentrations was negligible. The slumps of the mixes as shown in Figs. 5(b) and 5(c) varied between 180-250 mm. It is known that the workability of alkali activated fly ash mortar and concrete is dependent on the water content of the mixes. From the results of a molar ratio analysis as shown in Table 2, the ratios of H_2O/Na_2O^* of the mixes with complete test results ranged between 8.02 - 14.38. Fig. 6 shows the plot of slump and H_2O/Na_2O^* molar ratio, it is confirmed that the important parameter affecting the slump of alkali activated fly ash concrete was the H_2O/Na_2O^* molar ratio. The increase in the H_2O/Na_2O^* molar ratio within the range of 8.02 to 9.23 (Table 2; Fig. 6) had a very strong influence on slump as it increased the slump from approximately 100 mm to 200 mm. The additional increase in the H_2O/Na_2O^* molar ratio led to a smaller increase in the slumps since the values were approaching the obtainable maximum slump values.

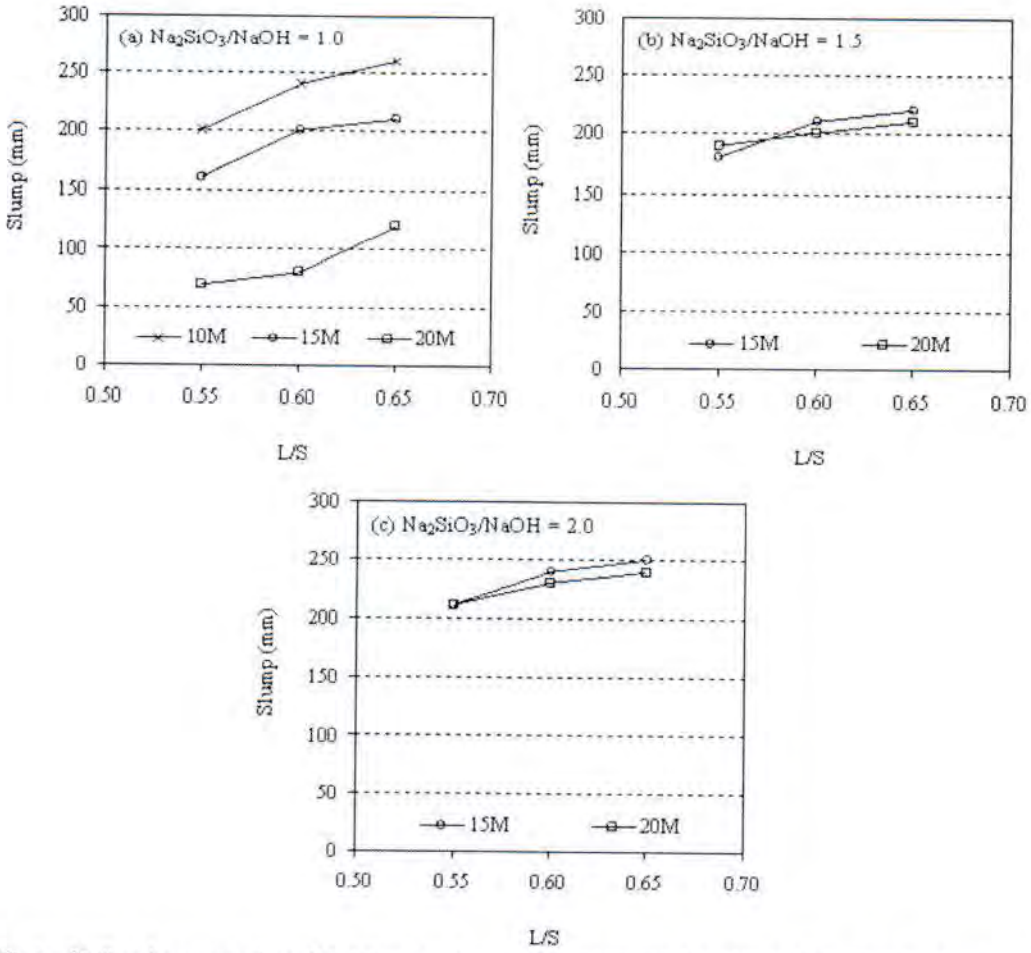


Fig. 5. Effects of L/S and concentration of NaOH on the slump of the mixes with delay time of 1 hour, curing temperature of 60 °C, curing duration of 1 day: (a) $Na_2SiO_3/NaOH$ = 1.0, (b) $Na_2SiO_3/NaOH$ = 1.5 and (c) $Na_2SiO_3/NaOH$ = 2.0

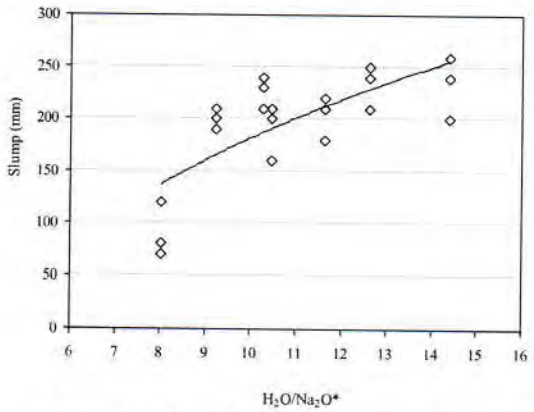


Fig. 6. Effect of molar ratio of H_2O/Na_2O in activator (H_2O/Na_2O*) on the slump of mix with delay time of 1 hour, curing temperature of 60 °C and curing duration of 1 day

4.2.2. Strength of the AAHCFA concretes

In the presence of calcium, it has been reported that it is possible to have polymeric gel and C-S-H gel forming simultaneously (Alonso and Palomo, 2001; Yip et al., 2005). The C-S-H gel is believed to be different from the one resulting from the hydration of Portland cement. At high alkalinity (Ms = 1.2), the polymeric gel contributes to the strength of the binder whereas C-S-H gel contribute significantly to the binder compressive strength at lower alkalinity (Ms = 2.0) (Yip et al., 2005). In this study, the Ms of the mixes with complete test results ranged between 0.58-1.15 as shown in Table 2; therefore, polymeric gel should be the dominant phase contributing to the strength of the AAHCFA concretes.

The results of the compressive strength are shown in Fig. 7. The strength of AAHCFA concrete increased with increasing NaOH concentration and decreasing $Na_2SiO_3/NaOH$ ratio. The increase in strength with increasing NaOH concentration was directly related to the ability of the dissolution of silica and alumina into the solution (Rattanasak and Chindaprasirt, 2009). The dissolution from fly ash particles is usually better in higher NaOH concentrations. Regarding the effect of $Na_2SiO_3/NaOH$ ratio, the low $Na_2SiO_3/NaOH$ ratio of 1.0 resulted in high strength concrete compared to those of higher $Na_2SiO_3/NaOH$ ratios of 1.5 and 2.0. A similar strength reduction of alkali-activated mortar was reported for solutions of high

Na_2SiO_3/NaOH ratio of 2.0 and NaOH concentrations of 10M and 15M (Rattanasak and Chindaprasirt, 2009). The reduction in strength with high Na_2SiO_3/NaOH ratio should again relate to the amount of silica and alumina dissolved into the solution. At high Na_2SiO_3/NaOH ratio, the amount of silicate is high and the water content is also high since this Na_2SiO_3 contained relatively high amount of water. At high Na_2SiO_3/NaOH ratio, the amount of NaOH was low and the dissolving of both silica and alumina were also low. The alkali-activated fly ash products with high silica to alumina ration were obtained. The strength reduction was likely related to the increase in the water content of the mixes and the high silica to alumina ratio of the products (Detphan and Chindaprasirt, 2009; Fletcher et al., 2005).

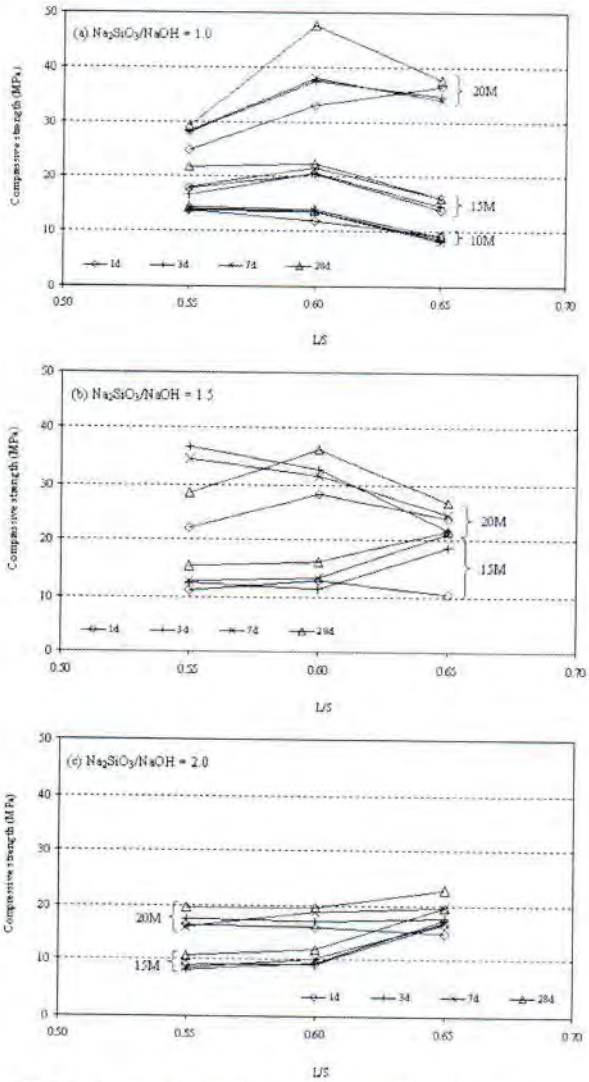


Fig. 7. Effects of L/S and concentration of NaOH on the compressive strength of the mixes with delay time of 1 hour, curing temperature of 60 °C, curing duration of 1 day: (a) Na_2SiO_3/NaOH = 1.0, (b) Na_2SiO_3/NaOH = 1.5 and (c) Na_2SiO_3/NaOH = 2.0

The L/S ratio also had a small effect on the compressive strength. At low NaOH concentration of 10M, the compressive strengths of the mixes with L/S ratios of 0.55 and 0.60 were approximately the same, but the strengths of the mixes with L/S ratio of 0.65 were slightly lower. At high alkali liquid content (L/S ratio of 0.65), the mixes contained low amount of fly ash. This should result in the lower amount of silica and alumina dissolved into the solution and also in a higher water volume that will evaporate leaving empty spaces in the microstructures.

At Na_2SiO_3/NaOH ratio of 1 and NaOH concentrations of 15M and 20M, the mixes with L/S ratio of 0.60 gave optimum strengths as shown in Fig. 7(a). At the lower L/S ratio of 0.55, the amount of liquid was low and the dissolving of the silica and alumina was therefore slowed down as the results of the increased concentration of the silica and alumina in the solution. Water is an essential part of polymerization and hydration reaction. However, the increase in the water content as a result of the increase in the L/S ratio produced a weak matrix in a similar manner to the high water to cement ratio in the Portland cement system.

As mentioned before, the sodium silicate solution used in this test was high in water content and the workability and strength results were therefore influenced by this. Furthermore, the results reported on the influence of the high calcium content might have been influenced by the method of mixing the alkali-activated fly ash concrete adopted.

5. Conclusions

The effects of several parameters on the slump and strength of alkali-activated high calcium fly ash (AAHCFA) concrete have been investigated. Based on results obtained with the materials and the method of mixing used in this experiment, the following conclusions could be made.

1. The use of high calcium fly ash and NaOH with low concentration of 10M resulted in relatively fast setting of the alkali-activated fly ash concrete.
2. The workability of AAHCFA concrete was related to the molar ratio of H_2O/Na_2O in activator. The L/S ratio and NaOH concentration also had some effects on the workability.
3. The compressive strength increased with the increase in the NaOH concentrations and reduced with the increase in the Na_2SiO_3/NaOH ratio. The L/S ratio also had some effect on strength but to a lesser extent.
4. The AAHCFA concretes with high strengths were obtained when the delay time of 1 hour, the heat curing temperature of 60 °C and the heat curing duration of 1 day were employed.

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Cement mortars hybridized with zeolite and zeolite-like materials made of lignite bottom ash for heavy metal encapsulation

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ABSTRACT

Bottom ash (BA) from Mae Moh lignite power plant was used to synthesize zeolite and zeolite-like materials. Low temperature synthesis (100–110 °C) was completed using SiO_2 to Al_2O_3 with molar ratios of 2.94 and 2.92, respectively. Factors investigated that affect synthesis include particle size distribution, pretreatment of BA, concentration of alkali solution and liquid to solid ratio. The synthesized product qualities were characterized by mineralogical composition, morphology, specific surface area, pore size, pore volume and cation exchange capacity. Natrolite-K zeolite (NAT-K) was obtained with a solution of BA and 7 M KOH. Zeolite-like material (potassium aluminosilicate hydrate: KASH) was obtained using very fine BA and 9 M KOH solution. The NAT-K, KASH and BA powders were used to replace type I Portland cement at 0, 5, 10, 20 and 30% by weight to produce composite materials for heavy metal encapsulation. The compressive strength and bulk density of the NAT-K- or KASH-hybridized cement mortars were tested at 1, 7 and 28 days. The heavy metal encapsulation capacity was also tested using the 28-day cement mortar containing either 5 wt% NAT-K or KASH adsorbed with Cr, Ni and Cd ions. The results showed that 5 wt% of NAT-K could improve early strength of cement mortar and the 28-day specimens with 5–10 wt% of NAT-K replacement had compressive strength similar to that of the normal cement mortar. The NAT-K and KASH encapsulate Cr, Ni and Cd ions in the structures of cement mortar matrices more than 97%.

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1. Introduction

Worldwide, the coal industry annually produces several million metric tons of by-products such as fly ash (FA), bottom ash, boiler slag and flue gas desulfurization material (Ríos and Williams, 2008). The yearly output of lignite bottom ash (BA) produced at the Mae Moh power plant in Thailand is approximately 0.8 MT, and it is discarded in landfills as solid wastes. The BA needs proper grinding to obtain a reasonably fine particle size for use as pozzolan (Sathonsaowaphak et al., 2009). The BA from the coal industry contains heavy metals and is harmful to the environment. It is often used as a low-cost replacement for more expensive sand in the production of concrete blocks. In many countries, it is used as a base course in road construction (Cheriaf et al., 1999). Synthesis of zeolites from BA is one of the promising ways to create a more environmentally friendly use of the unused solid waste. One of the good examples is synthesis of zeolite A from BA obtained from coal-fired boilers within the paper industries in Thailand (Chareonpanich et al., 2011). The BA obtained from the paper industry contains more crystalline silica content than that obtained from steam boilers at Mae Moh power plant. Moreover, due to the different coal source, their chemical and mineralogical compositions are not similar. In this study, low temperature zeolite synthesis from lignite BA obtained from Mae Moh power plant is investigated.

Zeolite has a crystalline aluminosilicate structure with a SiO_4 tetrahedra framework. Parts of the structure are substituted with AlO_4 tetrahedra which require charge-compensating cations. These tetrahedral units are connected with each other as repeating units forming 3-D porous framework structures in a molecular size (Kadono et al., 2008). The advantage of zeolites over resins, apart

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from their much lower cost, is their ion selectivity. Because of the characteristics of zeolite structures and their adsorbent properties, they have been applied as chemical sieve, water softener and adsorbents (Hui et al., 2005). Various types of zeolites can be synthesized from different source materials and under different conditions. BA, like fly ash, is considered as a starting material because of its promising chemical and mineralogical compositions and abundant availability. Although coming from the same source, mineralogical compositions of BA are totally different from FA due to their combustion temperature. For example, FA contains inert material such a mullite which is not easy to be dissolved (Chindaprasirt and Pimraksa, 2008). However, BA has been utilized less because its particle size is large and grinding is required to reduce the particle size and to increase its reactivity.

In previous work, we found that the optimum refluxing conditions for zeolite synthesis from Mae Moh BA with $d_{[4,3]}$ of 23 micron and Si/Al molar ratio of 1.5 or SiO_2/Al_2O_3 ratio of 3.06 were 5 M KOH solution, liquid to BA ratio (L/S ratio) of 8 and reaction time of 24 h (Pimraksa et al., 2010). This resulted in the formation of a zeolite-like material in the form of potassium aluminum silicate hydrate (KASH) ($KAlSiO_4.15H_2O$) as a main composition and phillipsite-K ($K_2[Al_2Si_{2.2}O_{6.4}].2H_2O$) as a minor phase. When 3 M NaOH solutions were used, there was no zeolite formation. This research, therefore, aims to study further the synthesis of zeolite phases from Mae Moh BA to discover more potential uses of BA for heavy metal encapsulation. Various factors affecting this synthesis, including KOH concentration, liquid to solid ratio, iron content and particle size distribution of BA were investigated. The quality of the synthesized zeolite is characterized in terms of mineralogical composition, microstructure, pore size, pore volume and CEC.

There are many kinds of zeolites suitable for use in encapsulation. Among those that perform best for ion exchange are the ones with a large number of negative charges in the framework. For ion adsorption capacity, zeolites with a large number of cavities and large surface areas in the framework works best (Alex and Dong-ke, 2003). Zeolite-like materials have also been considered for adsorption applications because of their high specific surface area (Gao et al., 2009). Waste encapsulation is now in high demand as huge amount of toxic industrial wastes have been disposed of in landfills. Therefore, it is very important to find a high potential waste encapsulation material. Zeolites possess some pozzolanic properties and they can be used as a pozzolanic material by blending with normal cement (Poona et al., 1999; Jana, 2007). They contribute to concrete strength mainly through the pozzolanic reaction, similar to other widely used pozzolans such as silica fume, metakaolin and fly ash. The zeolite is a meta-stable phase that readily undergoes dissolution under basic conditions with different manner from BA and one of the most reactive pozzolans such a metakaolin due to their molecular structures (Pelisser et al., 2012). The demand for such supplementary cementing materials has been markedly increasing in order to reduce cement production to cope with global warming (Yilmaz et al., 2007). In addition to the strength improvement, zeolites, when present in cement and concrete structures, also play an important role in the encapsulation of several types of heavy metals (Atkins et al., 1995; Olmo et al., 2003; Ok et al., 2007). Both the pozzolanic reactivity and waste encapsulation of zeolites are thus of much interest to cement chemists, concrete technologists and environmental scientists. Therefore, this study aims to use BA obtained from the Mae Moh power plant (Thailand) as a starting material for zeolite synthesis and to find the optimum condition for synthesis. The pozzolanic reactivity of the synthesized zeolite is then studied and compared with the ground BA. A comparison in pozzolanic reactivity of BA synthesized zeolites and BA was performed in this study for the first time. Not only pozzolanic reactivity, the heavy metal (chromium (III), nickel (II) and cadmium (II)) encapsulation ability of the zeolite materials and zeolite-like-hybridized cement mortars is also studied. It is commonly known, that Cr, Ni and Cd ions are typically found in electroplating wastes (Telukdarie et al., 2006). Moreover, Cr ion is one of the carcinogenic metals which can be very harmful to the ground and water, seriously concerned in many countries which run a leather industry as their main market. Active absorbers for those heavy metal removal are, therefore, very important for mitigation of the negative impact (Giannetti et al., 2004). The knowledge obtained from this study will no doubt lay a solid groundwork for the conversion of lignite BA into zeolite and zeolite-like materials, for waste encapsulation using zeolite-hybridized cement material as well as for the utilization of BA in a high potential way.

2. Experimental methods

2.1. Materials

Lignite BA used for zeolite synthesis was obtained from the Mae Moh power plant. The BA was ground by ball milling to obtain various particle size distributions. The BA volumetric mean diameter ($d_{[4,3]}$) after grinding for 12, 24 and 48 h were 13.3, 6.6 and 3.0 μm, respectively. The ground BA was treated to remove the iron compound using the looped magnetic separator until the iron content was lowered by 50%. The chemical composition of BA determined using X-ray fluorescence spectrometry (XRF) is shown in Table 1. BA was stirred in 5–9 M KOH solutions for 24 h in a 25 °C room to investigate the concentrations of reactive cations (Si^{4+} and Al^{3+}). The investigated condition, shown in Table 2, was determined to be the best condition based on the results of a previous study (Pimraksa et al., 2010). The reactive ions were measured using Atomic Absorption Spectroscopy (AAS). The total content of heavy metals contained in BA and type I Portland cement were determined using AAS and Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) carried out in accordance with ASTM D3688-78.

2.2. Zeolite synthesis

The as-received BA and the BA from which iron was removed BA, with SiO_2/Al_2O_3 molar ratios of 2.94 and 2.92, respectively, were used as starting materials. The conditions of zeolite synthesis are shown in Table 2. The effects of ground BA particle size, iron oxide removal from BA, KOH concentration and liquid to solid ratios on zeolite quality were studied. It was shown that the zeolite phase obtained from the refluxing method was better than that from the hydrothermal method (Pimraksa et al., 2010). Therefore, the refluxing method was selected for synthesis. The ground BA was stirred with the KOH solution for 30 min to allow the dissolution of silicate and aluminate ions. Refluxing was carried out at 100–110 °C for 24 h. The reaction time and temperature were taken from

Table 1
Chemical compositions of as-received BA and magnetically treated BA.

Compositions	As-received BA (%)	Magnetic treated BA (%)
SiO_2	38.69	41.19
Al_2O_3	22.25	24.19
Fe_2O_3	13.75	6.89
CaO	13.16	13.14
MgO	2.83	2.62
Na_2O	0.53	0.73
K_2O	1.97	2.25
TiO_2	0.39	0.38
SO_3	0.82	0.71
P_2O_5	0.16	0.16
LOI	5.19	3.50

Table 2
Conditions for synthesis.

No.	Particle size, $[d]_{4,3}$ (μm)	Iron compound removal	KOH concentration (molar)	Liquid:solid ratio (L/S ratio)
1	13.3	✓	5	8
2	6.6	✗	5	8
3	3.0	✓	5	8
4	6.6	✗	5	6
5	6.6	✗	5	10
6	6.6	✓	5	8
7	6.6	✗	7	8
8	6.6	✓	7	8
9	6.6	✗	9	8
10	6.6	✓	9	8
11	3.0	✗	9	8
12	3.0	✓	9	8
13	3.0	✗	7	8
14	3.0	✓	7	8

a previous work (Pimraksa et al., 2010). The solid products were filtered and washed with deionized water until the pH of the filtrate reached 10. The sample was then dried at 110 °C for 24 h. The solid phases obtained after drying were characterized in terms of the mineralogical composition using X-Ray Diffractometry (XRD) and morphology using Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Specific surface area was determined using Brunauer–Emmett–Teller (BET) and mercury porosimetry (MIP) was used to determined pore sizes. The cation exchange capacity (CEC) was measured using the ammonium exchange capacity by the titration method in accordance with the method of the soil analysis method (Rhoades, 1982). The exchangeable cations of the zeolites were replaced by NH_4^+ using 1 N ammonium acetate solution.

2.3. NAT-K and KASH used as hybrid materials

The cement mortar samples were prepared using a water to cement ratio of 0.6 and cement to sand ratio of 1:2.75, by weight. The synthesized NAT-K, KASH and BA were used to replace Portland cement by weight at 0%, 5%, 10%, 20% and 30%. The prepared mortars were cast in $2 \times 2 \times 2$ cm^3 brass molds. The samples were removed from the molds after 1 day and then cured in a lime-saturated solution in a temperature-controlled room at 25–27 °C until testing. The compressive strength was tested at 1, 7 and 28 days using a universal strength testing machine (Tinius Olsen, H50KT). Microstructure investigations using XRD and SEM-EDS were conducted on the cement pastes at 1, 7 and 28 days. The hydration of the cement pastes was stopped by soaking in acetone for 2 days and drying at 60 °C until a constant weight was obtained.

2.4. Waste encapsulation capacity of cement mortars hybridized with NAT-K and KASH

The $Cr(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$ and $Cd(N_2O_3)_2.4H_2O$ solutions were used as sources of Cr^{3+}, Ni^{2+} and Cd^{2+} ions, respectively, where 100 ppm of each solution was prepared. 100 g of NAT-K, KASH and BA were soaked separately in 100 ppm solutions of Cr^{3+}, Ni^{2+} and Cd^{2+} for 24 h. The amount of heavy metal adsorption on each material was confirmed by ICP detection, which was performed on the solutions after soaking. The heavy metals adsorbed on the materials were then dried at 60 °C until constant weights were obtained. To prepare the cement mortar, 5 wt% of heavy metal-adsorbed materials were used to replace Portland cement. Adsorbed heavy metal contents on hybrid materials before leaching test were calculated from the used material by weight obtained from the heavy metal adsorption test. After 28 days, the cured mortars were tested for leaching of heavy metal in accordance with TCLP. The $2 \times 2 \times 2$ cm^3 mortar specimen was soaked in diluted acetic acid solution with a solid to liquid ratio of 1:20. The solution was then subjected to circulation using magnetic stirring for 20 ± 2 h in accordance with DIN 38414-S4. The leachate solutions were analyzed for heavy metal concentration using ICP-MS. The heavy metal encapsulation capacity was estimated by the subtraction of the adsorbed heavy metal content and the leached heavy metal content.

3. Results and discussion

3.1. Materials

Chemical compositions of as-received BA and magnetic treated BA are shown in Table 3. Mineralogical compositions of as-received BA consisted of anorthite ($CaAl_2Si_2O_8$), augite ($(Na, Ca, K)_2(Al, Si)_2O_6$), quartz ($SiO_2$), maghemite ($\gamma$-$Fe_2O_3$), magnetite ($Fe_3O_4$) and glassy phase. With the use of magnetic separation, the iron oxide content mostly in the form of magnetite was reduced by 50 wt%. Therefore, the starting materials without iron removal and with iron removal contained SiO_2/Al_2O_3 molar ratios of 2.94 and 2.92, respectively. The amounts of dissolved aluminum and silicon species as described by Si/Al ratios in various synthesized conditions are shown in Table 3. The starting SiO_2/Al_2O_3 and Si/Al ratio of BA was 2.94 and 1.74, respectively. The reactive Si^{4+} and Al^{3+} ions dissolved from BA with 5 M KOH solution were 871 and 527 ppm, respectively, giving a Si/Al ratio of 1.65. This ratio was slightly lower than that of BA confirming that there was some undissolved silica left behind with the alkali activation. With a decrease in particle size from 13.3 to 3.0 μm, the Si/Al ratios decreased. The aluminum

Table 3
Dissolved aluminum (Al^{3+}) and silicon (Si^{4+}) contents, Si/Al ratios of BA activated by various synthesized conditions and specific surface areas of synthesized products.

Particle sizes (μm)	Iron removal	KOH conc. (M)	Liquid to solid ratios	Dissolved amounts (ppm)			Major products	Spec. surf. areas of products (m^2/g)
				Si	Al	Si/Al ratios		
13.3	✓	5	8	767	415	1.85	NAT-K	18.26
6.6	✗	5	8	927	582	1.60	NAT-K	20.66
3.0	✓	5	8	1157	768	1.51	NAT-K	19.39
6.6	✗	5	6	1052	658	1.60	NAT-K	21.74
6.6	✗	5	10	1149	757	1.52	NAT-K	22.81
6.6	✓	5	8	1030	642	1.60	NAT-K	23.43
6.6	✗	7	8	1186	669	1.77	NAT-K	26.56
6.6	✓	7	8	1424	891	1.60	NAT-K	30.92
6.6	✗	9	8	1234	746	1.65	KASH	33.28
6.6	✓	9	8	1280	771	1.65	KASH	32.55
3.0	✗	9	8	1511	931	1.62	KASH	30.19
3.0	✓	9	8	1544	966	1.60	KASH	30.94
3.0	✗	7	8	1403	875	1.60	KASH	33.42
3.0	✓	7	8	1533	977	1.57	KASH	36.97

phases with the smaller particle sizes were more susceptible to dissolution. However, for the same particle size, the use of a high L/S ratio resulted in low Si/Al. For a high KOH concentration, the Si/Al ratio tended to increase because of the increased susceptibility of the silicate phases. When the fine particle size and high KOH concentration were used, the leaching of both aluminate and silicate phases was enhanced.

The total heavy metal concentrations of BA and Portland cement type I are shown in Table 4. The major heavy metals contained in BA were Mn (556.75 ppm), Se (270.81 ppm), Zn (83.47 ppm) and Ni (72.80 ppm). For ordinary Portland cement, the major heavy metals were Zn (956.62 ppm), Mn (431.18 ppm), Cu (281.87 ppm) and Cr (75.30 ppm). Both of them consisted mainly of Mn and Zn. The Portland cement contained a large amount of Zn likely due to the utilization of Zn-bearing waste, such as used tires, as alternative fuel, which leads to the changes in chemical reaction of cement minerals (Trezza, 2007). The Mn was likely present in BA, as it was commonly found in some minerals in coal mines (Larsen and Mann, 2005).

3.2. Zeolite synthesis

Four factors, including particle size, liquid/solid ratio (L/S ratio), KOH concentration and iron compound removal, were considered. Fig. 1 shows the results of the XRD patterns of products obtained from different BA particle sizes. With the same refluxing condition (100–110 °C for 24 h and 5 M KOH), 6.6 μm BA showed the highest peak intensity of zeolite in a form of natrolite-K ($(K_{0.988}Na_{0.012})(AlSi_{1.5}O_5)(H_2O)$ or NAT-K) which was observed at $2\theta = 12.8^{\circ}$. To form NAT-K, SiO_2/Al_2O_3 or Si/Al molar ratios of about 3.0 or 1.5 were theoretically required. The starting SiO_2/Al_2O_3 and Si/Al ratios of used BA were 2.94 and 1.47, respectively, which conformed to the requirement of the NAT-K chemical pattern. Using a similar synthesis routine but with a different BA particle size, the obtained zeolite type was different from the previous work. With 23 μm BA used in the previous work, zeolite-like material in the form of potassium aluminum silicate hydrates ($KAlSiO_4.15H_2O$) with a Si/Al ratio of 1.0 and a small amount of zeolite (phillipsite-K) with a Si/Al ratio of 1.1 were obtained (Pimraksa et al., 2010). It was shown that for coarse BA, some of the silicon ion bearing phases did not dissolve. In this work, for the fine BA, quartz, augite and glassy phases changed to NAT-K with a Si/Al ratio of 1.5. However, anorthite ((Ca, Na) (Al, Si)$_2$ Si_2O_8) which was one of the inert silicon-bearing mineral was still left behind. The natrolite zeolite group was one of the key players for ion exchange and adsorption (Noroozifar et al., 2009; Singh et al., 2011); therefore, it was used for waste encapsulation in this study. With the use of 3.0, 6.6 and 13.3 μm BA, in addition to NAT-K formation, calcium silicate hydrate in the form of jusite ((Ca, Na, K)$_5$(Si, Al)$_6O_{15}.5H_2O$) and rosenhahnite ($Ca_3Si_3O_9.H_2O$) and non-hydrated and iron-bearing products such as hedenbergite (Ca(Fe, Mg) $(SiO_3)_2$), were also found as minority species. With respect to the effect of particle size, the reduction in BA particle size from 13.3 to 6.6 μm facilitated the dissolubility of Si^{4+} and Al^{3+} and other ions such as Fe^{3+} and Ti^{4+} because of the increase in the surface areas resulting from the broken edges. This hindered zeolite precipitation (Wang et al., 2008) and led to the formation of a more stable phase of potassium aluminum silicate hydrate.

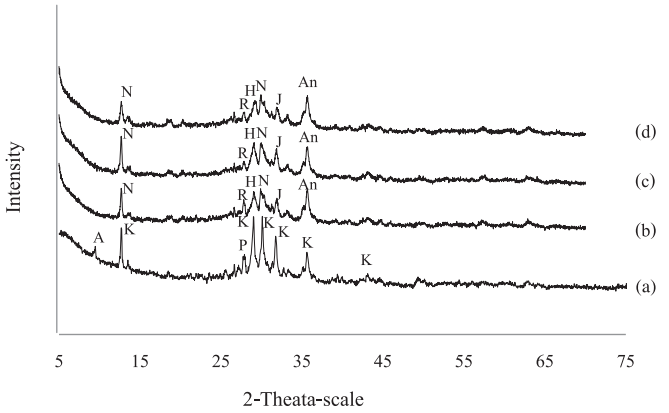


Fig. 1. XRD-pattern of products obtained from different BA particle sizes (a) 23 μm, (b) 13.3 μm, (c) 6.6 μm and (d) 3.2 μm. N = Natrolite-K [$K_{15.8}Na_{0.2}(Al_{16}Si_{24}O_{80}).16H_2O$], An = Anorthite [$(Ca,Na)(Al,Si)_2Si_2O_8$], H = Hedenbergite [$Ca(Fe, Mg)(SiO_3)_2$], J = Jusite [$(Ca,Na,K)_5(Si,Al)_6O_{15}.5H_2O$], R = Rosenhanite [$Ca_3Si_3O_9.H_2O$], Q= Quartz [$SiO_2$], P = Philipsite-K, K = Potasium Aluminum Silicate Hydrate [$KAlSiO_4.1.5H_2O$], A = Aluminum Titanium Phosphorus Silicon Oxide

The XRD results of the synthesized products for the L/S ratios 6, 8 and 10 are shown in Fig. 2(a), (b) and (c). The tests were performed using 6.6 μm BA, 5 M KOH solution and 100–110 °C for 24 h refluxing. The highest peak intensity of NAT-K was obtained when the L/S ratio was 8. At the dissolution stage, the increase in the L/S ratio resulted in the increased solubility of Si^{4+} and Al^{3+} including the counter ions such as Fe^{3+}. Walex et al. (2008) found that at a high L/S ratio, the dissolution of raw materials in an alkaline solution increased and also contributed to a high degree of crystallization. However, for practical applications, the favorable condition for dissolution was not desirable for zeolite crystallization. The system with the high L/S ratio contained a high water content, which caused the suppression of ion saturation and crystallization. As a result, 6.6 μm BA with an L/S ratio of 8 was chosen for further experimentation in the removal of iron oxide compounds from BA.

Table 3 shows the result of iron oxide contents removed from BA. The reduction of iron oxide was approximately 50% when BA was treated by the looped magnetic separator. According to the XRD patterns of synthesized products shown in Fig. 3(a) and (b), the NAT-K peak intensities of treated and untreated BA in 5 M KOH were quite similar, with a slight decrease in anorthite phase. All iron oxides in BA were not dissolved in the 5 M KOH solution and thus could not form precipitates of insoluble iron hydroxides. The insoluble $Fe(OH)_3$ acted as an inducer for the formation of hydrogarnet which could then compete with the zeolitization reaction (Wang et al., 2008).

Slightly higher KOH concentrations of 7 M and 9 M were used to compare the untreated BA and the magnetically treated BA. The results shown in Fig. 3(c) and (d) suggested that the use of treated BA and 7 M KOH produced the partial collapse of the anorthite structure and the NAT-K quantity was enhanced. For 9 M KOH, the XRD patterns shown in Fig. 3(e) and (f) revealed the crystals of potassium aluminum silicate hydrate (KASH: $KAlSiO_4.15H_2O$) with the presence of a small amount of kaliophilite ($KAlSiO_4$). However,

Table 4
Total heavy metal contents of BA and ordinary Portland cement (OPC); unit: ppm.

Samples	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn
BA	8.06	<0.01	59.25	58.60	<0.01	556.75	72.81	<0.01	270.81	83.47
OPC	4.16	2.36	75.30	281.87	<0.01	431.18	35.36	68.45	<0.01	956.62

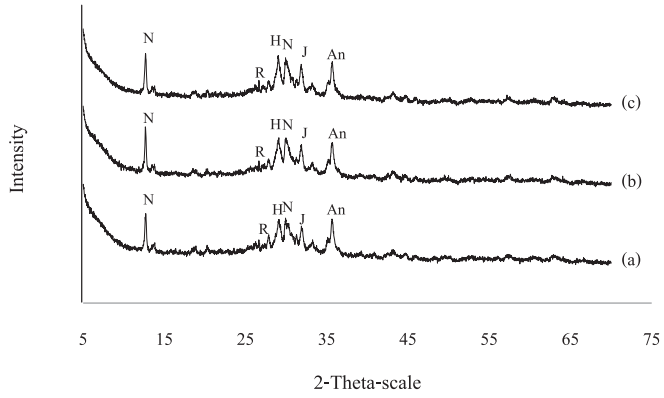


Fig. 2. XRD-patterns of products obtained from different L/S ratios (a) 6, (b) 8 and (c) 10. N = Natrolite-K [$K_{15.8}Na_{0.2}(Al_{16}Si_{24}O_{80}).16H2O$], An = Anorthite [$(Ca,Na)(Al,Si)_2Si_2O_8$], H = Hedenbergite [$Ca(Fe, Mg)(SiO_3)_2$], J = Jusite [$(Ca,Na,K)_5(Si,Al)_6O_{15}.5H_2O$], R = Rosenhanite [$Ca_3Si_3O_9.H_2O$]

the dissolved Si^{4+} and Al^{3+} concentrations were slightly different from that of 7 M KOH. At this high alkali concentration, the more stable phases of KASH and kaliophilite in the form of a tectosilicate Al–Si framework structure were developed. However, kaliophilite contained no zeolitic water in its structure. Fig. 4(a)–(d) show the XRD patterns of KASH obtained at various synthesized conditions. For 6.6 μm BA using 9 M KOH, KASH was formed. Increase in the fineness of BA to 3.0 μm did not increase the specific surface area of the matrix. With 7 M KOH, the surface area increased and approached the highest value (36.97 m^2/g). This was even superior to NAT-K when using magnetically treated BA. For the same starting material particle size, KASH possessed a higher surface area than NAT-K as shown in Table 3 because of the finer crystal sizes.

Thus, the highly purified NAT-K with high specific surface area (30.92 m^2/g) could be synthesized from magnetically treated 6.6 μm BA in 7 M KOH using L/S of 8 and 100–110 °C of refluxing for

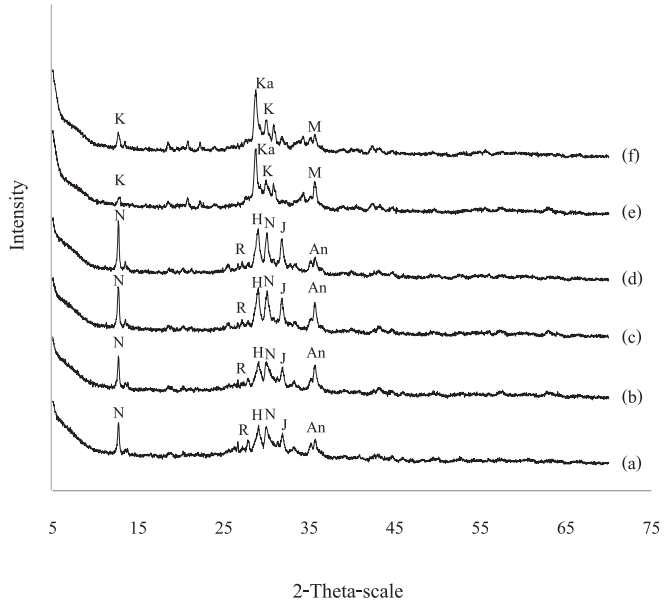


Fig. 3. XRD-patterns of products obtained from 6.6 μm BA with different synthesis conditions (a) untreated BA and 5 M KOH, (b) treated BA and 5 M KOH, (c) untreated BA and 7 KOH, (d) treated BA and 7 M KOH, (e) untreated BA and 9 M KOH and (f) treated BA and 9 M KOH. N = Natrolite-K [$K_{15.8}Na_{0.2}(Al_{16}Si_{24}O_{80}).16H_2O$], An = Anorthite [$(Ca,Na)(Al,Si)_2Si_2O_8$], H = Hedenbergite [$Ca(Fe, Mg)(SiO_3)_2$], J = Jusite [$(Ca,Na,K)_5(Si,Al)_6O_{15}.5H_2O$], R = Rosenhanite [$Ca_3Si_3O_9.H_2O$], K = Potassium aluminum silicate hydrate [$KAlSiO_4.1.5H_2O$], Ka = Kaliophillite [$KAlSiO_4$], M = Maghemite [Fe_2O_3]

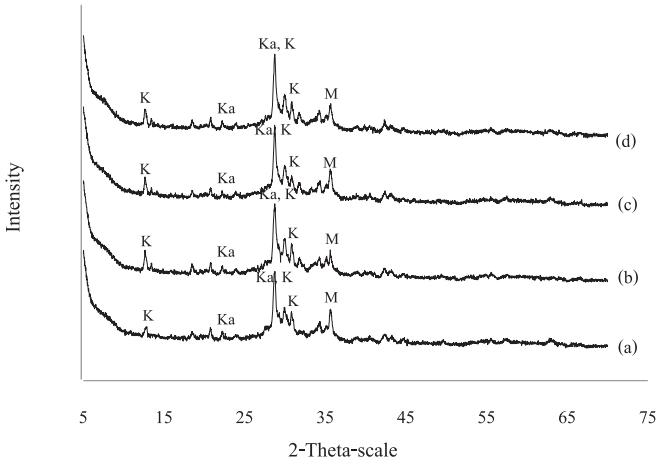


Fig. 4. XRD-patterns of products obtained from 3.0 μm BA with different synthesis conditions (a) untreated BA and 7 M KOH, (b) treated BA and 7 M KOH, (c) untreated BA and 9 M KOH and (d) treated BA and 9 M KOH. K = Potassium aluminum silicate hydrate [$KAlSiO_4.1.5H_2O$], Ka = Kaliophillite [$KAlSiO_4$], M = Maghemite [Fe_2O_3]

24 h. The best condition of KASH synthesis was similar to that of NAT-K regardless of the BA particle size. It is noted that the particle size of BA is very critical to provide the proper amount of dissolved aluminum and silicon species. The CEC values of 6.6 μm BA, NAT-K and KASH were 8.9, 160.9 and 196.7 cmol(+)/kg, respectively. The zeolite-like material (KASH) was capable of exchanging the cations similarly to the NAT-K. Moreover, its CEC value, like the specific surface area, was superior to that of NAT-K. From the synthesis, the reactive glassy phases with some crystalline phases of BA were

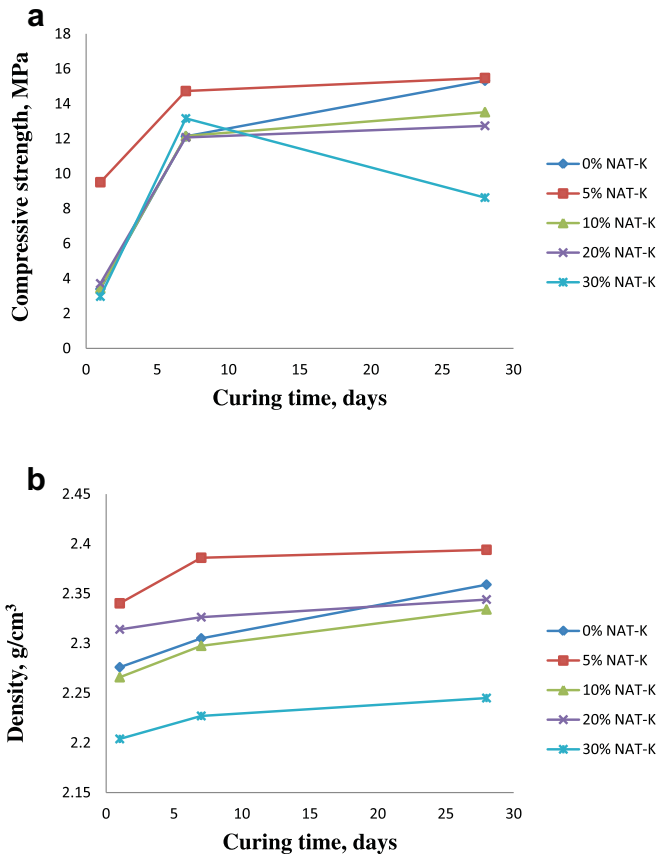


Fig. 5. (a) Strength development and (b) density of NAT-K-blended cement mortars.

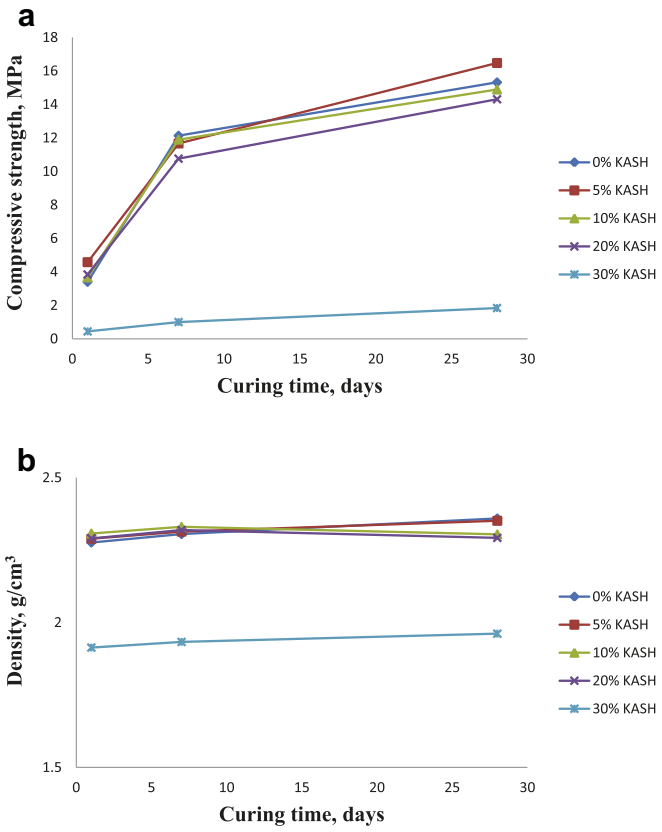


Fig. 6. (a) Strength development and (b) density of KASH-blended cement mortars.

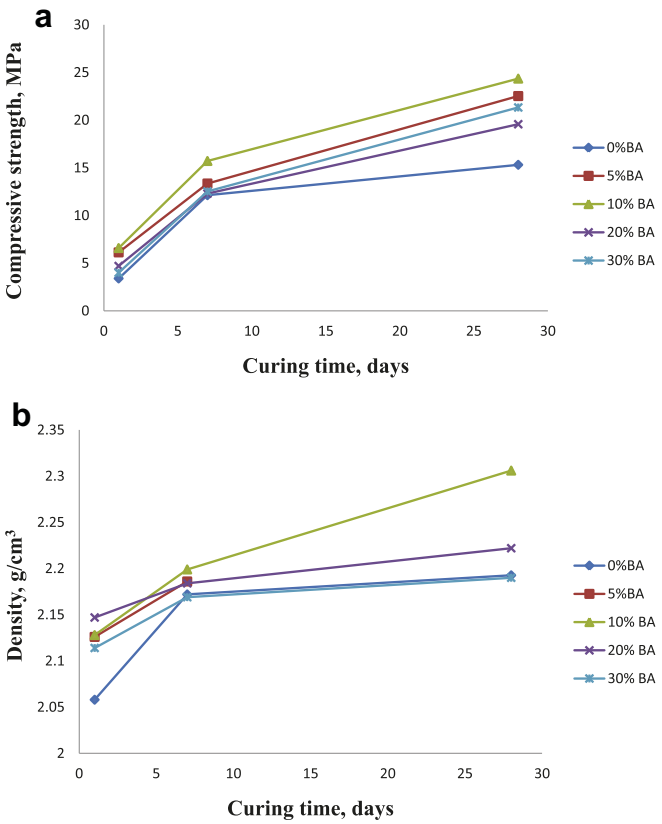


Fig. 7. (a) Strength development and (b) density of BA-blended cement mortars.

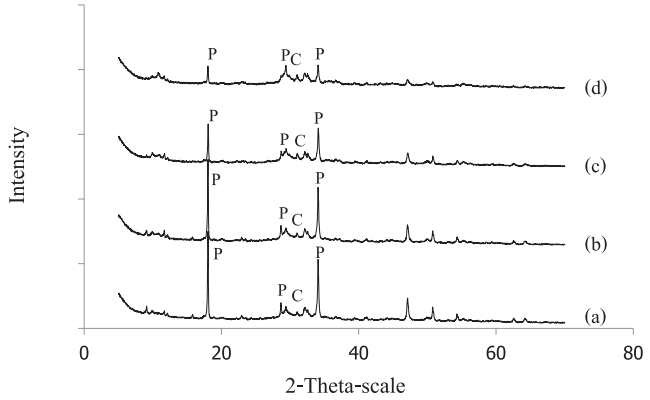


Fig. 8. XRD patterns of NAT-K used as supplementary cementing material for (a) 5 wt%, (b) 10 wt%, (c) 20 wt% and (d) 30 wt% at 28-day curing time. P = Portlandite [$Ca(OH)_2$], C = Calcite [$CaCO_3$]

transformed to zeolite phase (NAT-K) and zeolite-like material (KASH).

3.3. NAT-K and KASH used as hybrid materials

3.3.1. Mechanical property of NAT-K and KASH hybridized cement mortars

Fig. 5 shows the compressive strength and density of NAT-K-blended cement. The 1-day and 28-day compressive strengths of Portland cement mortar were 3.4 and 15.3 MPa, respectively. For 5 wt% zeolite replacement, the 1-day mortar strength increased substantially to 9.5 MPa indicating that the early strength of zeolitic cement was greater than that of the BA-blended cement, similar to the result shown in other works (Jana, 2007). The increase in the early strength should come from the ion exchange between Ca^{2+} in the cement matrix and K^{+} in the zeolite structure, resulting in the increase in pH; hence, the hydration was accelerated. A small amount of NAT-K improved the early strength of mortar. The density also increased with the NAT-K addition. Addition of a natural zeolite such as clinoptilolite improved the strength of the cement concrete due, not only to the pozzolanic effect, but also to the microfiller effect (Jana, 2007). After curing for 28 days, the compressive strength of 5 wt% NAT-K-blended mortar was slightly higher than that of Portland cement mortar. Different from the result in this study, a report from Caputo et al.

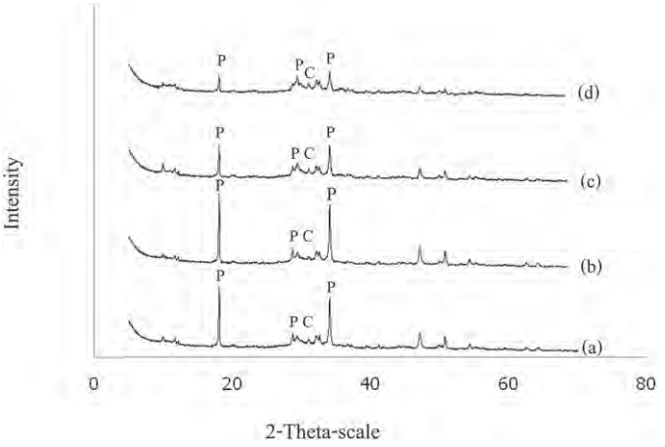


Fig. 9. XRD patterns of KASH used as supplementary cementing material for (a) 5 wt%, (b) 10 wt%, (c) 20 wt% and (d) 30 wt% at 28-day curing time. P = Portlandite [$Ca(OH)_2$], C = Calcite [$CaCO_3$]

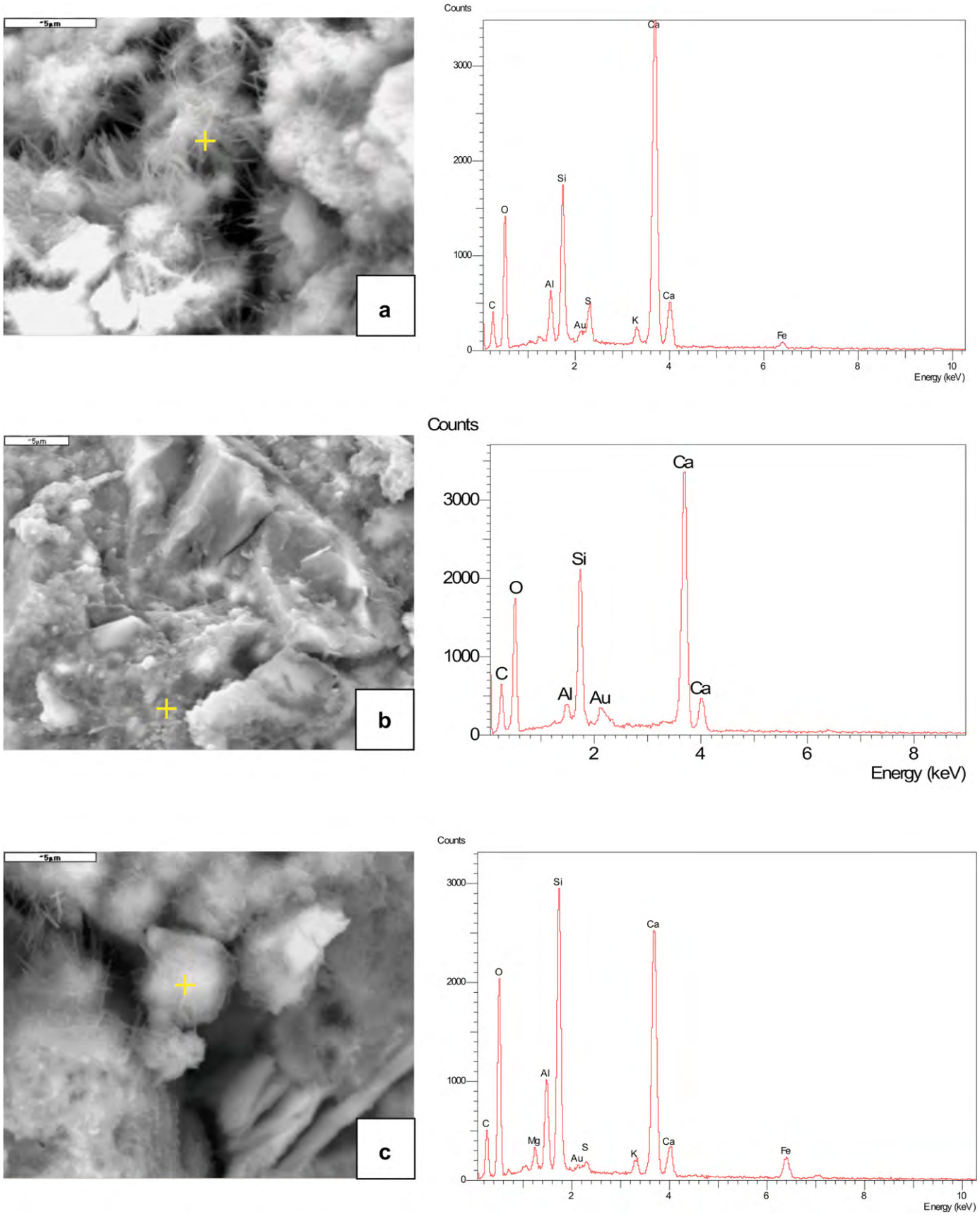
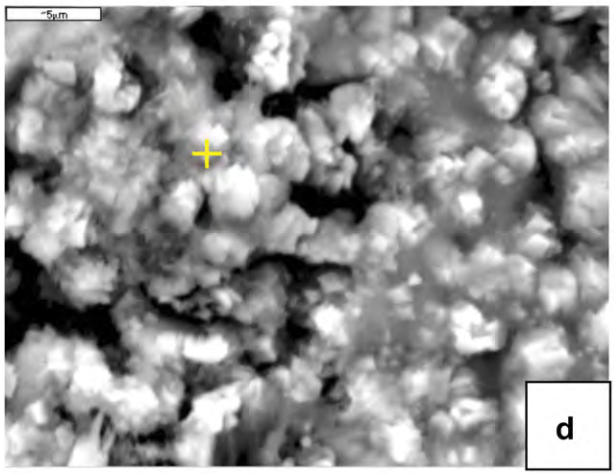
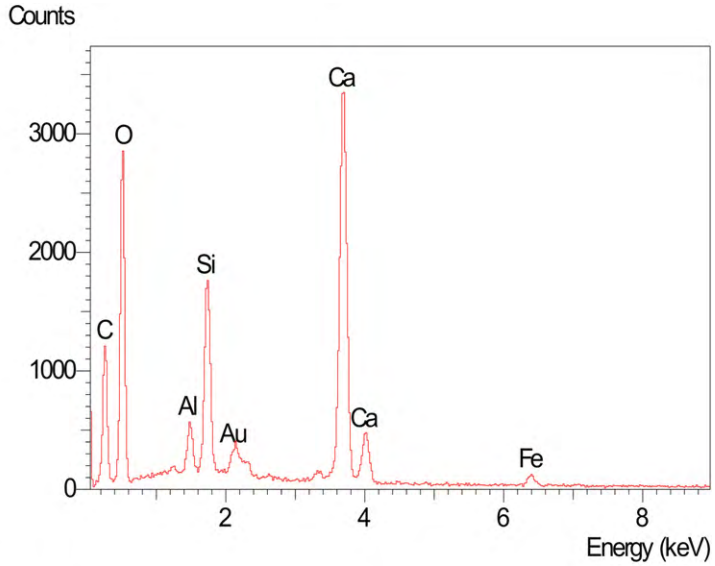
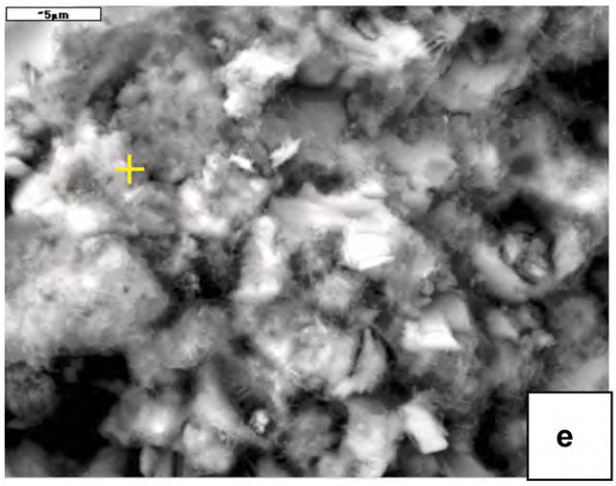
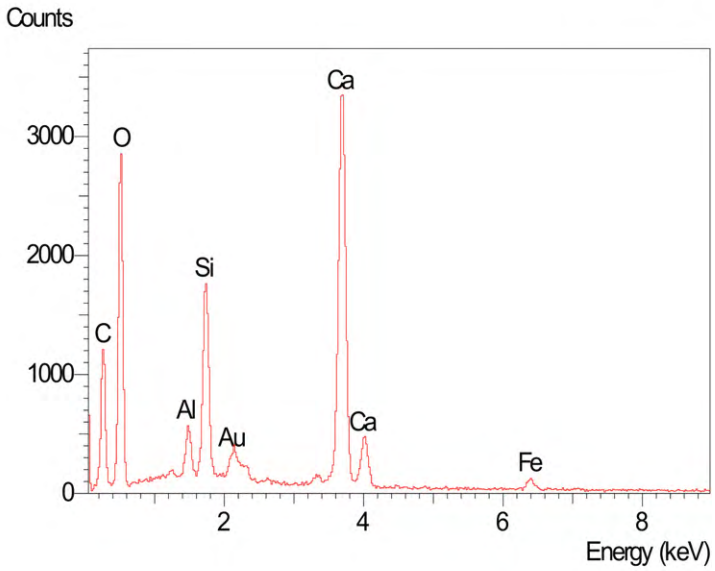


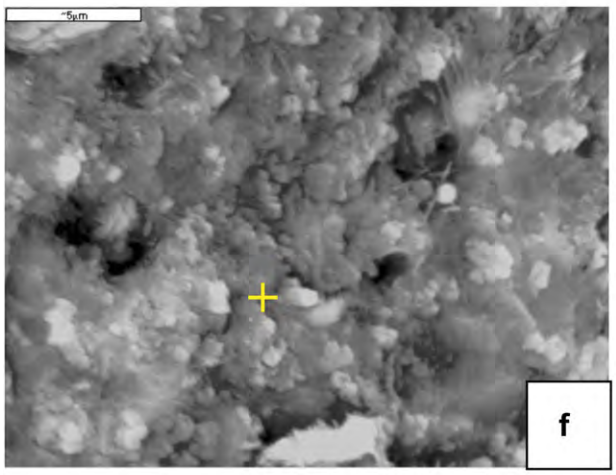
Fig. 10. SEM photomicrographs of (a) 1 day of cement mortar with no replacement (×5000), (b) 28 days of cement mortar with no replacement (×3500), (c) 7 days of 5 wt% NAT-K-replaced cement mix (×5000), (d) 28 days of 5 wt% NAT-K-replaced cement mix (×3500), (e) 7 days of 5 wt% KASH-replaced cement mix (×3500) and (f) 28 days of 5 wt% KASH-replaced cement mix.











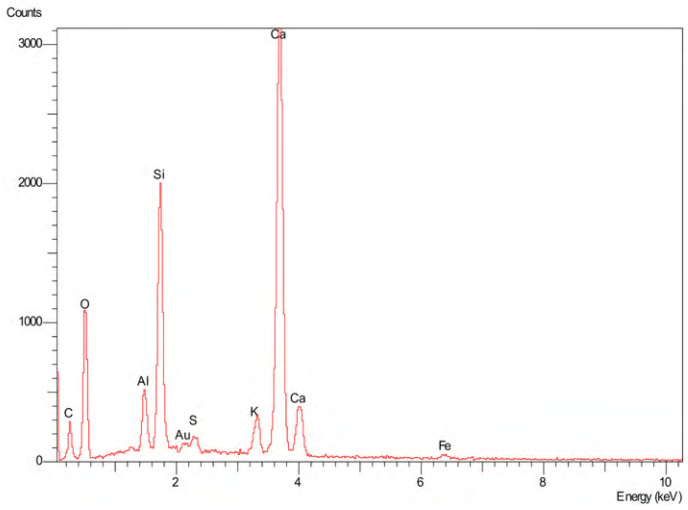


Fig. 10. (*continued*).

(2008) showed that LTA and FAU zeolites which contained very similar Si/Al molar ratio did not improve the early strength of cement mortar. This was owing to the different characteristics of NAT-K from those zeolites in which NAT-K had higher basic site density resulting in the better pozzolanic reactivity. An increase in NAT-K content to 10 wt% resulted in a mortar with similar strength at 7 days but with lower strength at 28 days compared with that of the control. The density substantially decreased with the replacement of 30 wt% NAT-K. With 20 and 30 wt% NAT-K replacement, their strength values were identical to that of normal cement mortar at 7 days curing and were lower at 28 days curing. The results were in good agreement with other researchers (Perraki et al., 2003; Yılmaz and Ediz, 2008) which indicated that the use of zeolite resulted in a smaller amount of Portland cement used. This led to less $Ca(OH)_2$ from cement hydration which was not sufficient for the pozzolanic reaction. In addition, the strength over time of zeolite-blended mortar was superior to that of the Portland cement mortar when the fine cement was used (Perraki et al., 2010; Canpolat et al., 2004; Un, 2005). The density greatly decreased with the addition of 30 wt% NAT-K. The zeolitic phase used in this investigation was highly porous and greatly affected the properties of the blended cement.

The strength development of KASH blended cement mortars was also investigated and shown in Fig. 6. There was no difference in compressive strength values when KASH was used to replace Portland cement up to 10 wt%. The compressive strengths at 1, 7 and 28 days were 4.5, 12.0 and 15.0 MPa, respectively. Their density was approximately 2.3 g/cm^3 for the range of KASH replacement of 5–20 wt%. With 20 wt% replacement, the strength slightly decreased. For the 30 wt% replacement, the 28-day strength and density were drastically reduced to 2.0 MPa and 1.9 g/cm^3, respectively, because of the high specific surface of KASH. Thus, the workability of the mortar was drastically reduced with the presence of the high amount of KASH at the fixed water content. This led to difficulty in the compaction and the reduced strength.

The mortar with only 6.6 μm BA only provided the best strength when compared to those with NAT-K and KASH, as shown in Fig. 7. The addition with 10 wt% BA attained the highest compressive strength. The density of the BA-blended mortar was also improved. The fine BA possessed a high surface area and increased the pozzolanic activity; hence, the strength of the mortars was increased (Jaturapitakkul and Cheerarot, 2003). The use of 5 wt% NAT-K, KASH and BA produced mortars with strengths higher than that of the control. Particularly, the use of BA resulted in mortar with improved strength at the later age because of the good pozzolanic reaction. BA that was mainly composed of the aluminosilicate glassy phase dissolved more readily in the lime solution than those of NAT-K and KASH.

3.3.2. Microstructures of NAT-K and KASH hybridized cement mortars

Fig. 8(a)–(d) show XRD patterns of 28-day paste containing NAT-K. Portlandite ($Ca(OH)_2$) from cement hydration was easily detected in all samples. The higher the NAT-K content, the less $Ca(OH)_2$ was left behind because of less cement in the mixes. After the pozzolanic reaction, binding compounds, such as calcium silicate hydrate (C-S-H) and calcium aluminosilicate hydrate (C-A-S-H), should be expected. Because of their semicrystalline characteristics and the XRD peak overlapping with portlandite, C-S-H and C-A-S-H were difficult to be identified. Fig. 9(a)–(d) show XRD-patterns of 28-day paste containing KASH. Again, the portlandite was easily identified and the binding phases were difficult to detect, similar to the NAT-K paste. Therefore, the pozzolanic reaction was confirmed by the reduction in the portlandite and the strength improvement of the cement mix with the presences of 5 wt% of NAT-K, KASH and BA.

Fig. 10 shows the photomicrographs of the hydration products with and without the supplementary cementing materials. At an early age (1 day), as shown in Fig. 10(a), ettringite and unreacted C_2S phases were found in normal cement. Potassium, which was found by EDS, was from the originally used BA. At 28 days, shown in Fig. 10(b), C-S-H was distributed quite evenly in the matrix and was easy to detect. For the 5 wt% NAT-K paste cured for 7 days, shown in Fig. 10(c), C-A-S-H was found at the surfaces of the NAT-K particles indicating the progress of the pozzolanic reaction. The reduction in the portlandite XRD peaks was also evident, which indicated the lime consumption of NAT-K. At the late curing age, shown in Fig. 10(d), C-A-S-H was found as a major phase. For 5 wt% KASH in Fig. 10(e) and (f), C-A-S-H can be detected in 7- and 28-day cured mortar.

3.3.3. Heavy metal adsorption capacity

Table 5 shows the percentages of heavy metal adsorption on NAT-K, KASH and BA. The cation exchange capacity (CEC) values of NAT-K and KASH were much higher than that of BA because of molecular pores and negative charges contained in their structures. Thus, NAT-K and KASH gave considerably higher adsorption of Ni and Cd than BA. NAT-K and KASH showed a similar adsorption capacity of 99.5–99.8% for Cr^{3+}, 97.5–98.0% for Ni^{2+} adsorption and 95.0% for Cd^{2+} adsorptions. The ionic radii of Cr, Ni and Cd were 0.097, 0.072 and 0.052 nm, respectively. The smaller ionic radii and the higher ionic valency led to the higher ionic strength. The increase in pH also resulted in an increase in Cd^{2+} adsorption (Hetzer et al., 2006; Quintelas et al., 2009). However, BA showed the effective adsorption for Cr ions and the poor adsorption for Ni and Cd ions. The small ionic radius and the high ionic valency of the Cr ion led to the higher ionic strength. Several researchers (Bayat, 2002; Mohan and Gandhimathi, 2009) reported that the functional oxidized groups of SiO_2 and Al_2O_3, as well as a basic testing condition, resulted in the negatively charged surfaces. The surface of the SiO_2 tended to form SiOH groups, which acted as a weak acid, and their surface charges were pH dependent. The negative charge for the high pH and the positive charge for the low pH would exist, and the positive charge was prone to dispel the positive ion. BA surfaces adsorbed the positive charges, which were attracted to the $Cr(OH)_3$ and $[Cr(OH)_6]^{3-}$ and $[Cr(OH)_4]^{-}$ at pH ~ 6–8 (Mollah et al., 1992). This induced Cr ion adsorption on BA surfaces. However, the pelletized lignite fly ash from the work of Papandreou et al. (2007) showed the same Cd^{2+} adsorption capacity on BA as this work at around pH 6.3. Its adsorption could reach 100% above pH 9.

However, in this work, the heavy metal adsorption was carried out without pH adjustment. The initial and final pH of the systems containing NAT-K, KASH and BA soaked in $Cr(NO_3)_3.9H_2O$, $Ni(NO_3)_2.6H_2O$ and $Cd(NO_3)_2.4H_2O$ solutions were ranged from weak acid to the neutral condition (pH ~ 6–8). In this condition, the NAT-K and KASH were highly effective in the adsorption of Cr, Ni and Cd ions. The heavy metal adsorption that occurred was because of ion exchange with K^+ for NAT-K and electrostatic attractive forces for KASH and BA. In multi-metal system, the zeolite adsorption mechanism was different. It was reported that, except for ion exchange, the formation of solid metal hydroxide occurred and depended on the ion species (Jha et al., 2009). For example in binary system of Cd^{2+} and Ni^{2+}, Jha et al. suggested that

Table 5
Capacity of heavy metal adsorption on NAT-K, KASH and BA; unit: percentage (%).

	CEC[a] cmol(+)/kg	Cr^{3+} adsorption	Ni^{2+} adsorption	Cd^{2+} adsorption
NAT-K	160.91	99.8	98.0	95.0
KASH	196.68	99.5	97.5	95.0
BA	8.87	95.0	29.0	30.0

[a] CEC, cation exchange capacity.

Table 6
Concentrations of Cr, Ni and Cd ions leached from cement mortars blended with hybrid materials.

Hybrid materials	Adsorbed concentration in 100 g zeolite (ppm)			Adsorbed concentration in cement mix (ppm)			Leached concentration (ppm)			Percentage of adsorption (%)		
	Cr	Ni	Cd	Cr	Ni	Cd	Cr	Ni	Cd	Cr	Ni	Cd
NAT-K	72.81	55.68	67.51	3.64	2.78	3.37	0.08	0.06	0.48	97.6	97.9	85.8
KASH	72.82	55.52	67.59	3.64	2.77	3.38	0.08	0.03	0.47	98.0	98.7	86.0
BA	69.75	16.5	23.55	3.49	0.83	1.18	0.21	0.10	0.30	94.0	88.0	74.5

the Ni^{2+} removal was caused by ion exchange with monovalent cation contained in zeolite structure, while Cd^{2+} removal involved the formation of metal hydroxide. In this study, Ni^{2+} was, therefore, removed by K^{+} exchange and Cd^{2+} was precipitated in the form of cadmium hydroxide. For tertiary system, Jha et al. investigated the combination of Ni^{2+}, Cd^{2+} and Cu^{2+}. In this case, Ni^{2+} and Cd^{2+} were removed mainly via ion exchange and Cu^{2+} was done by metal hydroxide precipitation. In this study, for Cr^{3+} instead of Cu^{2+} combined with Ni^{2+} and Cd^{2+}, the Cr^{3+} removal was performed via both cation exchange due to its ionic strength and new phase formation as $CaCrO_4$ in Portland cement based system that also enhanced the cement strength (Shi and Fernandez-Jimenez, 2006). Therefore, the removal of Ni^{2+} and Cd^{2+} should be dependent on the metal hydroxide precipitation.

3.3.4. Leaching of heavy metal encapsulated in cement mortar matrix

The results of the leaching test of heavy metal from mortars are shown in Table 6. KASH gave a slightly better encapsulation than NAT-K. NAT-K and KASH encapsulated 97.6% Cr, 97.9% Ni and 85.8% Cd and 98.0% Cr, 98.7% Ni and 86.0% Cd, respectively. BA gave a slightly lower performance with the encapsulation of 94.0% Cr, 88.0 Ni and 74.5% Cd. NAT-K, KASH and BA when mixed with Portland cement played a role in the pozzolanic reaction. Silicate and aluminate phases contained in NAT-K, KASH and BA dissolved and reacted with hydrated lime resulting in a very fine C-S-H binding phase. The zeolitic frameworks of NAT-K and KASH should be partly disturbed and co-exist with the cement hydration and pozzolanic reaction products. The heavy metal encapsulation mechanism thus relied on the remaining NAT-K or KASH and the C-S-H binding phase. Cement paste was highly alkaline and was expected to have negatively charged surfaces that repelled the metal anionic species. According to Mollah's work (Mollah et al., 1992), some Cr ions could substitute the Si^{4+} in a C-S-H structure. In addition, after the pozzolanic reaction, the density of cement mortars blended with 5 wt% NAT-K, KASH or BA was enhanced, which was good for heavy metal encapsulation. The Cd ion adsorption capacities of NAT-K, KASH and BA were comparable to the previous work (Ok et al., 2007), although the used zeolite content was much lower in this work. The zeolite–Portland cement of the Ok et al.'s work adsorbed Cd ion at the same value. This was possibly due to the partly chemical destruction of hydration reaction products and zeolite after being subjected to 400 °C heating. The use of a small amount of NAT-K and KASH produced mortars with improved strength and good heavy metal encapsulation capacity.

4. Conclusions

The conclusions are given as follows:

1) The NAT-K zeolite and KASH zeolite-like material can be produced from lignite BA obtained from the Mae Moh power plant. For NAT-K, the optimum conditions for synthesis were obtained with 6.6 μm BA, pretreatment by iron oxide removal, and refluxing with 7 M KOH at a temperature range of 100–110 °C for 24 h. For KASH, the optimum conditions for synthesis were obtained with 3.0 and 6.6 μm BA, pretreatment by iron oxide removal, and refluxing with 9 M KOH at a temperature range of 100–110 °C for 24 h.
2) Hybridized with NAT-K, the early strength and the density of the cement mortars could be improved. For 5 wt% replacement, the strength and density increased substantially due not only to the pozzolanic effect but also to the microfiller effect. With an increase in the replacement level, the gain in strength was reduced. For 10 wt% NAT-K replacement, the compressive strengths were comparable to normal cement mortar. KASH can replace cement up to 10% with no compressive strength reduction when compared to normal Portland cement mortar.
3) Both NAT-K and KASH can partially replace Portland cement and be used for heavy metal encapsulation. KASH gave a slightly better performance than NAT-K. They can encapsulate approximately 97% Cr, 98% Ni and 84% Cd which is better than BA

Acknowledgments

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High-Calcium Bottom Ash Geopolymer: Sorptivity, Pore Size, and Resistance to Sodium Sulfate Attack

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Abstract: The resistance to sulfate attack, compressive strength, sorptivity, and pore size of high-calcium bottom ash geopolymer mortars were studied. Ground lignite bottom ashes (BAs) with median particle sizes of 16, 25, and 32 μm were used. NaOH, sodium silicate, and temperature curing were used to activate the geopolymerization. Results showed that relatively high strengths of 40.0–54.5 MPa were obtained for the high-calcium bottom ash geopolymer mortars. The use of fine BA improved the strength and resistance to sulfate attack of mortars. The good performances were attributable to the high degree of reaction of fine BA and the associated low amount of large pores (0.05–100 μm) compared with those of coarse BA. The incorporation of water improved the workability of mixes, and the compressive strength, sorptivity, and resistance to sulfate attack decreased due to the increase in large pores. **DOI: 10.1061/(ASCE)MT.1943-5533.0000560.** © *2013 American Society of Civil Engineers.*

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Introduction

Portland cement is an energy intensive product because it consumes a large amount of energy. Its production releases approximately 7% of the green house gas produced annually (Malhotra 2002). Efforts have, therefore, been made to reduce the use of portland cement by introducing other supplementary cementitious materials (SCM). Another form of cement that is more environmental-friendly, such as geopolymer, is now receiving more attention (Davidovits 1999; Duxson et al. 2007). The source materials are normally fly ash (Palomo et al. 1999) and metakaolin because they contain large amounts of silica and alumina. The geopolymerization process normally involves the activation of source materials with alkaline solutions such as sodium hydroxide and potassium hydroxide, sodium silicate, and temperature curing (Detphan and Chindaprasirt 2009; Van Jaarsveld et al. 2002).

Bottom ash (BA) is a waste that results from coal burning to produce electricity in power plant. The major output of BA in Thailand is from pulverized coal combustion (PCC) at Mae Moh power plant in the north. The annual output is approximately 0.6 million tons (Wongkeo and Chaipanich 2010) and is disposed at landfills. It has been shown that BA has similar chemical constituents to fly ash, but with different particle sizes and shapes, BA can be used as an SCM to replace part of portland cement (Cheriaf et al. 1999; Jaturapitakkul and Cheerarot 2003). Because its particle size is larger than fly ash, it has to be ground to increase the reactivity. The ground BA has also been successfully used as a source material for making geopolymers (Chindaprasirt et al. 2009; Sathonsaowaphak et al. 2009).

The durability aspect of concrete is an important issue. Reinforced concrete and cementitious composites confront several harmful phenomena such as chloride penetration, carbonation, acid attack, sulfate attack, and the penetration of hazardous liquids or solutions, even by water (Gordon et al. 2011). Sulfate is one of the major problems affecting the performance of concrete. The mechanism of sulfate attack results in expansion and strength reduction (Atahan and Dikme 2011; Lee et al. 2005). Blended cement technology by incorporating SCM in concrete mixes has been selected to mitigate the durability problems of concrete. Most SCM, when incorporated into blended cement concrete to resist sulfate attack, showed satisfactory performance (Bonakdar and Mobasher 2010; Chindaprasirt et al. 2007c). Efforts to study the durability of geopolymer have recently been conducted (Bakharev 2005; Fernandez-Jimenez et al. 2007; Pacheco-Torgal et al. 2012; Thokchom et al. 2010). Thus far, the study has been limited to fly ash and metakaolin geopolymers, and very little work has been done on high calcium BA. The mechanisms of sulfate attack on portland cement and geopolymers are expected to be different because of the large difference in the amount of calcium (Bakharev et al. 2003) and the different chemical roles played by calcium in these systems.

The sorptivity or absorption of water is related to the ability of water or fluid to move into mortar and concrete and is, therefore,

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related to the durability property. Water absorbed in reinforced concrete structures coupled with oxygen may cause steel reinforcements to corrode. Water can go into concrete by means of capillary action of pore systems. Additionally, the resistance to this mechanism is consistent with that of liquid ingress with regard to sulfate and chloride solutions. As expected, the resistance to sorptivity is high when the rate or coefficient of sorptivity is low. The resistance to the sorptivity of concretes is inversely proportioned to the water/binder ratio (Ghrici et al. 2007) and porosity (Gonen and Yazicioglu 2007).

Mercury intrusion porosimetry (MIP) has been widely used to confirm the pore size distribution and porosity of cement paste with other properties; namely, mechanical properties, physical properties, and microstructures (Chindaprasirt et al. 2007b; Poon et al. 2006). The use of MIP has been extended to study the porosity of geopolymers from fly ash, metakaolin, and other alkali activated material (Kong et al. 2007; Zuda et al. 2010). The MIP technique has some limitations due to the ink-bottle effect, however it has been successfully used to compare the pores of similar products (Zuda et al. 2010). Information regarding the MIP of BA geopolymer is crucial to understand its strength and resistance to sulfate and water sorptivity.

Research Significance

High calcium BA geopolymers with various fineness of BA, with and without extra water, were made and tested to assess the effects of BA fineness and water content of geopolymer. The compressive strength, water sorptivity, pore size distribution by MIP, and resistance to sulfate attack are the subjects of this research.

Experimental Details

Materials

The lignite bottom ash was obtained from Mae Moh power station in northern Thailand. To study the effects of BA fineness, three finenesses were used: fine BA (F), medium BA (M) and coarse BA (C), with corresponding median particle sizes of 16, 25, and 32 μm and Blaine finenesses of 5,000, 3,400, and 2,100 cm^2/g, respectively. The X-ray diffraction (XRD) analysis of the BA is given in Fig. 1. The broad hump that showed the amorphous phase of BA was located at the two theta angle at approximately 20–35°, and the peaks of crystal of anorthite, augite, and gehlenite were also observed.

The particle size distributions of fine, medium, and coarse BA are shown in Fig. 2. The chemical composition of BA is shown in

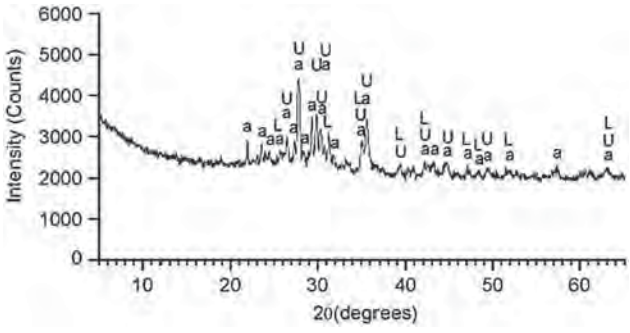


Fig. 1. XRD graph of ground BA

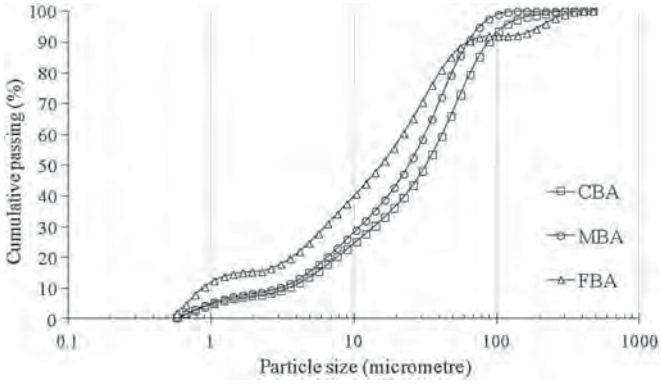


Fig. 2. Gradation curve of each BA fineness

Table 1. The SiO_2 and Al_2O_3 contents were reasonably high at 39.3 and 21.3%. Because this bottom ash was from lignite coal, CaO content was high at 16.5%. Sodium silicate solution (NS) with 13.8% Na_2O, 32.2% SiO_2, and 54.0% H_2O, and 10 M NaOH solution (NH) were used as alkaline activators. Local river sand with specific gravity of 2.62 and fineness modulus of 2.85 in saturated surface dry condition was used to make the geopolymer mortars. The gradation of the sand is shown in Fig. 3.

Mix Proportions, Mixing, and Curing

The mix proportions of geopolymer mortars were taken from a previous research study (Sathonsaowaphak et al. 2009) and consisted of a sand/BA ratio of 2.75, liquid alkaline/BA ratio of 0.6, and NS/NH ratio of 1.50. To study the effects of water content, two series of mixes with different water contents were used. For Series A, no extra water was added to the mixes. For Series B, extra water at a water/ash ratio of 0.08 (total liquid/ash ratio of 0.68) was incorporated to the mixes to obtain relatively workable mortars for comparison purposes. The addition of extra water results in dilution of the alkali solutions, and hence, affects the leaching of silica and alumina (Rattanasak and Chindaprasirt 2009). The mix proportions are shown in Table 2.

Mixing was conducted in an air-conditioned room at 25°C to eliminate the effect of temperature variation. The mixing procedure involved mixing of the BA and NH for 5 min. Sand and extra water (if needed) were then incorporated and mixing was conducted for five more minutes. This was followed by the addition of NS with a final mixing of 5 min. The mortar mixtures were then cast into molds, which were wrapped with clingfilm to avoid moisture loss. They were left in the laboratory at 25°C for one hour and then cured at 75°C for 48 h. The specimens were demolded and kept in a controlled room at 23°C and 50% relative humidity until they reached testing age.

For the mixing of paste, the same mixing procedure was used, except sand was not included. The paste mixtures were cast in cylindrical molds of 25 mm in diameter and 50 mm in length, and the same curing regime was used. The paste samples were used to determine the distribution of pore sizes of geopolymer using MIP. The paste samples were used because they gave more accurate results than the mortar samples. Certain differences in pore structure were attributable to interfacial transition zone effects between mortars and pastes. The comparison was, therefore, limited to the same type of materials; i.e., paste has been widely used to study the pore size distribution for cementitious materials (Chindaprasirt et al. 2007b).

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Table 1. Composition of High Calcium Lignite BA

Chemical	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	TiO_2	MgO	K_2O	P_2O_5	SO_3	LOI
Composition (%)	39.3	21.3	16.5	13.5	1.0	0.4	2.6	2.1	0.2	1.5	1.4

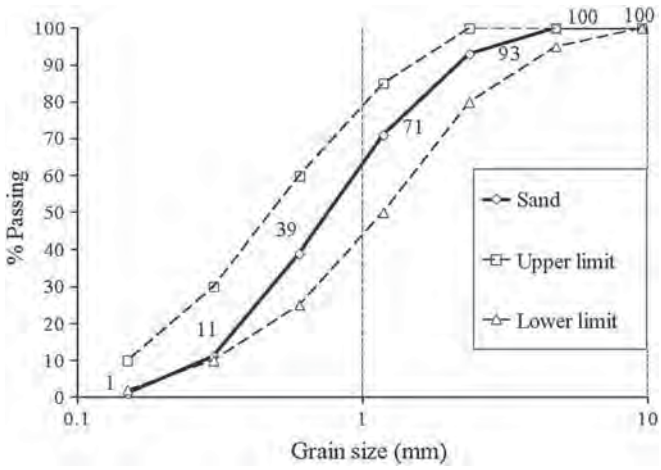


Fig. 3. Gradation curve of sand

Test Methods

Compressive Strength Test

For compressive strength tests (ASTM 2002), $50 \times 50 \times 50$ mm cube specimens were used. The mortars were cast in two layers with tamping. In the final step, specimens were vibrated for 10 s using a vibrating table. The prepared samples were tested for compressive strength at 7, 28, 90, 180, and 360 days. The reported compressive strengths were the average of three samples.

Pore Size

The measurements on intruded volume and pore size distribution of paste were conducted using MIP with the capability of measuring pore size diameter down to 7 nm. The samples were obtained by chiseling from the middle part of the hardened geopolymer paste cylinders and immersing in acetone for 48 h to stop the geopolymerization. After that, the samples were oven-dried at a temperature of 60°C for 24 h. Samples used were 3–6 mm thick and 1–1.5 g. The mercury volume was normalized for each sample weight. The applied pressures were between 9.3 and 206.5 MPa. The mercury contact angle and surface tension were 140° and 0.480 N/m.

Rate of Sorptivity

Mortar discs cut from the parent 100×200 mm mortar cylinder were used as samples for the determination of rate of sorptivity (ASTM 2011). The tests were performed at the age of seven days. The side-curved surface of the specimen was sealed with waterproof tape to allow water to penetrate into the specimen from the bottom end. The specimens were placed upright and supported to allow a sufficient gap of 100 mm for water to be absorbed by capillary suction. A 5-mm head of water above the bottom of the specimen was chosen for this investigation. Weights of the specimens before and after immersion were determined after 1, 5, 10, 20, and 30 min and 1, 2, 3, 4, 5, and 6 h of immersion. The weight of water absorbed and the rate of sorptivity were then calculated.

Sulfate Resistance

Mortar bars with dimensions of $25 \times 25 \times 285$ mm were used to test the sulfate resistance (ASTM 2010). They were immersed in 10% sodium sulfate solution after the age of seven days in a 23°C controlled room, and were tested for sulfate-induced expansion and weight change until 360 days of immersed time. The sulfate solution was replaced with fresh solution weekly for the first month and monthly thereafter. The reported results were the average of four samples. The weight changes of the samples were also recorded.

Results and Discussion

Compressive Strength

The compressive strengths of mortars are given in Table 3. It was evident that the strength of geopolymer mortars was affected by the fineness of BA and extra water. Series A mixes with no extra water gave high compressive strengths at 28 days of 40.0–54.5 MPa. The extra water is sometimes needed to improve the workability of the mixes (Sathonsaowaphak et al. 2009). The addition of extra water in a water/ash ratio of 0.08 drastically reduced the compressive strengths to 13.5–22.5 MPa. Although water was needed for the geopolymerization process and workability, the excess water reduced the strength of geopolymer mortars (Chindaprasirt et al. 2007a; Sathonsaowaphak et al. 2009). The leaching of silica and alumina was reduced because extra water diluted the concentration of base solution.

Table 2. Mix Proportions of the Geopolymer Mortars

Mix	Type of BA	BA (g)	NS (g)	NH (g)	Water (g)	Sand (g)
AF	F	100.0	35.8	23.9	0.0	275.0
AM	M	100.0	35.8	23.9	0.0	275.0
AC	C	100.0	35.8	23.9	0.0	275.0
BF	F	100.0	35.8	23.9	8.0	275.0
BM	M	100.0	35.8	23.9	8.0	275.0
BC	C	100.0	35.8	23.9	8.0	275.0

Note: 10 M NH, sand/BA = 2.75, liquid alkaline/BA = 0.597, NS/NH = 1.50.

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Table 3. Compressive Strengths and Rates of Sorptivity of Geopolymer Mortars

Mix	Compressive strength (MPa)					Rate of sorptivity ($\mu m/s^{1/2}$)
	7 days	28 days	90 days	180 days	360 days	7 days
AF	48.5	54.5	51.5	61.5	55.5	6.1
AM	46.0	48.0	46.5	49.5	39.5	7.6
AC	43.0	40.0	32.5	35.0	36.5	11.0
BF	16.0	22.5	22.0	22.5	23.5	14.0
BM	16.0	15.0	15.0	16.5	13.5	16.0
BC	16.5	13.5	13.5	11.5	15.0	40.0

The fineness of BA also contributed to the compressive strength of mortar. For Series A using fine BA (AF mix), the strengths of mortars were highest. The compressive strengths of AF, AM, and AC mixes at 28 days were 54.5, 48.0, and 40.0 MPa, respectively. For Series B, relatively high strengths of the mix using fine BA compared to the mixes using medium and coarse BA were also observed. A similar increase in strengths of geopolymer mortars with the increase in the fineness of BA has been reported (Sathonsaowaphak et al. 2009).

The development of strength was also affected by the ash fineness. For fine BA, the strength developments after seven days of AF and BF mortars were clearly observed. The compressive strengths of AF mortars at 7, 28, 90, 180, and 360 days were 48.5, 54.5, 51.5, 61.5, and 55.5 MPa, respectively. The compressive strengths of BF mortars at the same ages were 16.0, 22.5, 22.0, 22.5, and 23.5 MPa, respectively. For the coarser ashes, the strength developments after seven days of AM, AC, BM, and BC mortars were not observed. The BA with high fineness and high surface area could dissolve more silica and alumina and resulted in the increase in geopolymerization and strength. In addition, a large portion of BA particles were porous and contributed to the low strength of geopolymer mortars (Chindaprasirt et al. 2009). Grinding helped to destroy the pores of BA particles (Sathonsaowaphak et al. 2009) and thus improved the strength of geopolymer mortars. Some losses of strengths of geopolymer concretes were observed at the later age of 365 days. Shrinkage cracking (Wongpa et al. 2010) and sodium and carbon dioxide reaction (Pacheco-Torgal et al. 2007) were proposed as the reasons.

Volume Intrusion of MIP

The results of volume intrusion of the MIP of geopolymer pastes are shown in Fig. 4. The volume intrusion (VI) down to 0.007 μm was dependent on the BA fineness and amount of extra water. In general, the amount of VI increased gradually with the decreasing pore diameter. For fine BA, the increases in VI values were initially lower thanthose of medium BA and coarse BA. The threshold VI values of slightly higher than 0.02 m^3/Mg at a pore diameter of 0.02 μm were quite prominent for both AF and BF pastes. For the medium BA, the threshold values were not as distinct as those of fine BA. They were located at VI of 0.04 m^3/Mg at pore diameter of 0.025 μm and VI of 0.06 m^3/Mg at pore diameter of 0.03 μm for AM and BM pastes, respectively. This indicated that the extra water and the increase in the BA median particle size resulted in the increase in large pores. The results of VI of coarse BA paste clearly reflected this observation. The leaching of alumina and silica was dependent on the contact area of ash particles and base solution (Rattanasak and Chindaprasirt 2009). The fine BA with high surface area eased the dissolution of silica, alumina, and calcium, which resulted in higher geopolymerization (Sathonsaowaphak et al. 2009) and a higher amount of calcium silicate hydrate (C-S-H) (Somna et al. 2011) than those of coarser BA.

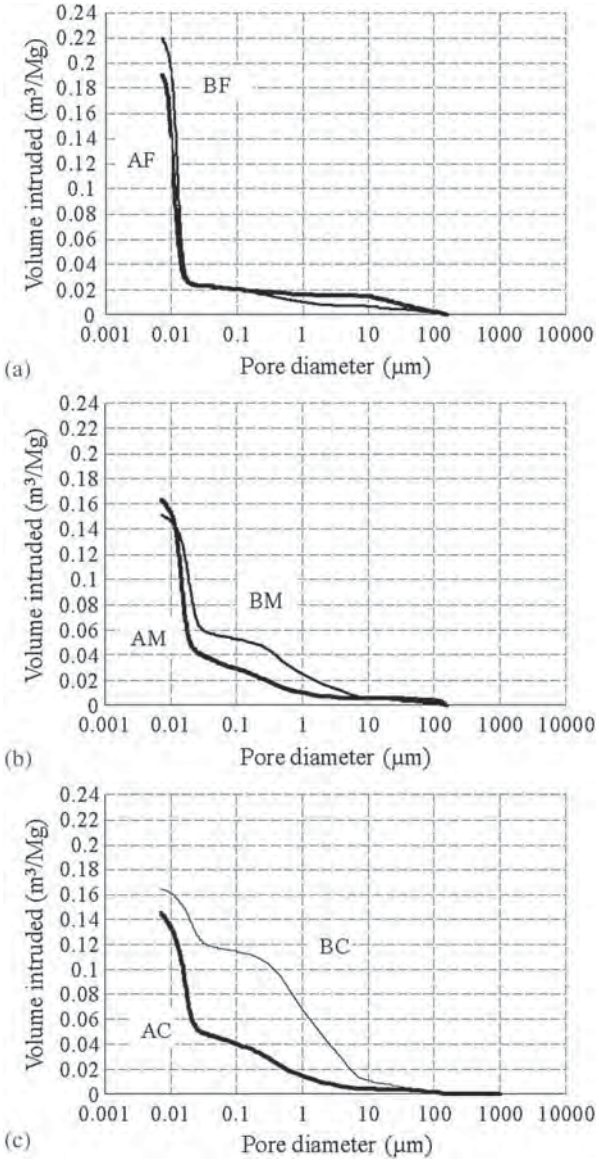


Fig. 4. Intruded volume of MIP of geopolymer pastes: (a) AF and BF pastes; (b) AM and BM pastes; (c) AC and BC pastes

This produced a denser matrix and higher compressive strength mortars than those with coarser BA and with extra water.

The increase in VI was very high at the approximate pore size of 0.01–0.02 μm. For fine BA, a significantly higher percentage of small pores at approximately 0.01 μm could be observed, compared to that of large pores (larger than 0.02 μm). The high rate of increase was reduced with the addition of extra water and

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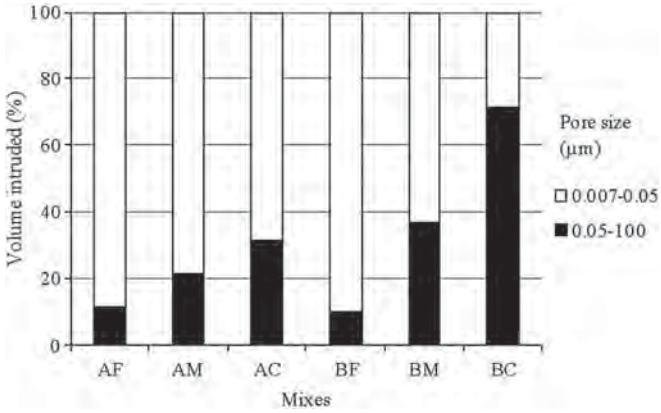


Fig. 5. Percentage of intruded volume of MIP

reduction in fineness of BA. These results suggested an increase in gel pore (approximately 0.01–0.02 μm) and the corresponding increase in gel formation.

To further compare the results, the amount of small pores and large pores were identified, as shown in Fig. 5. The small pores were pores with sizes up to 0.05 μm, which included small capillary pores (Chindaprasirt et al. 2007b). The percentages of VI of small and large pores were clearly affected by the water/ash ratio and fineness of BA. The percentage of VI of large pores between 0.05–100 μm of AF and BF pastes was low at 10%. The percentages of VI increased with the decrease in fineness of BA and with the addition of extra water. The percentages of large pores of AM and AC pastes were 21 and 33%, compared to 37 and 70% of those of BM and BC pastes. The geopolymer porosity was affected by the water/ash ratio (Skvara et al. 2006). The addition of extra water increased the porosity of the geopolymer paste. The incorporation of water effectively improved the workability of geopolymer, with some reductions in strength (Chindaprasirt et al. 2007a). Excess water also diluted the liquid and thus slowed down the dissolution and reaction of geopolymer (Sathonsaowaphak et al. 2009). The increase in porosity and dilution of liquid alkaline activator were the primary reasons for the reduction in strength.

Rate of Sorptivity

The results in Table 3 showed that the rate of sorptivity of mortar decreased with the increase in fineness of BA. The rate of sorptivity of AF, AM, and AC mortars were 6.1, 7.6, and 11.0 $\mu m/s^{1/2}$, respectively. The sorption versus time$^{1/2}$ curves were linear and very close to the straight line. The relatively low sorptivity indicated that the pores were too small to take up water. The use of fine BA resulted in a dense and strong matrix and the decrease in the rate of sorptivity values, as expected. The obtained rate of sorptivity values were similar to those of portland cement or portland blended cement concrete of 5.0–30.0 $\mu m/s^{1/2}$ (Ghrici et al. 2007; Gonen and Yazicioglu 2007; Keleştemur and Demirel 2010). The addition of water to improve the workability resulted in mixes with less dense matrices and the rate of sorptivity values increased more than those of Series A. The rate of sorptivity values of BF, BM, and BC mixes were 14.0, 16.0, and 40.0 $\mu m/s^{1/2}$, respectively. These rate of sorptivity values were approximately 2.5–4 times higher than the corresponding values of Series A. The rate of sorptivity values of BF and BM at 14.0 and 16.0 $\mu m/s^{1/2}$ were within the normal range of those of portland cement mortar. However, the rate of sorptivity value of BC of 40.0 $\mu m/s^{1/2}$ was higher than those of portland cement. The high rate of sorptivity of the BC mix corresponded with a large amount of large pores, indicated by the MIP results (Fig. 4).

Sulfate Resistance

The results of mortar bar expansion are given in Fig. 6(a). The expansion of mortar bars was found to depend on the fineness of the BA and the water content of mixture. The expansions of Series B, which contained extra water, were significantly higher than those of Series A. After immersion for 360 days, the expansions of Series B were between 215 and 325 microstrains, whereas those of Series A were between 80 and 160 microstrains. The results correlated with the results of pore size and strength. The mix with extra water content and a large amount of large pores exhibited high expansion and low strength. For the effect of fineness of BA, the expansions were lower with the use of fine BA. For Series A, the expansions after a 360-day immersion were 80, 125, and 160 microstrains for AF, AM, and AC mortars, respectively. For Series B, the trend of the results was similar to the expansions after 360 days of 215, 280, and 325 microstrains for BM, BF, and BC mortars, respectively.

The values of expansion of 215–315 and 230–335 microstrains for Series B mixes after 270 and 360 days of immersion in 10% sulfate solution were still lower than those of mortars made from portland cement replaced with 20–25% fly ash immersed in 5–10% sodium sulfate solution (Chindaprasirt et al. 2007c; Nehdi and Hayek 2005). The expansions of mortars made from portland cement replaced with 20–40% fly ash immersed for 360 days in 5% sodium sulfate solution were between 500 and 750 microstrains (Chindaprasirt et al. 2007c).

The results of the weight change of geopolymer mortar bar immersed in sulfate solution are shown in Fig. 6(b). The weight gains were dependent on the fineness of BA and water content. For Series B mixes with extra water, the weight gains were high at 2–5% and those of Series A mixes were lower than 2% after 180–360 days of

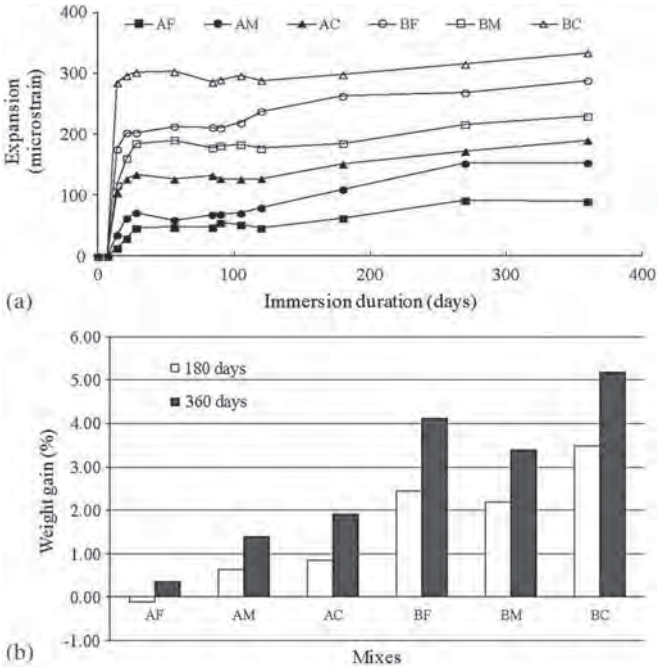


Fig. 6. Change in length and weight of mortar bars in 10% sodium sulfate solution after 180–360 days of immersion: (a) length change; (b) percentages of weight change

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immersion. In fact, the initial weight gains of AF and AM mortars were very low, and significant weight gains were obtained after a period of immersion. The weight gain increased with the increasing amount of large pores. For the effect of fineness, the fine BA performed better than the coarse BA. The fine BA geopolymer was denser and contained fewer large pores than the coarse BA geopolymer.

The expansion of high calcium BA geopolymer mortar immersed in sodium sulfate solution was attributable to the formation of ettringite and gypsum crystal (Bakharev 2005; Sata et al. 2012). The high calcium content of BA reacted with sulfate ion and formed the calcium sulfate, which precipitated within the pores of matrix. It was also reported that the calcium reacted and formed C-S-H, and coexisted with the geopolymer gel (Somna et al. 2011). In addition, the sulfate also reacted with other ions such as aluminum and formed ettringite (calcium sulfoaluminate hydrate). The formation of both gypsum crystals and ettringite contributed to the expansion of mortar bars. After immersion in sodium sulfate solution, mortars made from coarse BA and those with extra water with a low degree of geopolymerization and large amount of large pores contained a large amount of ettringite and gypsum, and thus showed large expansion and weight gain. In the study of fly ash geopolymer samples immersed in sodium and magnesium sulfate solutions, the ettringite phase was identified using XRD (Bakharev 2005). Other sulfate products were also likely to be present after the sulfate attack.

Conclusions

Based on the obtained data, the following conclusions were made:

1. The high calcium bottom ash geopolymer with relatively high compressive strengths of 40.0–54.5 MPa at 28 days were obtained with the use of finely ground BA, 10 M NaOH, sodium silicate solution with temperature curing at 75°C for 48 h. The fine BA gave a high compressive strength due to an increase in reactivity through a more increased surface area than medium and coarse BA.
2. The strengths of high calcium bottom ash geopolymer mortar were dependent on BA fineness and the amount of water in the mixes. The addition of extra water at a water/ash ratio of 0.08 significantly improved the workability of mixes. However, the 28-day compressive strengths were significantly reduced to 13.5–22.5 MPa.
3. The threshold values of the intruded volume, pore sizes of paste, and rate of sorptivity of mortar of high calcium bottom ash geopolymer were dependent on the fineness of BA and extra water. The pastes with low percentages of large pores and mortars with low rates of sorptivity were obtained with mixes with no extra water and with fine BA.
4. The resistance to sulfate attack of high calcium bottom ash geopolymer mortar was excellent, because the expansion of mortar bars after immersion in the 10% sodium sulfate solution for 360 days were low. The expansion was primarily related to the formation of ettringite and gypsum.

Acknowledgments

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Properties of high calcium fly ash geopolymer pastes with Portland cement as an additive

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Abstract: The effect of Portland cement (OPC) addition on the properties of high calcium fly ash geopolymer pastes was investigated in the paper. OPC partially replaced fly ash (FA) at the dosages of 0, 5%, 10%, and 15% by mass of binder. Sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) solutions were used as the liquid portion in the mixture: NaOH 10 mol/L, Na_2SiO_3/NaOH with a mass ratio of 2.0, and alkaline liquid/binder (L/B) with a mass ratio of 0.6. The curing at 60°C for 24 h was used to accelerate the geopolymerization. The setting time of all fresh pastes, porosity, and compressive strength of the pastes at the stages of 1, 7, 28, and 90 d were tested. The elastic modulus and strain capacity of the pastes at the stage of 7 d were determined. It is revealed that the use of OPC as an additive to replace part of FA results in the decreases in the setting time, porosity, and strain capacity of the paste specimens, while the compressive strength and elastic modulus seem to increase.

Keywords: geopolymers; Portland cement; fly ash; compressive strength; porosity; elastic moduli

1. Introduction

Currently, Portland cement (OPC) is used extensively as a cementitious material for construction and building. However, the process of producing OPC also results in environmental problems and releases a large amount of green house gas [1]. Therefore, the effort focuses on how to replace part of OPC with by-products or natural materials. Recently, a new and more environmental friendly binding material, called geopolymer, was developed [2]. Geopolymer is normally made from a source material containing silica and alumina, and activated with alkali solution.

Fly ash (FA) is a by-product from lignite coal burning from Mae Moh Power Station in northern Thailand. The annual output is approximately 3 million tons. This FA consists mainly of silicon dioxide (SiO_2), aluminum trioxide (Al_2O_3), and calcium oxide (CaO). High CaO is the normal feature of high calcium fly ash. The use of FA as pozzolan in concrete is constantly increasing because it improves the properties of concrete, namely, workability, durability, and long-term strength in hardened concrete [3-4]. It has been also shown that this high calcium fly ash is suitable as a source material for making good geopolymer [5-6]. The high calcium content of fly ash leads to the formation of calcium silicate hydrate which coexists with the aluminosilicate geopolymer products [7-8]. The coexistence of calcium silicate hydrate (C-S-H) phase with the geopolymeric gel has been proved to improve the mechanical properties of final products [9]. In addition, it has been suggested that, for geopolymer containing various Ca compounds, the calcium enters into the geopolymer network, possibly acting as the charge-balancing cation [10].

The reaction of fly ash and alkali solution is an endothermal process and thus requires the extra heat [11-

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12]. In the production of fly ash geopolymer, a moderate heat is usually incorporated to accelerate the geopolymerization. The reaction of OPC with water is an exothermal process and generates heat. The addition of OPC in a fly ash geopolymer system should be beneficial not only on the mechanical properties but on the setting and reaction of the system. The amount of OPC as an additive should not be large. The heat generated by OPC hydration should assist the geopolymerization process.

This paper studied the properties of geopolymer pastes made from high calcium FA with OPC as an additive. The knowledge would be beneficial to the future applications of geopolymeric materials.

2. Experimental

2.1. Materials

A high calcium fly ash (FA) from Mae Moh Power Plant in northern Thailand and Portland cement Type I (OPC) were used in this study. Sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) with 13.89% Na_2O, 32.15% SiO_2, and 46.04% H_2O by mass were used as a liquid portion in the mixture to activate the geopolymerization.

Table 1 shows the chemical composition of FA and OPC. The physical properties of materials are shown in Table 2. The specific gravity of FA and OPC are 2.61 and 3.16, respectively. The median particle sizes of FA and OPC are 8.5 and 14.6 μm with the corresponding Blaine fineness values of 4300 and 3600 cm^2/g, respectively.

2.2. Mix proportion of geopolymer pastes

The mix proportions of geopolymer pastes are shown in Table 3. The control, FA5PC, FA10PC, and FA15PC pastes are geopolymer pastes with 0%, 5%, 10%, and 15% OPC by mass of binder. The constant ratio of liquid alkaline to binder by mass (L/B, 0.60) and the ratio of Na_2SiO_3 to NaOH by mass (2.0) based on the previous research [13] were used for all mixtures. The NaOH and Na_2SiO_3 solutions were first mixed together and used as the liquid solution. FA and OPC were dry and mixed until homogenous. Thereafter, the liquid solution was added, and mixing of pastes was done for 5 min.

Table 1. Chemical composition of materials **wt%**

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
FA	29.32	12.96	15.64	25.79	2.94	2.93	2.83	7.29	0.30
OPC	20.80	4.70	3.40	65.30	1.50	0.40	0.10	2.70	0.90

Table 2. Physical properties of materials

Materials	Specific gravity	Median particle size, d_{50} / μm	Blaine fineness / ($cm^2 \cdot g^{-1}$)
FA	2.61	8.5	4300
OPC	3.16	14.6	3600

Table 3. Mix proportions of geopolymer pastes

Mix No.	Symbol	Mix proportion / wt%		SiO_2/Al_2O_3 mole ratio
		FA	OPC	
1	Control	100	0	3.26
2	FA5PC	95	5	3.28
3	FA10PC	90	10	3.30
4	FA15PC	85	15	3.33

2.3. Setting time and compressive strength of geopolymer pastes

After mixing, the setting time of geopolymer pastes were tested in accordance with ASTM C191 [14]. The reported setting times of geopolymer pastes were the average of three samples.

Cube moulds of 50 mm×50 mm×50 mm were used for the compressive strength tests of geopolymer pastes. The specimens were prepared in accordance with ASTM C109 [15]. The moulds were wrapped with vinyl sheets to protect the moisture loss and left standing for 1 h. Then, the specimens were placed in the oven for heat curing at 60°C for 24 h. After the heat curing, the specimens were kept in the laboratory to cool down and demoulded the next day. At last, they were kept in a 23°C control room. The reported compressive strengths of geopolymer pastes are the average of five samples.

2.4. Porosity of geopolymer pastes

Cylindrical specimens with 50 mm in diameter and 100 mm in height were prepared for the porosity measurement of geopolymer paste specimens. The specimens were cured in a 23°C control room and tested after curing time of 1, 7,

28, and 90 d. The porosity was calculated using Eq. (1). Moreover, the water absorption of geopolymer pastes was also tested. The porosity and water absorption were determined as described in ASTM C642 [16]. The methods for measuring porosity and water absorption were used successfully in a number of researches [17-20]. The reported results are the average of three samples.

$$\begin{cases} p = \dfrac{B-A}{B-C} \times 100\% \\ w = \dfrac{B-A}{A} \times 100\% \end{cases} \quad (1)$$

where p is the vacuum saturation porosity; w the vacuum saturation water absorption; A the weight of the oven-dried sample, g; B the weight in air of the saturated sample, g; and C the weight in water of the saturated sample, g.

3. Results and discussion

3.1. Setting time

The setting time of geopolymer pastes at various replacement levels of OPC are shown in Fig. 1. The initial setting time of control, FA5PC, FA10PC, and FA15PC pastes are 30, 27, 20, and 15 min, and the final setting time of these pastes are 58, 47, 38, and 26 min, respectively. The setting time of geopolymer pastes obviously decreased with the increase in the replacement of OPC, indicating the faster activation of the pastes. The addition of calcium in soluble or partly soluble states significantly accelerated the setting and hardening of geopolymer pastes [6, 21]. Readily available free Ca ions from OPC and high-calcium FA also reacted and formed C-S-H and calcium aluminosilicate hydrate (C-A-S-H) [22-23]. The higher Ca content with the reduced amount of SiO_2 and Al_2O_3 of binders led to a higher reaction degree [24]. The faster setting time of FA-OPC paste could be advantages in the repair binding materials or in other conditions where fast setting is required.

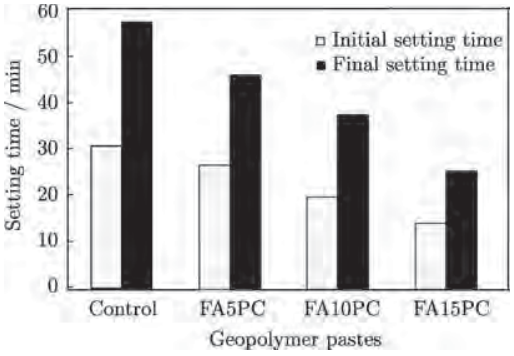


Fig. 1. Setting time of geopolymer pastes.

3.2. Compressive strength

The compressive strengths of geopolymer pastes at various replacement levels of OPC are shown in Fig. 2. The compressive strengths of geopolymer pastes obviously increased with the increase in replacement levels of OPC and curing time. When the content of OPC increased, the compressive strength of geopolymer pastes was significantly improved due to the increased amount of Ca content, which altered the microstructure of geopolymer gels [21, 25]. These results agreed with previous researches [22, 26]. The increase in Ca led to a high compressive strength mix due to the additional formation of C-S-H and C-A-S-H gels, which modified the microstructure of the paste. C-S-H and C-A-S-H within geopolymeric binder could work as a micro-aggregate, thereby enhanced the durability and compressive strength [21, 27]. The reaction with SiO_2 and Al_2O_3 of binder reduced the $Ca(OH)_2$ content of the system, and the pore structure was refined in a similar way as the pozzolanic reaction in the blended cement paste [28]. As shown in Fig. 2, for the low replacement levels of OPC in control and FA5PC mixes, the rates of strength improvement are low after curing for 28 d. However, the rates are high for the high OPC replacement levels in FA10PC and FA15PC mixes. This was associated with the reaction of OPC and pozzolanic reactions to form additional C-S-H and C-A-S-H. The increase in compressive strength at the later stage in this system was very useful, as this could compensate for the possible strength reduction at the later stage often observed [29].

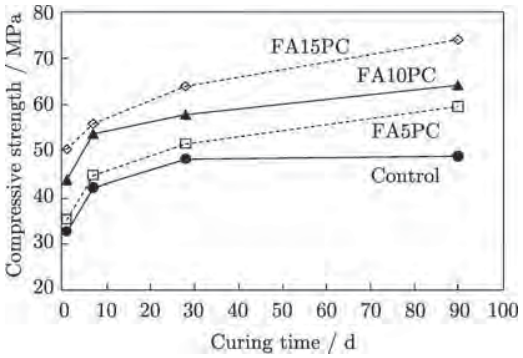


Fig. 2. Compressive strength of geopolymer pastes.

3.3. Porosity and water absorption

The results of porosity and water absorption of geopolymer pastes are shown in Table 4. The porosities at all stages of pastes are lowered with the increases in the replacement level of OPC and curing time. For example, the porosities at 28 d of control, FA5PC, FA10PC, and FA15PC pastes are 14.6%, 13.3%, 12.4%, and 12.0%, respectively, and the porosities of FA10PC pastes at 1, 7, 28, and 90 d are 15.5%, 12.9%, 12.4%, and 12.0%, respectively. The water absorption capacity decreases with the increase in curing time as expected. The water adsorption values were slightly less than the absorptions, as some of pores were not readily accessible. The results corresponded well with the strength behavior. The increase in OPC content

led to a higher compressive strength and reduced porosity. The reduced porosity and increased density were the results of pore structure refinement from coarser to finer [30-32].

Table 4. Porosity and water absorption of geopolymer pastes

Mixes	Porosity / %				Water absorption (7 d) / %
	1 d	7 d	28 d	90 d	
Control	18.5	15.2	14.6	14.3	10.2
FA5PC	17.9	14.6	13.3	12.5	9.5
FA10PC	15.5	12.9	12.4	12.0	8.7
FA15PC	13.4	12.6	12.0	11.1	8.5

3.4. Stress-strain and elastic modulus of geopolymer pastes

The relationships between stress and strain of geopolymer pastes curing for 7 d are shown in Table 5 and Fig. 3. The chord modulus was determined as described in ASTM C469 [33]. The values of elastic modulus and compressive strength increased with the OPC replacement levels. The denser and stronger pastes with the addition of OPC resulted in the increase in elastic modulus. The elastic modulus values of normal strength Portland cement pastes were reported to be between 12.5 and 17.5 GPa [34-35], which were similar to that of geopolymer pastes without OPC. The addition of OPC produced additional C-S-H and C-A-S-H within geopolymeric binder and acted as a micro-aggregate, which enhanced the compressive strength [21, 27] and increased the elastic modulus of the pastes. For the strain capacity, the strains at peak stress (strain capacity) were lowered with the increase in the OPC replacement level. The strain capacity at peak stress tended to reduce, whereas the elastic modulus tended to increase with the increase in the OPC content compared to those of the control paste.

Table 5. Strain capacity (ε_p) and elastic modulus (E) of geopolymer pastes curing for 7 d

Mixes	ε_p	E / GPa
Control	0.00302	13.7
FA5PC	0.00247	15.2
FA10PC	0.00238	19.4
FA15PC	0.00230	23.2

Fig. 4 shows the relationship between elastic modulus and compressive strength of geopolymer pastes. The elastic modulus tended to increase linearly with the square root of ultimate compressive strength. The equation predicting this relationship can be written as

$$E = 8.507\sqrt{f'_c} - 41.649 \quad (2)$$

where E stands for the elastic modulus, GPa; and f'_c the ultimate compressive strength, MPa.

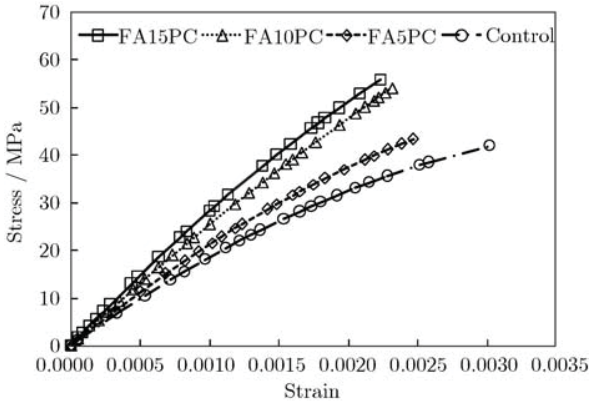


Fig. 3. Relationship between stress and strain of geopolymer pastes.

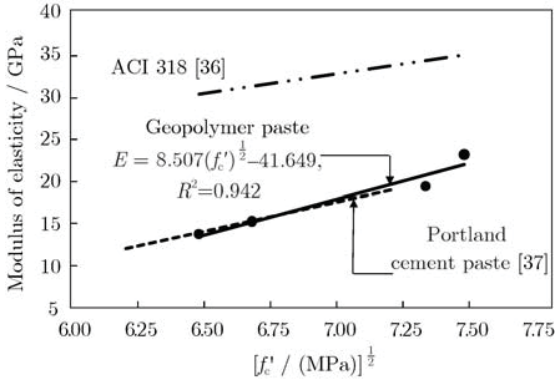


Fig. 4. Relationship between elastic modulus and compressive strength of geopolymer pastes.

As shown in Fig. 4, the elastic modulus values of geopolymer pastes in this study are approximately half of those given by ACI 318 for Portland cement concrete [36], and similar to those of the Portland cement paste with the similar strengths (between 38.5 and 52.2 MPa) [34, 37]. The elastic modulus of inorganic polymer concrete (IPC) depends primarily on the SiO_2/Al_2O_3 mole ratios by mass [38]. In this study, the SiO_2/Al_2O_3 mole ratio of mixes varied in a narrow range between 3.26-3.33, as shown in Table 3, and its effects on the strength and elastic modulus would be small. The influences on the elastic modulus and

strength were, therefore, from the addition of OPC. The increased calcium reacted and formed additional C-S-H and C-A-S-H. The results also suggested that the increase in OPC content was very useful in terms of improvement in the stiffness of this inorganic polymer matrix.

3.5. Relationship between compressive strength and porosity of geopolymer pastes

The relationship between compressive strength and porosity of geopolymer pastes is shown in Fig. 5, which can be presented in the form of Eq. (3). The similar relationship between strength and porosity of Portland cement pastes from previous research [39] was also reported for comparison. A slightly lower in the strength and porosity curve obtained from this study could be attributed to the difference in the measuring of porosity. The values obtained from the vacuum saturation porosity, as described in ASTM C642, was slightly lower than that obtained from the mercury intrusion porosimetry (MIP).

$$f'_c = 211.711 \exp(-0.103p) \quad (3)$$

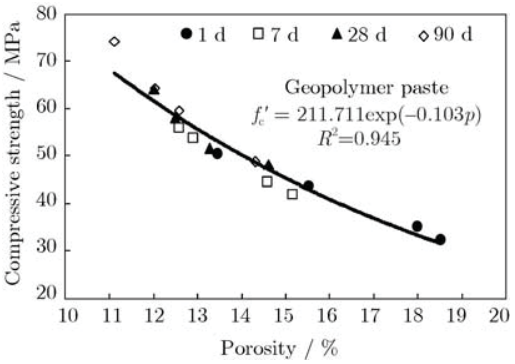


Fig. 5. Relationship between porosity and compressive strength of geopolymer pastes.

The results indicated that increasing the compressive strength of geopolymer pastes corresponded to the reduction in porosity. The addition of OPC resulted in the rich of $Ca(OH)_2$, and increased C-S-H and C-A-S-H phases, which refined the pore structure of geopolymer pastes [40] and increased the compressive strength and elastic modulus of geopolymer pastes.

3.6. SEM analysis

The SEM photos of FA and FA10PC geopolymer pastes are shown in Fig. 6. The FA paste contains a larger number of non-reacted and/or partially reacted fly ash particles embedded in a continuous matrix. For FA10PC paste, a less number of fly ash particles are observed, and the matrix appears denser than that of the FA paste. The use of high calcium fly ash resulted in the formation of C-S-H which co-existed with geopolymer products [7-8]. The incorporation of Portland cement resulted in the less amount of fly ash used and also the formation of additional C-S-H and C-A-S-H, which also would coexist with geopolymer products. This led to the overall increase in the strength of geopolymer products.

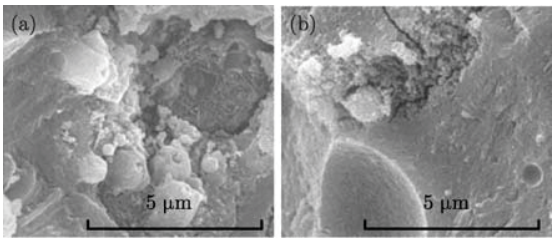


Fig. 6. SEM images of geopolymer pastes: (a) FA; (b) FA10PC.

4. Conclusions

(1) The use of OPC to partially replace FA results in the reduction of setting time due to the increase in calcium content, which accelerates the setting and hardening of geopolymer pastes. The initial and final setting times of geopolymer pastes are between 15-30 min and 26-58 min, respectively.

(2) The incorporation of OPC increases the strength of FA geopolymer mixes due to the formation of additional C-S-H and C-A-S-H gel, which modifies the microstructure and pore of geopolymer pastes. The relatively high compressive strength (curing for 28 d, 64.0 MPa) can be obtained with the replacement of 15wt% OPC.

(3) The incorporation of OPC also increases the elastic modulus and reduces the pore of geopolymer pastes. Additional C-S-H and C-A-S-H are formed and filled the pore to make dense and strong geopolymer pastes.

(4) The strain capacity at peak stress of geopolymer pastes, however, is reduced with the increase in OPC content. The dense and strong pastes are obtained at the compensation of less deformation in terms of strain at peak stress.

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Properties of pervious geopolymer concrete using recycled aggregates

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HIGHLIGHTS

- Recycled aggregates (RAs) were used to make pervious geopolymer concrete (PGC).
- PGCs were prepared from high-calcium fly ash geopolymer binder and two different types of RA.
- Mechanical properties, total void ratio, and water permeability were tested.
- These RA could be used as coarse aggregates to produce PGC with acceptable properties.

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ABSTRACT

In this paper, the use of recycled aggregates (RAs) for making pervious geopolymer concrete (PGC) was studied. PGCs were prepared from high-calcium fly ash (FA), sodium silicate (Na_2SiO_3) solution, sodium hydroxide (NaOH) solution, and two different types of RA viz., crushed structural concrete member (RC) and crushed clay brick (RB). The results were also compared with those of natural coarse aggregate (NA). Compressive strength, splitting tensile strength, total void ratio, and water permeability coefficient of the PGCs were determined. The results indicate that both RC and RB can be used as recycled coarse aggregates for making PGC with acceptable properties.

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1. Introduction

Pervious concrete is a special concrete that contains continuous voids and possesses high water permeability compared to normal concrete. It has been developed as an environmentally friendly material for use in water purification, permeable pavement, acoustic absorption, thermal insulation, and other applications in civil engineering and architecture [1–3]. Generally, the sizes of connected pore in pervious concrete range from 2 to 8 mm in diameter with void content between 15% and 35% and compressive strength between 2.8 and 28.0 MPa [4]. Typically, pervious concrete consists of binder, coarse aggregates, water, and admixture.

It is generally known that cement manufacturing is an energy intensive process and releases a large amount of green house gas to the atmosphere. The cement industry contributes about 7% by weight of the total carbon dioxide emissions [5]. Therefore, the use of supplementary materials to partially replace Portland cement and alternative cementing materials should be developed in order to reduce the use of Portland cement [6–8]. Geopolymer binder is one such alternative cement which is synthesized by mixing aluminosilicate material and high alkali solutions [9]. It utilizes by-products such as fly ash or metakaolin as aluminosilicate source to react with high alkali solutions of sodium or potassium based. Fly ash geopolymers have been studied by several researchers and were found to have high early strength, high later age strength, and excellent resistance to sulfate and acid attack [9–12].

In addition, the use of waste such as recycled aggregate in concrete is beneficial for the environment. The use of these materials can reduce wastes to landfill and reduce consumption of natural material resources. The studies with respect to the applicability of recycled aggregate in concrete have been conducted around the world [13–16]. However, most researchers have focused on the mechanical properties of recycled aggregate as a test element and its application in normal cement concrete. The study on the use of recycled aggregate in pervious concrete especially that made with fly ash geopolymer binder is now at the very beginning.

The strength and void ratio of pervious geopolymer concrete were studied with high-calcium fly ash as a source material [17]. Pervious fly ash geopolymer concretes (PGCs) were prepared with Na_2SiO_3 and NaOH solutions, and natural coarse aggregate with FA

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to coarse aggregate ratio of 1:8 by weight and constant Na_2SiO_3/NaOH ratio of 0.50. The results indicate that the high-calcium fly ash geopolymer binder could be used to produce pervious concrete with satisfactory mechanical properties. In this study, recycled coarse aggregates from crushed structural concrete members and crushed clay bricks were used to replace natural coarse aggregate for PGC. The effects of NaOH concentrations on the properties of PGC were evaluated. The results were also compared with PGC containing natural coarse aggregate.

2. Materials and methods

2.1. Materials

High-calcium fly ash (FA) was procured from Mae Moh Electricity Power Station in northern Thailand. The FA had a median particle size of 50 μm, a Blaine fineness of 2250 cm^2/g, and 45% (by weight) retained on 45 μm sieve. SiO_2, Al_2O_3, and Fe_2O_3 made up 71.7% of the FA whereas the CaO content was 19.4%. It can be classified as Class C pozzolan according to ASTM C618 [18]. Three concentrations of sodium hydroxide solution (NaOH) at 10, 15, and 20 M, and a commercial grade sodium silicate solution (Na_2SiO_3) with 15.32% Na_2O, 32.87% SiO_2 and 51.81% water were used. The NaOH solution was prepared by dissolving NaOH pellets in distilled water. For example, 10 M NaOH was obtained from 400 gm of NaOH pellets and 1 l of distilled water. Sodium silicate solution was used without any modification.

Three types of single-size coarse aggregates with 4.5–9.5 mm diameter were used in this study. The first was natural coarse aggregate from crushed limestone (NA), the second was a recycled aggregate from crushed structural concrete (RC) obtained from the strength test in laboratory, and the last was a recycled aggregate from crushed broken clay brick obtained from construction site (RB). RC was from the concretes with compressive strengths of 30–40 MPa and RB was from local clay bricks with compressive strengths of 5.0–9.0 MPa. Fig. 1 shows the coarse aggregates used in this study and their properties are shown in Table 1. The specific gravity (SG) of NA was 2.72 and the dry-rodded density was 1550 kg/m^3. The SG slightly RC was slightly lower at 2.53 as it contained NA and some adhered mortar. The SG of RB was significantly lower at 2.02 reflecting the different material from NA and RB altogether. The dry-rodded density of RC and RB were lower than that of NA while the water absorptions were higher as expected. The mortar content of RC was 65%. The Los Angeles abrasion loss of NA, RC, and RB were 30.2%, 43.3%, and 42.4%, respectively. The high water absorption and high Los Angeles abrasion loss of RC and RB were due to the residues of cement mortar attached on aggregate surface and the high porosity of the recycled aggregate [16,19].



(a) NA



(b) RC



(c) RB

Fig. 1. Comparison of coarse aggregates.

2.2. Mix proportions, mixing, casting, and curing

All pervious geopolymer concretes (PGCs) were produced with FA to coarse aggregate ratio of 1–8 by weight. The Na_2SiO_3/NaOH and alkali liquid (LA)/FA ratios were kept constant at 0.50 and 0.45, respectively. The typical mixture consisted of 221 kg/m^3 FA, 33 kg/m^3 Na_2SiO_3, 66 kg/m^3 NaOH, and 1768 kg/m^3 of coarse aggregate. The parameters of this study were the types of coarse aggregates (NA, RC, and RB) and the NaOH concentrations (10, 15, and 20 M). The mix proportions of PGC are shown in Table 2. The symbol RC10 means the PGC with RC as coarse aggregate and 10 M NaOH.

The mixing of PGC was done in an air conditioned room at 25 °C. FA and NaOH were mixed in a pan-type mixer for 5 min. Coarse aggregate was then added and mixed for 4 min. Finally, Na_2SiO_3 solution was added and mixed for another minute. The total mixing time was 10 min.

After mixing, PGC were cast in 100 × 200 mm cylindrical molds and compacted on a vibrating table. The specimens were immediately wrapped with vinyl sheet to protect from moisture loss and kept in the controlled 25 °C room for 1 h. After that, they were placed in an oven for heat curing at 60 °C for 48 h. After the heat curing, the specimens were put in the laboratory to cool down and demoulded the next day. The specimens were then wrapped with vinyl sheet and stored in the controlled room at 23 ± 2 °C and 50% RH until the testing age. Fig. 2 shows the specimens of PGC containing NA, RC, and RB.

2.3. Testing methods

The compressive and splitting tensile strengths of PGC were determined at the age of 7 days in accordance with ASTM C39 [20] and ASTM C496 [21]. The results were presented as the average value of three specimens.

The total void ratio and water permeability coefficient of PGC were tested using 100 × 200 mm cylindrical specimen. The total void ratio was calculated using Eq. (1) [22] and the reported values were the average of three specimens

$$V = \left(1 - \frac{(W_2 - W_1)}{\rho_w \mathrm{Vol}}\right) \times 100 \quad (1)$$

where V is the total void ratio (%), W_1 is the weight of specimen under water (g), W_2 is the saturated weight of specimen (g), ρ_w is the density of water (g/cm^3), and Vol is the volume of specimen (cm^3).

After the total void ratio test, the specimen was placed in the water permeability test set-up as shown in Fig. 3. The water permeability coefficient of PGC was tested using the constant head method and carried out when a steady state flow was reached. The coefficients of water permeability (k) were the averages of three specimens and calculated following Darcy's law [4,23,24] as shown in following equation:

$$k = \frac{QL}{HAt} \quad (2)$$

where k is the coefficient of water permeability (cm/s), Q is the quantity of water collected (cm^3) over time t (s), L is the length of specimen (cm), H is the water head (cm), and A is the cross sectional area of specimen (cm^2).

3. Results and discussions

3.1. Density, compressive strength, and splitting tensile strength

The results of density, compressive strength, and splitting tensile strength tests of PGC are shown in Table. 3. The densities of PGCs were between 1420 and 1840 kg/m^3 which were lower than that of the conventional concrete (about 2400 kg/m^3) due to the high void of pervious concrete. The NaOH concentration had no effect on the density of PGC. For example, the densities of RC10, RC15, and RC20 concretes were 1720, 1710, and 1730 kg/m^3,

Table 1
Properties of coarse aggregates (NA, RC, and RB).

Aggregates	Specific gravity	Dry-rodded density (kg/m^3)	Absorption (%)	Los Angeles abrasion loss (%)
NA	2.72	1590	0.21	30.2
RC	2.53	1340	4.58	43.3
RB	2.02	950	16.2	42.5

Table 2
Mix proportions of pervious geopolymer concretes (PGCs).

Mixes	Mix proportion (kg/m^3)							
	FA	Na_2SiO_3	NaOH (10 M)	NaOH (15 M)	NaOH (20 M)	Coarse aggregates		
						NA	RC	RB
NA10	221	33	66	–	–	1768	–	–
NA15	221	33	–	66	–	1768	–	–
NA20	221	33	–	–	66	1768	–	–
RC10	221	33	66	–	–	–	1768	–
RC15	221	33	–	66	–	–	1768	–
RC20	221	33	–	–	66	–	1768	–
RB10	221	33	66	–	–	–	–	1768
RB15	221	33	–	66	–	–	–	1768
RB20	221	33	–	–	66	–	–	1768

Note: Na_2SiO_3/NaOH = 0.50.

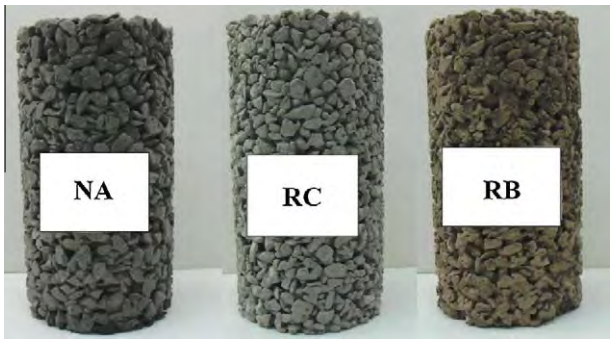


Fig. 2. Specimens of PGC containing NA, RC, and RB after demoulding.

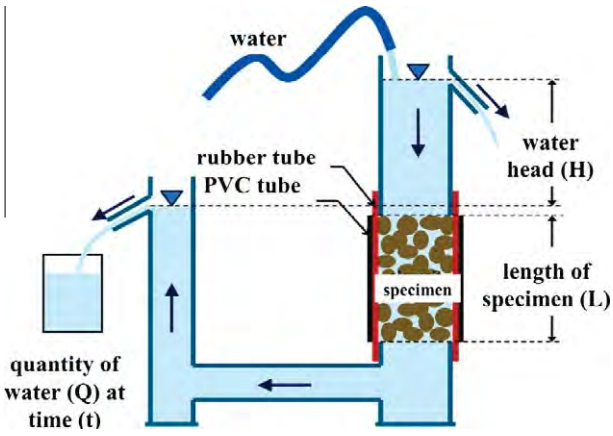


Fig. 3. Test set-up of water permeability.

respectively. The density of PGC containing RB as coarse aggregate was lowest with the average value of 1480 kg/m^3, while the densities of PGCs containing NA, and RC were higher at 1800 and 1720 kg/m^3. The dry-rodded density of aggregate and the density of PGC containing NA, RC, and RB were plotted in Fig. 4. As expected, the density of PGC increased as the dry-rodded density of aggregate increased. The relationship was a linear correlation with high R^2 value of 0.93 as shown in Eq. (3). This equation gives a prediction of the density of PGC based on a known dry-rodded density of aggregate

$$D = 0.51(D_r) + 1010 \quad (3)$$

where D is the density of pervious concrete (kg/m^3) and D_r is the dry-rodded density of aggregate (kg/m^3).

The compressive strengths of PGC containing NA were between 11.9 and 13.6 MPa and similar to the PGC containing a slightly larger aggregate with similar alkali liquid to fly ash ratio [17]. The use of recycled aggregate reduced the compressive strengths of PGC. The compressive strengths of PGC containing RC and RB were between 7.0–10.3, and 2.9–6.6 MPa, respectively. The highest compressive strength of 13.6 MPa occurred with NA10 and NA15 concretes, while the RB10 concrete showed the lowest compressive strength of 2.9 MPa. However, their compressive strengths were within the typical strength distribution reported [4].

At the same NaOH concentration, the compressive strengths of PGC containing NA were higher than those of RC and RB. For example, the compressive strength of NA15 was 13.6 MPa, while those of RC15 and RB15 were 10.0 and 4.0 MPa, respectively. The reduction in strength was due to the weakness of the attached mortar in recycled aggregate [25]. In addition, the low dry-rodded density and abrasion resistance of RC and RB also contributed to the low compressive strength [26]. The compressive strength of PGC was plotted as a function of dry-rodded density of aggregate as shown in Fig. 4. By linear regression, the empirical relationship with R^2 of 0.87 was derived as

$$f'_c = 0.0132(D_r) - 8.19 \quad (4)$$

where f'_c is the compressive strength of PGC (MPa) and D_r is the dry-rodded density of aggregate (kg/m^3).

The results also indicated that the optimum NaOH concentration to produce good strength PGC was 15–20 M. Since the formation of gel depended on the concentration of alkali OH ion, the low NaOH concentration resulted in a weak chemical reaction and slightly decreased compressive strength. The compressive strength increased with an increase in NaOH concentration mainly through the leaching of silica and alumina with high NaOH concentration

Table 3
Density, compressive strength, and splitting tensile strength of PGC at the age of 7 days.

Mixes	Density (kg/m^3)	Compressive strength (MPa)	Splitting tensile strength (MPa)
NA10	1840	13.6	1.6
NA15	1760	13.6	1.8
NA20	1810	11.9	1.5
RC10	1730	7.0	1.3
RC15	1710	10.0	1.4
RC20	1720	10.3	1.5
RB10	1420	2.9	0.4
RB15	1510	4.0	0.7
RB20	1520	6.6	0.9

[27]. However, an increase in alkali concentration enhanced strength development of geopolymer, but excess hydroxide ion concentration caused aluminosilicate gel precipitation at early stage and resulted also in low strength geopolymer [28,29]. The reduction of strength due to the increased in NaOH concentration from 15 M to 20 M could be observed in the NA aggregate. Similar to conventional concrete, the compressive strength of PGC improved when the density increased as shown in Fig. 5. The relationship between density and compressive strength of PGC was linear with R^2 equal to 0.84 and the function can be written as

$$f_c' = 0.0245(D) - 31.97 \quad (5)$$

where f_c' is the compressive strength (MPa) and D is the density of PGC (kg/m^3).

The splitting tensile strength of PGC ranged from 0.4 to 1.8 MPa. The results followed the same trend as those of the compressive strength. The splitting tensile strength values of PGC containing NA aggregate were higher than those of RC and RB aggregates. NA15 concrete gave the maximum splitting tensile strength of 1.8 MPa while RB10 concrete gave the lowest strength of 0.4 MPa. The average ratio of splitting tensile to compressive strengths of PGC was 14.4% which was slightly higher than 8–14% for conventional concrete and Portland cement concrete containing recycled aggregate [16,30,31] as shown in Fig. 6. This was due to the denser and stronger interfacial transition zone between aggregates and geopolymer binder compared with that of cement binder as a result of the use of soluble silicate [32].

The relationship between compressive strength and splitting tensile strength of PGC compared with the value suggested by ACI 318 [33] is shown in Fig. 7. The results showed that as compressive strength increased, the splitting tensile strength also increased. The splitting tensile strengths of PGC were slightly lower than that predicted by ACI 318 [33]. Eq. (6) was used for prediction the splitting tensile strength of PGC

$$f_{st} = 0.44(f_c')^{0.50} \quad (6)$$

where f_{st} is the splitting tensile strength (MPa) and f_c' is the compressive strength of PGC (MPa).

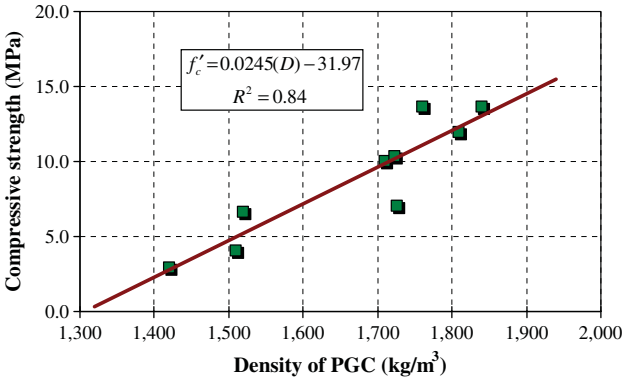


Fig. 5. Relationship between compressive strength at the age of 7 days and density of PGC.

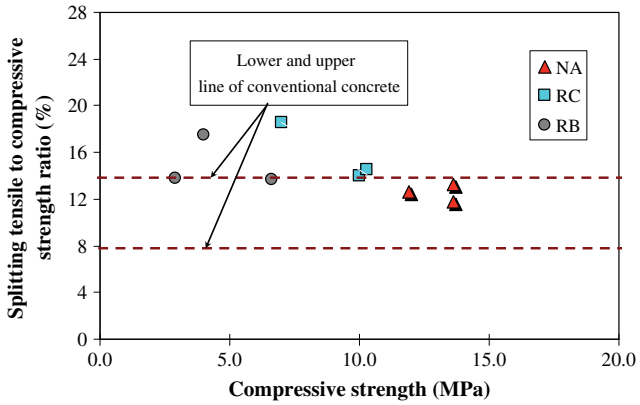


Fig. 6. Splitting tensile to compressive strength ratios and compressive strength of PGC at the age of 7 days.

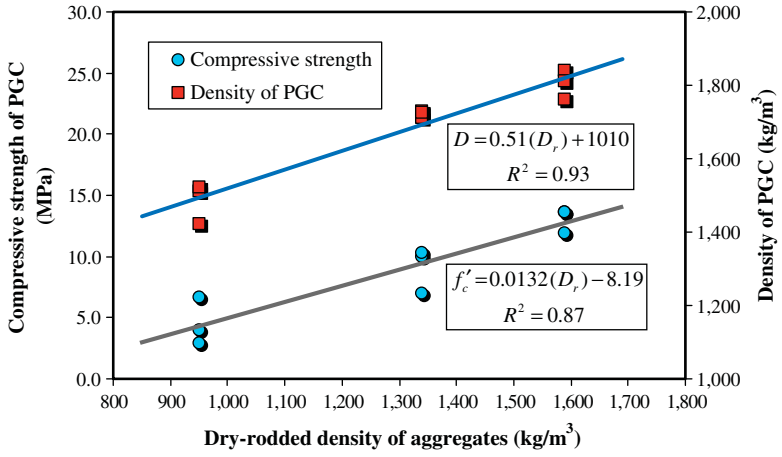


Fig. 4. Relationship between compressive strength at the age of 7 days, density of PGC and dry-rodded density of aggregates.

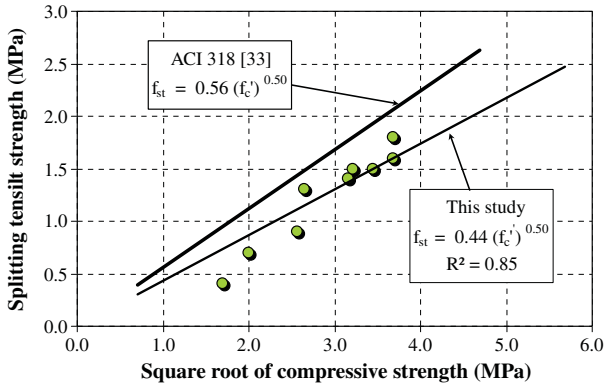


Fig. 7. Relationship between compressive strength and splitting tensile strength of PGC at the age of 7 days.

3.2. Fracture surfaces

Fig. 8 compares the PGC failure patterns of various aggregates and Figs. 9–11 show the fracture surfaces of PGC specimens after splitting tensile test. The majority of failure of PGC with NA aggregate occurred at the interface between geopolymer paste and aggregate. However, for RC aggregate, the fractures were at the attached mortar. As compare to normal aggregate and geopolymer paste, the poor quality due to its high porosity of the attached mortar had created the weak zones in PGC. When the PGC approached the ultimate load, the cracks passed though these zones instead of paste and coarse aggregate [25,34]. The failure surface of PGC containing RB showed fracture through the recycled aggregate particles indicating that RB aggregate was the weakest point. The RC and RB aggregate particles were not strong as suggested by their high Los Angeles abrasion losses (43.2% and 42.5%).

3.3. Total void ratio and water permeability coefficient

Table 4 shows the results of total void ratios and water permeability coefficient of PGC. The total void ratios of all PGC varied between 21.7% and 27.4% which were typical values of ACI 522 (15–35%). It was reported that PGCs with high total void ratios of 28.7–30.4% were successfully made with the use of a relatively large coarse aggregate of 12.5–20.0 mm [17]. The total void ratios of PGC containing NA slightly increased with the increasing NaOH concentrations. They were 24.2%, 25.3%, and 27.4% for NA10, NA15, and NA20 concretes, respectively. The use of RC in PGC at various NaOH concentrations showed nearly the same total void ratios of 26.8%, 26.9%, and 26.4% for RC10, RC15, and RC20, respectively. In the case of using RB in PGC, the total void ratios ranged from

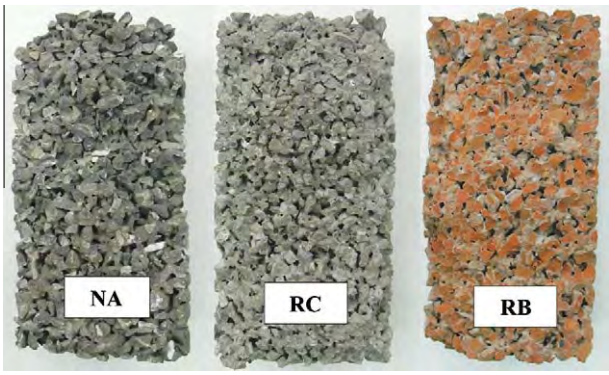


Fig. 8. Failure surface of PGC by splitting tensile strength.

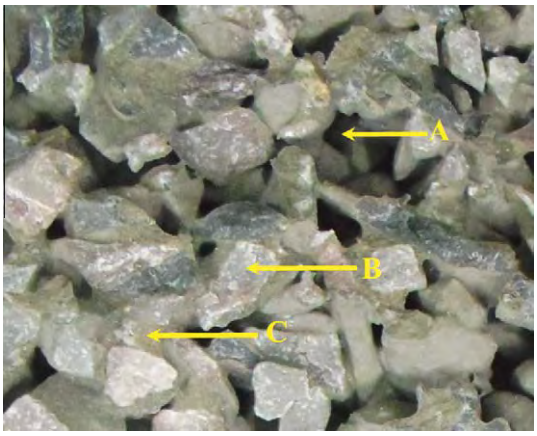


Fig. 9. Fracture surface of PGC containing NA; (A) void; (B) failure at bond; and (C) geopolymer paste.

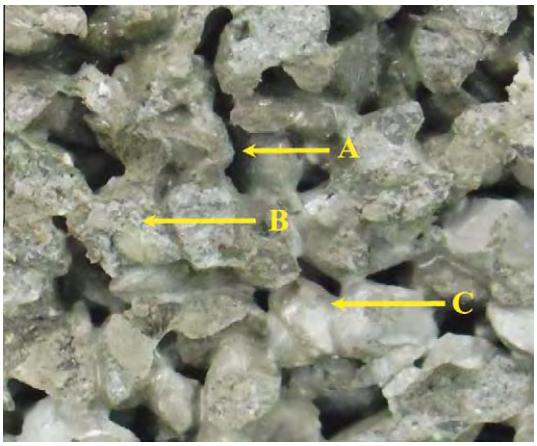


Fig. 10. Fracture surface of PGC containing RC; (A) void; (B) fractured RC at attached mortar; and (C) geopolymer paste.

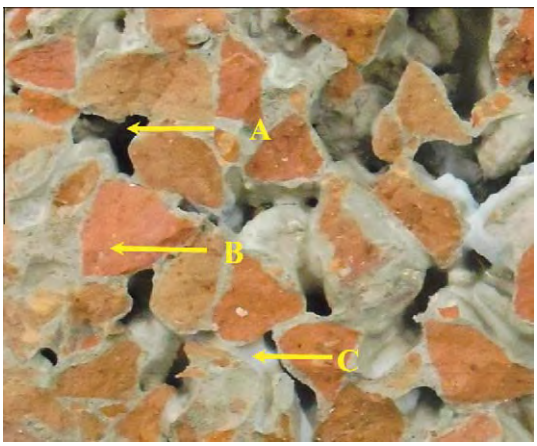


Fig. 11. Fracture surface of PGC containing RB; (A) void; (B) fractured RB; and (C) geopolymer paste.

21.7% to 23.7% which were lower than those of NA and RC. It could, therefore, be concluded that the total void ratios of the PGC with different NaOH concentrations but the same aggregate and geopolymer paste content were not very different.

With regard to the water permeability coefficient of PGC, the trend of the results was similar to that of the total void ratio. The low values of water permeability coefficients of 0.71–1.2 cm/s

Table 4
Total void ratio and water permeability coefficient of PGC at the age of 7 days.

Mixes	Total void ratio (%)	Water permeability coefficient (cm/s)
NA10	24.2	1.25
NA15	25.3	1.18
NA20	27.4	1.71
RC10	26.8	1.56
RC15	26.9	1.46
RC20	26.4	1.47
RB10	23.7	1.12
RB15	21.7	0.71
RB20	22.4	0.80

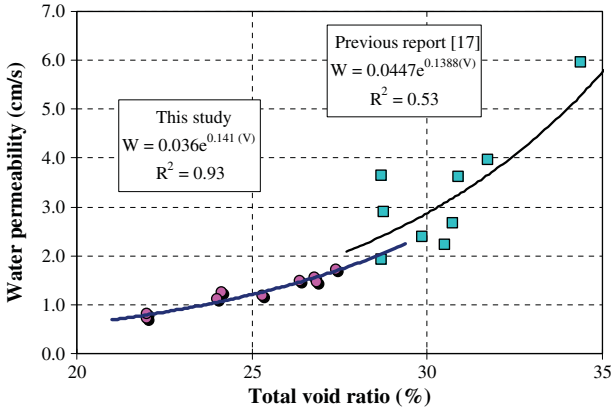


Fig. 12. Relationship between water permeability coefficient and total void ratio of PGC.

were achieved with PGC using RB aggregate. Also, the water permeability coefficient values of PGC with the same aggregate varied in a narrow range with different NaOH concentrations. Thus, the relationship between water permeability coefficient and total void ratio of all PGCs could be fitted as Eq. (7) as shown in Fig. 12. The R^2 value of 0.93 indicated a relatively strong relation between water permeability coefficient and total void ratio

$$k = 0.036e^{0.141(V)} \quad (7)$$

where k is coefficient of water permeability coefficient (cm/s) and V is total void ratio (%).

Similar trend of results was reported by the previous work [17] as shown in Fig. 12. The permeability of PGC increased exponentially with the void content similar to normal Portland cement pervious concrete [23].

4. Conclusions

The recycled aggregate from crushed structural concrete member (RC) and crushed clay bricks (RB) could be used as coarse aggregates for making pervious geopolymer concrete (PGC) using high-calcium fly ash as a source material. PGCs containing RC and RB gave lower compressive strengths than those containing natural aggregate (NA). However, the obtained compressive strengths of 2.9–10.3 MPa were within the typical strength distribution reported [4]. The relationships of density and compressive strength, splitting tensile and compressive strength, and total void ratio and water permeability coefficient in pervious high-calcium fly ash geopolymer concrete incorporating recycled coarse aggregates were similar to those of conventional pervious concrete. The total void ratio and water permeability coefficient of the PGCs with different NaOH concentrations but the same aggregate and geopolymer paste content were not very different. For the effect of NaOH concentrations, the high concentration 15–20 M NaOH gave PGC with higher strength than the low concentration 10 M NaOH.

The overall results indicate that it is feasible to use RC and RB as recycled coarse aggregates with high-calcium fly ash geopolymer binder for making pervious concrete with acceptable properties. However, the using RC and RB resulted in significant losses in strength as compared to a NA pervious concrete.

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Original Research Paper

Role of microwave radiation in curing the fly ash geopolymer

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ABSTRACT

Fly ash geopolymer requires rather long heat curing to obtain reasonable strength development at an early age. However, the long heat curing period limits the application of the fly ash geopolymer. High strength development and a reduction in heat curing duration have been considered for energy saving. Therefore, this research proposed a process using 90-W microwave radiation for 5 min followed by conventional heat curing for high-calcium fly ash geopolymer. Results showed that the compressive strengths of geopolymer with microwave radiation followed by conventional heat curing were comparable to those of the control cured at 65 °C for 24 h. Microwave radiation gave the enhanced densification. In addition, SEM images showed that the gels formed on the fly ash particles owing to the promoted dissolution of amorphous phases from fly ash. This method accelerated the geopolymerization and gave the high compressive strength comparable to the conventional curing.

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1. Introduction

Coal-fired power plants currently produce 40% of the global electricity for households and industries. Besides generating power energy, coal wastes, i.e. fly ash and bottom ash are obtained and utilized related to the environmental aspect [1,2]. In addition to the use of fly ash to partially replace Portland cement, the high content fly ash usage has been introduced and termed "geopolymer" which is a low heat cured alumino-silicate material [3]. Owing to the endothermic reaction, heat curing at 65 °C was employed in order to gain high early strength of lignite fly ash geopolymers with good physical and mechanical properties [4,5]. However, the 24-h or longer heat curing periods limit the application of geopolymer. Although the room temperature curing has been considered for energy saving, the prolonged curing duration was required to obtain reasonable strength for lignite fly ash geopolymer [6].

Heat curing has been applied to construction materials especially for the precast concrete to improve the strength development process. This concrete attains sufficient strength in short curing time, so the moulds can be reused, and the final products can be rapidly delivered to the site [7]. For the conventional heating technique, heat is distributed in the specimen from the exterior to the interior leading to the non-uniform and long heating period to attain the required temperature. In contrast, the microwave technique allows a uniform and fast heating due to the interaction between the polar molecules and microwave electric fields [7–11]. Application of microwave to the fresh concrete results in removal of water, collapse of capillary pore and densification of sample. However, microwave radiation is mostly used in concrete curing and the radiation period is usually long (more than 1 h with high wattage) [7,8]. This could limit the use of microwave curing due to the energy cost.

Therefore, this research proposed the process to reduce the microwave curing duration and energy using the short-time microwave radiation in addition to the convention heat curing for the fly ash geopolymer. Microwave radiation could play the role in the geopolymer formation and strength enhancement. Additionally, this method could shorten the curing time of geopolymer, accelerate the geopolymerization and give the high compressive strength at an early age compared to the conventional curing.

2. Experimental procedure

2.1. Materials

Coal fly ash from Mae Moh power plant in the north of Thailand was used as raw material. This fly ash was generated from the pulverized coal combustion process (1200 °C) using lignite coal as the feed. The properties of this fly ash are tabulated in Table 1. In addition to Al_2O_3 and SiO_2, this fly ash had high contents of CaO and magnetite (Fe_3O_4). Sodium hydroxide pellet (NaOH) dissolved in the deionized water to obtain 10 M NaOH solution, and sodium silicate solution (Na_2SiO_3) with SiO_2:Na_2O mass ratio of 3.2 was also used. The viscosities of 10 M NaOH and Na_2SiO_3 were 9.3, and 60.6 cps (centipoises), respectively. The graded river sand with fineness

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Table 1
Properties of fly ash.

Chemical composition (wt%)	SiO_2	39.2
	Al_2O_3	19.7
	CaO	16.9
	Fe_3O_4	12.1
	SO_3	2.8
	Others	9.3
Median particle size (μm)		19.0

modulus of 2.8 and specific gravity of 2.65 was employed to prepare the mortar specimen for strength test.

2.2. Geopolymer preparation

To prepare the liquor, 10 M NaOH and Na_2SiO_3 were mixed in a container with the Na_2SiO_3/NaOH mass ratio of 1.5. The liquor was then added to the fly ash in a pan mixer and the paste was thoroughly mixed. The fly ash-to-liquor mass ratio of 1.86 (fly ash = 65 wt% and liquor = 35 wt%). The paste was continuously mixed for 5 min and then cast into 50-mm cubic acrylic mould (1-cm thickness). The paste specimens were vibrated for 10 s and covered with cling film to avoid the moisture evaporation during the heat curing.

For geopolymer mortar preparation, sand was added to the paste mixture with the sand-to-fly ash mass ratio of 1.5 and mixed for another 2 min. The mixture was then cast into 50-mm cubic acrylic mould. The curing condition was the same as for the paste preparation. Compressive strength test was performed on the geopolymer mortars.

2.3. Microwave and conventional curing temperature profile

In this study, the 2.45-GHz household microwave and the conventional oven were employed. Owing to preliminary results, 90- and 180-W microwave power levels were applied on the geopolymer mortars for 3, 5 and 10 min to obtain the temperature profile at the middle of the samples. Higher wattage resulted in rapid evaporation in short time, heat evolution and cracks on the surface of specimens. Result is reported as an average of five samples.

In addition, the effect of microwave and conventional curing on the compressive strength of geopolymer mortar was evaluated. 90-W microwave curing for 5 min was selected in addition to the convention heat curing at 65 °C for 3, 6 and 12 h. After heat curing, specimens were cooled down and cured continuously at 25 °C. The compressive strength was tested at the age of 7 days. The reported results were the averages of five samples. Table 2 shows the curing conditions. Curing at 65 °C for 24 h (system 1) was the control.

2.4. XRD, SEM and degree of reaction

Geopolymer paste was prepared for the testing of XRD, SEM and degree of reaction. 90-W microwave radiation for 5 min in addition to the conventional heat curing at 65 °C for 3, 6 and 12 h was used. XRD and SEM analyses were performed on the hardened samples. In addition, degree of reaction was determined both on geopolymer paste and fly ash by identification of unreacted fly ash in specimen using the dissolution of the powdery sample in 2 M HCl and 5 wt% Na_2CO_3 [12–14]. The hardened geopolymer pastes were ground to obtain particles that passed a 150-μm sieve. A 100-mL beaker filled with powdered samples (5 g) and 2 M HCl (30 mL) was placed in a 60 °C water bath and stirred for 20 min to accelerate the dissolution. Solid phase was then filtered using a vacuum filter. The remaining solid was washed with warm water thrice to completely remove HCl. Acetone was applied in the last filtration to remove water before drying at 70 °C for 2 h. Degree of reaction was calculated using Eq. (1). The degree of reaction of the fly ash particles was also determined and assigned as "blank." All the results were subtracted with blank to obtain the corrected degree of reaction. The reported results were the averages of three samples.

$$\text{Degree of reaction} = \frac{m_{\text{sample}} - m_{\text{residue}}}{m_{\text{sample}}} \times 100 \quad (1)$$

where m_{sample} is the weight of powdery sample (g) and m_{residue} is the weight of dried residue (g).

3. Results and discussion

3.1. Temperature profile of microwave curing

The temperature profiles of the 50-mm cube geopolymer mortar are reported in Fig. 1. Application of 90- and 180-W microwave power levels generated high temperature in the specimen in a short period of time. At 5 min microwave radiation, 90- and 180-W gave slightly different temperatures. For 10-min microwave radiation, the temperature difference was noticeable. Increase in the microwave radiation time led to high temperature, however, longer radiation time and increase in wattage resulted in rapid evaporation, high heat evolution and sequential cracks on the surface of specimens owing to the energy beyond the requirement for water removal in materials [15]. For this reason, 90-W microwave radiation for 5 min was selected for further study.

3.2. Effect of microwave and conventional curing on the compressive strength

To study the effect of curing conditions on the properties of geopolymer mortars, the compressive strength was primarily focused in this section. Table 3 presents the strengths of the specimens

Table 2
Curing conditions of geopolymer.

System	Curing conditions	Note
1	65 °C oven curing for 1, 3, 6, 12 and 24 h	65 °C oven curing
2	65 °C oven curing for 1, 3, 6, 12 and 24 h → 90 W MW curing for 3 min	65 °C oven curing before MW radiation
3	90 W MW curing for 3 min	MW radiation only
4	90 W MW curing for 5 min	MW radiation only
5	90 W MW curing for 10 min	MW radiation only
6	90 W MW curing for 3 min → 65 °C oven curing for 1, 3, 6, 12 and 24 h	MW radiation before 65 °C oven curing
7	90 W MW curing for 5 min → 65 °C oven curing for 1, 3, 6 and 12 h	MW radiation before 65 °C oven curing
8	90 W MW curing for 10 min → 65 °C oven curing for 1, 3, 6 and 12 h	MW radiation before 65 °C oven curing
9	25 °C curing for 7 and 28 days (room temp., RT)	No heat curing

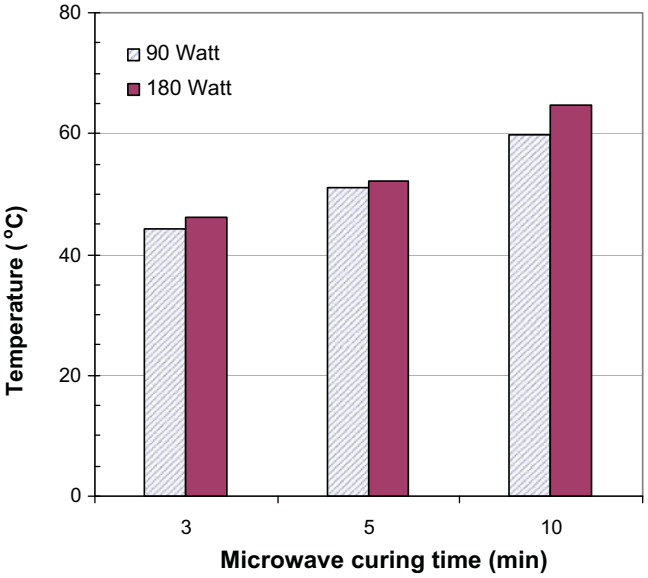


Fig. 1. Temperature profile of geopolymer mortar.

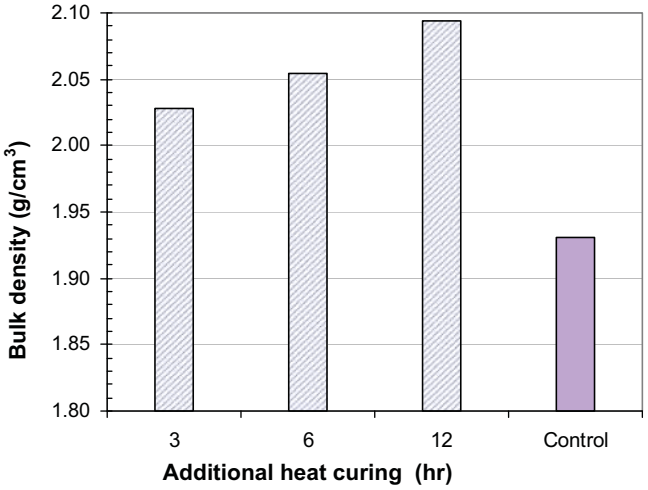


Fig. 2. Bulk density of geopolymer mortars with 90 W microwave radiation for 5 min.

Table 3
Compressive strengths of geopolymer mortars at various curing conditions.

System	Curing conditions	Compressive strength (MPa)						
		Additional curing time in 65 °C oven					RT	
		1 h	3 h	6 h	12 h	24 h	7 d	28 d
1	65 °C	13.0	15.7	22.2	21.2	***32.7***[a]		
2	65 °C → 90 W (3 min)	9.9	16.6	25.2	23.9	***32.4***		
3	90 W (3 min)						9.4	
4	90 W (5 min)						16.2	
5	90 W (10 min)						17.4	
6	90 W (3 min) → 65 °C	12.9	17.4	21.2	29.0	***33.8***	–	
7	90 W (5 min) → 65 °C	21.9	29.2	***35.5***	***42.5***			
8	90 W (10 min) → 65 °C	20.0	27.4	***34.6***	***41.4***			
9	25 °C (RT)						20.0	***35.8***

Bolditalic values = strengths equal to or higher than that of the control.
[a] Comparative strength (control).

cured with microwave radiation, heat curing and room temperature curing. Curing at 65 °C for 24 h (system 1) was the control and the strength result of this condition was compared to the others. The control had the compressive strength of 32.7 MPa. The strength of system 2 with the same heat curing time was similar at 32.4 MPa. From this result, it could be noted that the additional microwave radiation after the normal heat curing did not improve the strength of geopolymer. This was due to the complete geopolymerization after the optimum duration of heat curing. With no heat curing or room temperature curing (system 9), the specimens gained the strength with age and the strengths at 7 and 28 days were 20.0 and 35.8 MPa respectively. Without heat curing, the strength development of the fly ash geopolymer mortar was extremely slow. The heat curing contributed to the strength of geopolymer at the early age. However, the use of only microwave radiations for 3–10 min (systems 3–5) gave the samples with strength up to 28–50% of the control strength.

The use of microwave radiation followed by conventional heat curing provided the high strength gain of geopolymer as shown in systems 6–8. The optimum time of microwave radiation shortened the required time of conventional heat curing. For 3 min of 90-W radiation, the additional heating of 12 h slightly increased the strength of the geopolymer mortar to 29.0 MPa compared to 21.2 MPa of that with 6-h heat curing alone. To obtain the strength of over 32.7 MPa (control), the additional heat curing time of 24 h was still required owing to the low accelerated temperature of the microwave radiation (3 min of 90-W).

However, for the microwave radiation of 5–10 min, only 6-h additional heat curing was needed to obtain the strength equivalent to the control. Extension of radiation time to more than 10 min could increase the accelerated temperature beyond 65 °C and risked getting close to the boiling temperature of water. This resulted in rapid water evaporation, high pressure and subsequent cracks in sample.

The results of bulk densities of the geopolymer mortar (systems 6–8) are presented in Fig. 2. The microwave radiation enhanced the densification compared with those entirely cured with conventional heat curing. This result implied that the microwave radiation overcame the activation energy of geopolymerization. The microwave effect, in the presence of an external electric field, resulted in the densification of the matrices. In contrast to the conventional heating, the preferential interaction of the microwaves gave lower porosity leading to the accelerated densification [16]. High compressive strengths of the samples were, thus, achieved.

3.3. XRD patterns of microwave radiation cured geopolymers

Fig. 3 shows the X-ray diffraction (XRD) patterns of geopolymer pastes under microwave radiation followed by the conventional heat curing for 3, 6 and 12 h. The results of original fly ash and the 24-h heat cured sample (control) are also presented. Numerous peaks of crystalline quartz (SiO_2), calcium sulfate ($CaSO_4$) and calcium oxide (CaO) of this high calcium fly ash were identified. In addition, the XRD pattern of fly ash showed many sharp peaks owing to the crystalline phases in the sample.

For geopolymer pastes, the product was semi-crystalline with a high amount of amorphous gel as indicated by the broad hump and some sharp peaks of crystallinity. The broad hump of these pastes appeared at 22–38°, indicating the highly disorder silicate glass phase in geopolymer [17]. The calcium silicate compounds from the reaction between high calcium fly ash, silica and silicate solution were also detected. In addition, samples with microwave radiation exhibited the sharp peaks of crystalline phases with high degree of amorphous phase of the semi-crystalline geopolymer.

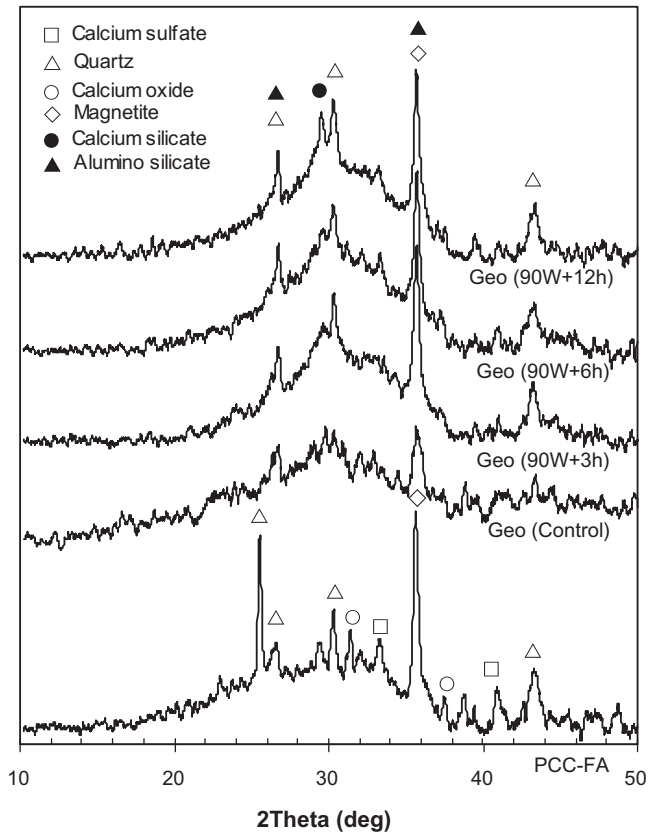


Fig. 3. XRD patterns of geopolymer pastes with microwave radiation and additional 65 °C heat curing.

Quartz and alumino-silicate compounds had an effect on both the physical and mechanical properties of the geopolymer. The presence of some of these crystalline products in geopolymer resulted in an increase in the compressive strength [18].

In addition, the dissolution of SiO_2 and Al_2O_3, especially from the glassy phase, was enhanced by the partial microwave radiation at the early stage of reaction [19]. Therefore, microwave radiation promoted the dissolution of Si and Al species from fly ash owing to the rapid heating up of an aqueous solution. Furthermore, the active water with hydrogen bond breaking under microwave radiation could independently attack Si–O and Al–O bonds leading to the enhancement of the dissolution of glassy phase of fly ash particles [19].

3.4. Microstructural study

Fig. 4 exhibits the SEM images of the geopolymer with partial microwave radiation (Fig. 4a–c) and the control sample with the heat curing for 24 h (Fig. 4d). The unreacted spherical fly ash, partially reacted grains of fly ash particles, and a continuous mass of geopolymer products were recognized. Gel formation on fly ash particles showed the dissolution of glassy phase in the alkaline solution. With microwave radiation as shown in Fig. 4a–c, a large number of gels was formed on the fly ash particles owing to the promoted dissolution of Si and Al species from fly ash with microwave radiation [19]. It was found that the prolonged radiation significantly retarded the nucleation of alumino-silicate gel [11,19]. Prolonged microwave radiation was thus not recommended. Increase in additional heat curing provided more reaction products on the fly ash particles. For the control sample, the partially reacted grains of fly ash particles were also observed. The gradual dissolution of the glassy phase of fly ash particles resulted in the normal formation of gel. The early-stage microwave radiation followed by the conventional heating effectively contributed to the geopolymerization of fly ash. Cracks and occupied fly ash pores were also found in the continuous mass of geopolymer products. Cracks were due to the moisture removal during heat curing.

The mechanism of microwave radiation in geopolymer curing could be explained as follows. Microwave radiation prior to conventional heat curing affected the strength gain of geopolymer. Early-stage of microwave radiation contributed to the gel formation of geopolymer. Applying the microwave to fresh sample promoted the dissolution of Si and Al species from fly ash owing to the rapid heating up of the aqueous solution. It stimulated the breaking of hydrogen bonds in water molecules. Gel formation on fly ash particles, as observed by SEM analysis, showed the

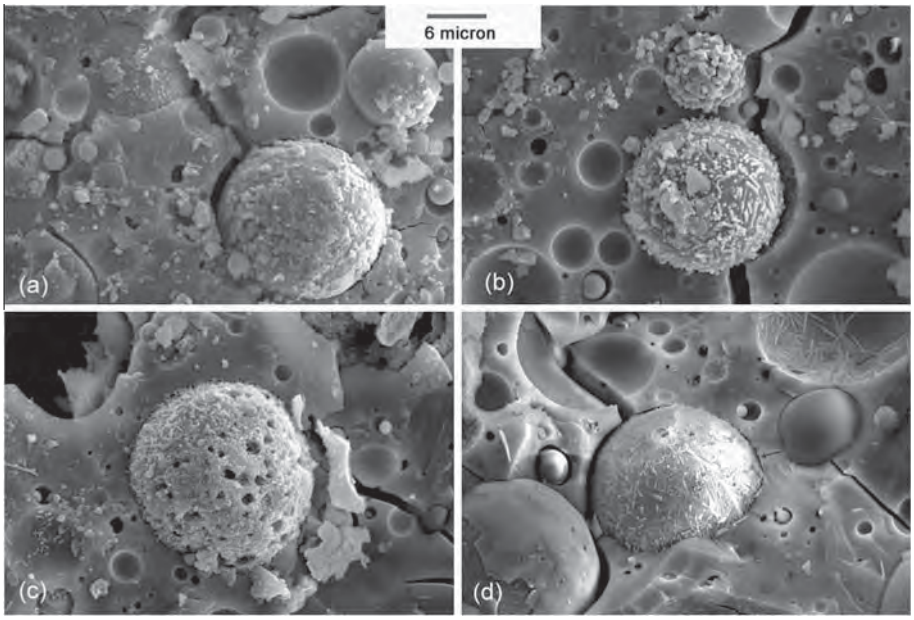


Fig. 4. Microstructure of geopolymer pastes with microwave radiation and additional 65 °C heat curing; (a) 3 h, (b) 6 h, (c) 12 h, and (d) Control.

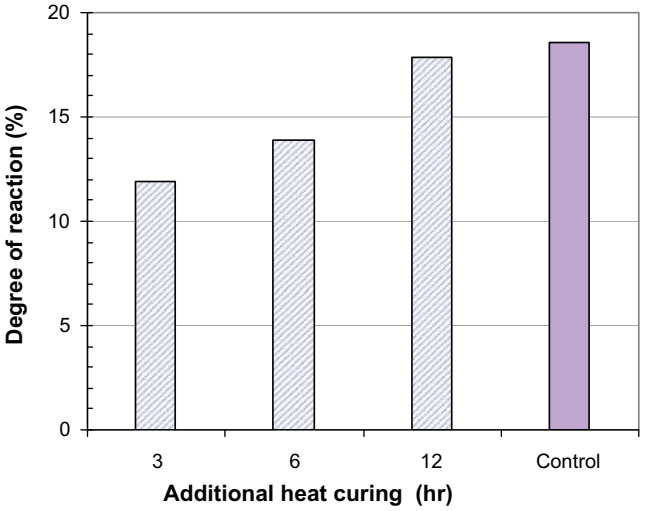


Fig. 5. Degree of reaction of fly ash geopolymer with microwave radiation.

dissolution of glassy phase in the alkaline solution. Higher densification of matrices compared with those cured in the electric oven could be obtained. Additional heat curing provided the additional reaction products. Therefore, the early-stage microwave radiation followed by the conventional heating effectively enhanced the geopolymerization. The main advantages are the reduction in curing time and energy and hence the associated reduced cost.

3.5. Degree of reaction

The degrees of reaction of geopolymer pastes with microwave radiation are presented in Fig. 5. With partial microwave radiation and heat curing for 3, 6, and 12 h, the degrees of reaction were 11.9%, 13.9% and 17.9%, respectively compared to 18.6% degree of reaction of the control. The control with entire 24-h heat curing had similar degree of reaction to that with microwave radiation and 12-h conventional curing. The results suggested that the time for normal curing could be reduced by half using the radiation. The results conformed to the results of the SEM and the strengths.

4. Conclusions

Microwave radiation effectively enhanced the geopolymerization and compressive strength of fly ah geopolymer. The microwave radiation followed by conventional heat curing reduced the heat curing time and energy. The 90-W microwave radiation for 5 min followed by 6-h at 65 °C additional heat curing produced geopolymer mortar with strength comparable to that of the control (24-h at 65 °C). The microwave radiation resulted in the densification of the matrices and increase in the bulk density of the samples. The mechanism of strength enhancement could be explained as follows.

1. Early-stage of microwave radiation promoted the dissolution of Si and Al species and enhanced the gel formation of geopolymer and stimulated the breaking of hydrogen bonds in water molecules.
2. Gel formation on fly ash particles resulted in higher densification of matrices.
3. The additional conventional heat curing provided the additional formation of reaction products.

Therefore, the early-stage microwave radiation followed by the conventional heating effectively contributed to the geopolymerization of fly ash geopolymer.

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ORIGINAL ARTICLE

Resistance to acid and sulfate solutions of microwave-assisted high calcium fly ash geopolymer

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Abstract In this paper, 90-W microwave radiation for 5 min plus a shortened heat curing period was applied to cure the fresh geopolymer paste. Results showed that microwave radiation contributed to the dissolution of fly ash in the alkaline solution. Numerous gel formations were observed in microscopic scale. This resulted in a dense composite and strong bonding between the fly ash and the geopolymer matrix leading to high strength gain compared to those of the control pastes cured at 65 °C for 24 h. In addition, resistances to the sulfuric acid and sulfate attacks of the microwave geopolymer were superior to that of the control as indicated by the relatively low strength loss. The microwave radiation also helped the geopolymer attaining thermal stability as the dense matrices were obtained.

Keywords Geopolymer · Microwave · Radiation · Fly ash · Durability

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1 Introduction

Recently, fly ash geopolymer is becoming a well known binding material. The pulverized combustion coal (PCC) fly ash contains both the amorphous and semi-crystalline silica and alumina. In an alkaline solution, they can be effectively converted to aluminosilicate material or geopolymer [1–4]. Fly ash composes of crystalline phases such as quartz and mullite in the interior and a glassy phase of silica and alumina at the surface layer [5]. This glassy phase plays an important role in geopolymer formation due to the high solubility in the alkaline solution. Room temperature (RT) curing can be employed, however the strength development is slow and prolonged curing is normally required to obtain reasonable strength [6]. Owing to the endothermic reaction of fly ash geopolymer, the heat curing of 60–90 °C for 24–48 h is usually employed in order to obtain the high early strength with good physical and mechanical properties [6–8]. However, the heat curing for 24–48 h is the major set back of the synthesis of the fly ash geopolymer.

Heat curing has been applied in concrete, especially for the precast concrete, to improve the strength in short curing time [9]. At present, a microwave radiation technique is utilized in the synthesis of zeolite and in the curing of concrete resulting in the shortening of heating process [9–11]. Microwave energy is directly transferred through the material and allows a fast and uniform heating due to the

interaction between the microwave electric fields and the polar molecules. Removal of water in the fresh concrete, collapse of capillary pore and densification of sample are achieved with microwave application [9, 10]. Improved microstructure can be obtained at an early age. Short-time curing process is preferred to reduce the energy consumption.

This paper presents the effect of microwave radiation on the strength and resistance to acid and sulfate solutions of fly ash geopolymer. In addition to the convention heat, microwave radiation was applied to accelerate the geopolymer formation. This method could shorten the curing time and provide a strong and durable geopolymer.

2 Experimental program

2.1 Materials and specimen preparation

Lignite coal fly ash from the pulverized coal combustion process (1200 °C) of an electric power plant in northern Thailand was used as raw material. The oxide compositions and particle size of this fly ash are tabulated in Table 1. The majority of fly ash compositions composed of Al_2O_3, SiO_2, CaO and magnetite (Fe_3O_4). 10 M sodium hydroxide (NaOH) solution was prepared by dissolving NaOH pellets in the distilled water [3]. Sodium silicate solution (Na_2SiO_3) with SiO_2-to-Na_2O weight ratio of 3.2 was also used. For mortar specimens for strength test, the graded river sand with fineness modulus of 2.8 and specific gravity of 2.65 was employed.

Table 1 Properties of fly ash

Chemical composition (wt%)	
SiO_2	39.2
Al_2O_3	19.7
CaO	16.9
Fe_3O_4	12.1
SO_3	2.9
K_2O	2.8
MgO	1.7
Na_2O	1.7
Others	1.9
Loss on ignition (%)	1.1
Median particle size (μm)	19.0

The geopolymer was prepared by mixing fly ash with the 10 M NaOH and Na_2SiO_3 solutions in a pan mixer. The mass ratio of Na_2SiO_3/10 M NaOH of 1.5 was used based on the previous research [3, 8]. The mass fraction of fly ash in the mixture was controlled at 0.65 (65 parts of fly ash and 35 parts of mixing solution). The paste was continuously mixed for 5 min and then cast into 50 mm cubic acrylic mould. The specimens were vibrated for 10 s to remove the air bubbles and then covered with cling film to avoid the moisture evaporation during the heat curing.

In the case of geopolymer mortar, sand was added to the paste mixture with the sand-to-fly ash mass ratio of 1.5 and mixed for another 2 min. The procedures for casting, vibration and curing of specimens were the same as those of paste. Compressive strength test was performed on the geopolymer mortars at the age of 7 days. The reported results were the average of five samples.

2.2 Microwave and conventional heat curing

In this study, microwave energy was generated by the household microwave oven with frequency of 2.45 GHz. In addition, the conventional oven was employed. From preliminary test, it was found that 90 W microwave power level applied to the geopolymer pastes for 5 min increased the specimen temperature to 60–65 °C. Higher watts and longer time microwave radiation resulted in high temperature, rapid evaporation, and crack formation on the surfaces of specimens. The specimens were then applied with the convention heat curing at 65 °C for 3, 6 and 12 h. These conditions were selected to compare with the control specimens with heat curing at 65 °C for 24 h. After heat curing, specimens were cooled down and cured in a controlled room at 25 °C.

2.3 XRD, SEM, TGA and durability test (acid and salt resistances)

Geopolymer paste was prepared for the testing of X-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetry (TGA) analyses. The specimens were broken into small sizes for XRD, SEM and TGA analyses. For the SEM analysis, small sample pieces were gold coated for the investigation of the microstructure. For the durability test; after 7 days of curing, the geopolymer mortars were then

Table 2 Compressive strengths of geopolymer mortars at various curing conditions

Sys.	Curing conditions	Compressive strength (MPa)					
		Curing time in oven at 65 °C				25 °C (RT)	
		3 h	6 h	12 h	24 h	7 days	28 days
1	65 °C				32.7[a]		
2	90 W (5 min) + 65 °C	29.2	35.5	42.5			
3	25 °C (RT)					20.0	35.8

[a] Control strength

immersed in 3%volH_2SO_4 and 5%wt$MgSO_4$ solutions. After immersion of 90 and 180 days, the strength tests were performed. Acid and sulfate resistances were expressed in the terms of strength loss. The reported results were the average of five samples.

3 Results and discussion

3.1 Compressive strength

The compressive strengths of geopolymer with 90-W microwave radiation and heat curing compared to those of normal heat curing and RT curing are shown in Table 2.

The control geopolymer was the mix with 65 °C curing for 24 h (system 1) and had the compressive strength of 32.7 MPa. The strength of system 1 was comparable to 35.8 MPa of the mix cured at RT (25 °C) for 28 days (system 3). Therefore, heat curing was preferable in terms of short curing time. System 2 was the mix with 90 W microwave radiation for 5 min incorporated with the conventional heat curing. The system 2 with 6 h heat curing produced the compressive strength of 35.5 MPa which was slightly higher than that of the control. The microwave radiation shortened the required time of heat curing and enhanced the strength development of the geopolymer paste. The presence of an electric field in microwave resulted in a lower porosity and the densification of the matrices [11].

3.2 Durability

The durability of geopolymer was presented in term of the strength after immersion for 3 and 6 months in the 3%volH_2SO_4 (pH = 0.85) and 5%wt$MgSO_4$ (pH = 9.85) compared with the control as shown in Figs. 1 and 2. H_2SO_4 acid is a strong acid and readily attacks calcium compound and other calcareous materials in

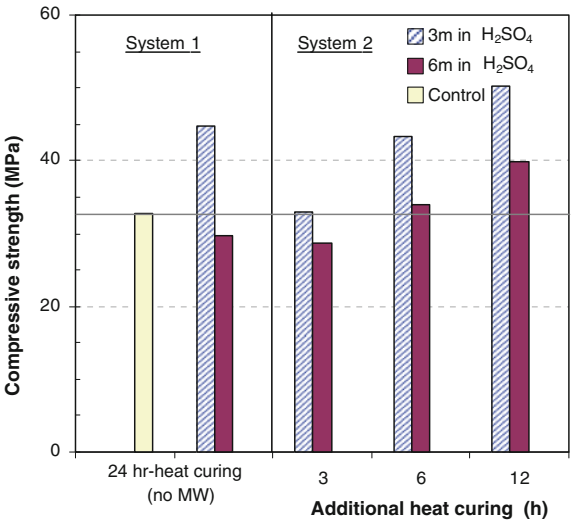


Fig. 1 Compressive strength of geopolymers under H_2SO_4 attack

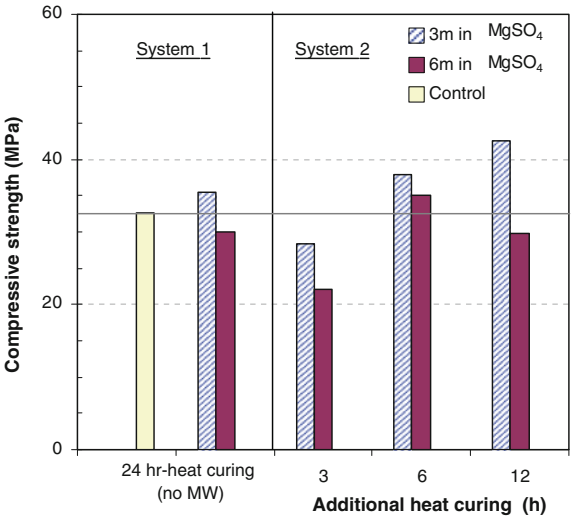


Fig. 2 Compressive strength of geopolymers under $MgSO_4$ attack

concrete. Owing to the microwave radiation, a dense matrix was achieved leading to a low leaching of calcium compounds by acid and a low strength loss. In the presence of moisture, the compressive strength of geopolymer developed with time due to additional pozzolanic reaction of high calcium fly ash. The compressive strengths after immersion in the H_2SO_4 for 3 months were all higher than that of the control. However, the strengths significantly decreased after 6 months immersion in the acid.

The reactions of geopolymer paste in H_2SO_4 solution consisted of the reaction between $Ca(OH)_2$ and H_2SO_4, and resulted in $CaSO_4$ which was easily leached out from the matrix (Eq. 1). The use of high calcium fly ash led to $Ca(OH)_2$ formation within geopolymer matrix and was identified from the XRD pattern. Internal $CaSO_4$ further reacted with aluminium compound in the fly ash leading to the formation of calcium sulfoaluminate or ettringite (Eq. 2). This ettringite caused the expansion, cracking and a loss of strength in the geopolymer. In addition, the calcium silicate hydrate (CSH) also reacted with H_2SO_4 and formed calcium sulfate and amorphous silica gel [12] which were easily destroyed by external physical forces (Eq. 3). These compounds and products were presented as indicated by the results of the XRD patterns.

$$Ca(OH)_2\ (s) + H_2SO_4\ (aq) \rightarrow CaSO_4 \cdot 2H_2O\ (s) \quad (1)$$

$$3CaO\ (s) + Al_2O_3\ (s) + 3CaSO_4\ (s) + 32H_2O\ (l) \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O\ (s) \quad (2)$$

$$3CaO \cdot SiO_2\ (s) + 3H_2SO_4\ (aq) + 3H_2O\ (l) \rightarrow 3CaSO_4 \cdot 2H_2O\ (s) + SiO_2\ (s) \quad (3)$$

The alumino-silicate network in geopolymer could also be attacked by hydrogen ions (H^+) from H_2SO_4 acid ionization. H^+ ruptured the alumino-silicate network at aluminium sites (–Al–O–Si–O–) and yielded silicic acid ($Si(OH)_4$) and aluminium ions (Al^{3+}) [13]. The breaking of oxy-aluminium bridge (–Al···O–Si–O) rendered the geopolymer paste susceptible to acid attack.

After immersion in the $MgSO_4$ solution, the compressive strengths of all geopolymer mortars were lower than those immersed in the H_2SO_4 solution for the same period. For the 6-month immersion in the $MgSO_4$ solution, only the samples with microwave radiation and 6-h heat curing gave the strength higher than that of the control. White substance on the surface of the samples was observed. The XRD pattern of this white substance is presented in Fig. 3 and indicated the presence of the magnesium hydroxide ($Mg(OH)_2$), silica (SiO_2), calcium magnesium silicate (Ca–Mg–Si–O) and magnesium silicate (Mg–Si–O) compounds.

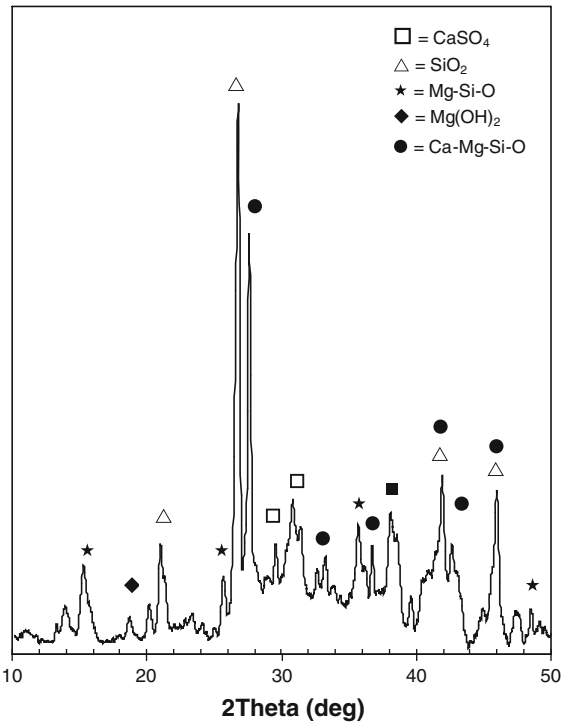


Fig. 3 XRD pattern of white substance after immersion in $MgSO_4$ solution

The reaction between Mg^{2+} ion, sulfate ion and hydroxyl ion (OH^-) from $Ca(OH)_2$ and NaOH in geopolymer matrix yielded the $Mg(OH)_2$ and calcium sulfate in the form of gypsum ($CaSO_4{\cdot}2H_2O$) as presented in Eq. 4 [12]. $Mg(OH)_2$ and gypsum are insoluble compound leading to the deposition on the material surface.

$$Mg^{2+}\ (aq) + SO_4^{2-}\ (aq) + Ca(OH)_2\ (s) + H_2O\ (l) \rightarrow Mg(OH)_2\ (s) + CaSO_4 \cdot 2H_2O\ (s) \quad (4)$$

In addition, decomposition of CSH phase also took place and resulted in the formation of amorphous hydrous silica (SiO_2) as shown in Eq. 5 [12].

$$3Mg^{2+}\ (aq) + 3SO_4^{2-}\ (aq) + 3CaO \cdot SiO_2\ (s) + 9H_2O\ (l) \rightarrow 3Mg(OH)_2\ (s) + 3[CaSO_4 \cdot 2H_2O]\ (s) + SiO_2\ (s) \quad (5)$$

The degradation of CSH phase in the present of $MgSO_4$ is significant faster and more thorough than that with other sulfate compounds. This was due to the low pH ($\sim$10.5) of saturated solution, which is too low to maintain the stability of CSH [12].

Concurrently, additional amount of gypsum, $Mg(OH)_2$ and magnesium silicate hydrate were also formed as shown in Eq. 6. The hydrated magnesium silicate possessed no binding capacity [12, 14]. The immersion in $MgSO_4$ solution, therefore, resulted in the deterioration of materials and lowered the compressive strength.

$$6Mg^{2+}\ (aq) + 6SO_4^{2-}\ (aq) + 2[3CaO \cdot SiO_2]\ (s) + 17H_2O\ (l) \rightarrow 3MgO \cdot 2SiO_2 \cdot 2H_2O\ (s) + 6[CaSO_4 \cdot 2H_2O]\ (s) + 3Mg(OH)_2\ (s) \quad (6)$$

In addition, sulfate ions (SO_4^{2-}) from $MgSO_4$ solution were strongly absorbed on surface of aluminosilicate owing to the strong interaction between SO_4^{2-} ions and aluminol edge site (Al–OH) on the surface of solid [15]. The SO_4^{2-} replaced –OH edge group, which was attached to Al ion leading to a high void ratio [15]. This replacement corresponded to the increased pores observed on geopolymer surface, and also affected the compressive strength of geopolymer.

3.3 Effect of microwave radiation on the geopolymer properties

XRD patterns of geopolymer pastes and fly ash are presented in Fig. 4. There were numerous sharp peaks of crystalline quartz (SiO_2), alumina (Al_2O_3), calcium sulfate ($CaSO_4$) and calcium oxide (CaO) identified in this fly ash. The crystalline phases appeared mainly in the core, whereas a glassy phase occupies the fly ash surface [5]. This glassy phase could be dissolved in alkaline solution forming geopolymer gel over the fly ash particles [3, 7]. In case of geopolymer pastes, the semi-crystalline gel was detected as indicated by both broad hump and some sharp peaks. The 22–38° 2θ broad hump of these pastes indicated the highly disorder glass phase in geopolymer [16]. In addition, new compounds of alumino-silicate (Al–Si–O) and calcium silicate (Ca–Si–O) were also detected. The Ca–Si–O was the same

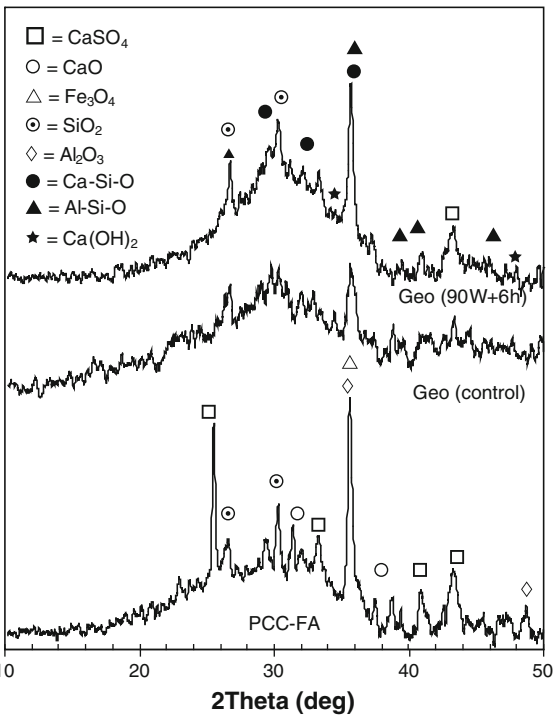


Fig. 4 Typical XRD patterns of geopolymer pastes and fly ash

product of the hydration of Portland cement. This was produced by the reaction between high calcium fly ash and NaOH/sodium silicate solutions. The crystalline quartz remained in the geopolymer paste owing to its low reactivity compared with the glassy phase on the fly ash particles [5].

Moreover, the samples with microwave radiation exhibited the sharp peaks of crystalline phases and the increase in height of hump peak compared with the control confirming the semi-crystalline geopolymer. The quartz, calcium- and alumino-silicate compounds had significant effects on the physical properties of the geopolymer. The presence of some of these crystalline products in geopolymer also enhanced the compressive strength [16].

Figure 5 shows the microstructure of the geopolymer with microwave radiation and the control. Partially reacted fly ash embedded in continuous mass of geopolymer products was readily observed. The gel formation on the fly ash surface confirmed the dissolution of the glassy phase in the alkaline solution and deposited on the fly ash surface [5]. Numerous gel formations occurred with microwave radiation. Microwave radiation promoted the dissolution of Si

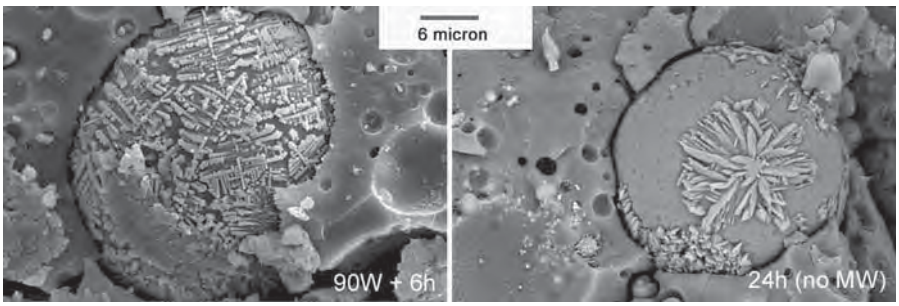


Fig. 5 Microstructure of geopolymer pastes

and Al species from the fly ash particles. In addition to the microwave energy, the additional heat curing contributed to more gel formation on the fly ash particles. With only heat curing, the gradual dissolution of the glassy phase on fly ash surface took place and led to less surface reaction compared with that with radiation. Cracks from the moisture removal during heat curing, voids and occupied fly ash pores were also detected in the geopolymer matrices.

Microwave radiation enhanced the dissolution rate at the early stage of geopolymerization compared with the conventional heat curing. It resulted in the rapid heating up of an aqueous alkaline solution by microwave energy, and the glassy SiO_2 and Al_2O_3 phases were easily leached out. In addition, the hydrogen bond between water molecules was broken under the microwave radiation and resulted in single water molecule. This molecule would consequently attack the Si–O and Al–O bonds of fly ash [5].

Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were used to determine the geopolymer's thermal stability and its fraction of volatile components by monitoring the weight change during heating of specimen. Figure 6 shows the TGA/DTG curves of fly ash and geopolymer pastes. Fly ash lost the weight at approximately 100, 400 and 700 °C owing to the evaporation of water, and decompositions of magnesite ($MgCO_3$) and calcium sulfate ($CaSO_4$) into CaO and SO_3, respectively.

For microwave radiation, a dense and strong sample was obtained as indicated by the low weight loss at high temperature compared with that of the control. Both the radiation and control geopolymers had a considerable weight loss at high temperature. This is probably due to the use of the alkaline solutions in the geopolymer mixture [16]. The geopolymer was, therefore, relatively stable at high temperature and

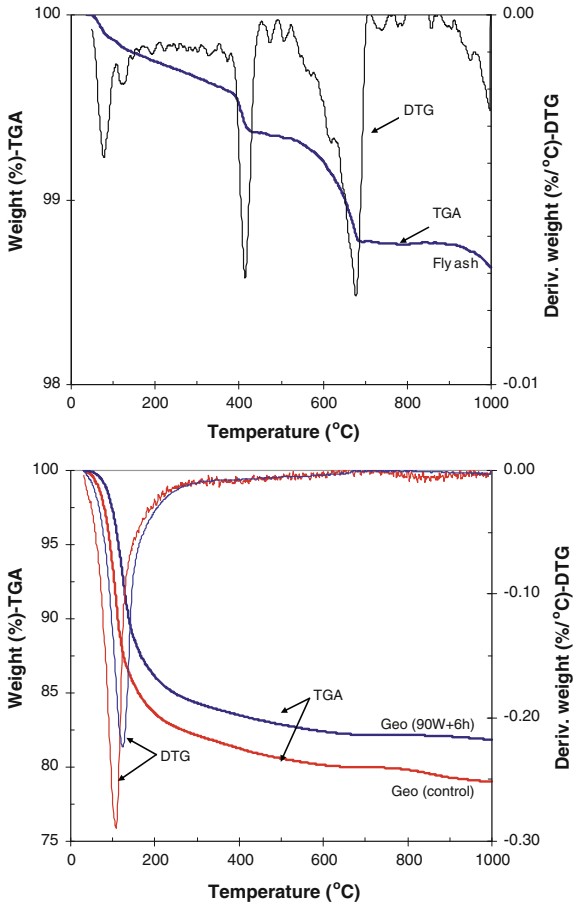


Fig. 6 TGA/DTG curves of geopolymer pastes

microwave radiation contributed to the dimensional stability of the geopolymer.

4 Conclusions

Microwave radiation and additional heat curing of geopolymer contributed to the dissolution of the

glassy phase on fly ash surface in alkaline solution. The microwave radiation shortened the required time of heat curing and enhanced the geopolymerization. A dense sample was achieved leading to a low strength loss under the acid and sulfate attacks compared with that of the control. However, gypsum, $Mg(OH)_2$, SiO_2, and magnesium silicate hydrate were formed and deposited onto the geopolymer surface during sulfate immersion. This caused the deterioration of materials and reflected in compressive strength loss. Numerous gel formations occurred with microwave radiation due to the promoted dissolution of Si and Al species from the fly ash surface. The geopolymer with microwave radiation possessed a dense sample with strong bonding leading to the dimensional stability of geopolymer.

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Cellular lightweight concrete containing high-calcium fly ash and natural zeolite

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Abstract: Cellular lightweight concrete (CLC) with the controlled density of approximately 800 kg/m^3 was made from a preformed foam, Type-I Portland cement (OPC), fly ash (FA), or natural zeolite (NZ), and its compressive strength, setting time, water absorption, and microstructure of were tested. High-calcium FA and NZ with the median particle sizes of 14.52 and 7.72 μm, respectively, were used to partially replace OPC at 0, 10wt%, 20wt%, and 30wt% of the binder (OPC and pozzolan admixture). A water-to-binder mass ratio (W/B) of 0.5 was used for all mixes. The testing results indicated that CLC containing 10wt% NZ had the highest compressive strength. The replacement of OPC with NZ decreased the total porosity and air void size but increased the capillary porosity of the CLC. The incorporation of a suitable amount of NZ decreased the setting time, total porosity, and pore size of the paste compared with the findings with the same amount of FA. The total porosity and cumulative pore volume decreased, whereas the gel and capillary pores increased as a result of adding both pozzolans at all replacement levels. The water absorption increased as the capillary porosity increased; this effect depended on the volume of air entrained and the type or amount of pozzolan.

Keywords: lightweight concrete; fly ash; zeolites; compressive strength; microstructure; water absorption

1. Introduction

Lightweight concrete has been widely used in wall panels, masonry blocks, roof decks, and precast concrete units in many building applications. There are many advantageous qualities of lightweight concrete, such as its low density, low thermal conductivity, reduction of dead load, fast building rate, and low haulage cost [1]. The air voids needed to produce lightweight concrete can be obtained using expanded lightweight aggregate materials, such as perlite, blast furnace slag, volcanic ash, and coal bottom ash. The air voids can also be formed in cement paste by adding the prepared foam to the unhardened mixture. Cellular lightweight concrete (CLC) is a well-known low-density product that contains blends of Portland cement, silica, pozzolan, and lime as well as a homogeneous void or cellular structure attained with gas-forming chemicals or foaming agents. Autoclave curing is usually employed for CLC that contains binder ingredients other than, or in addition to, Portland cement [2]. Density control is achieved by substituting macroscopic air cells for all or part of the fine aggregate. Normal-weight coarse aggregates are not usually used, but lightweight aggregates, both fine and coarse, are often found in CLC [3]. After molding, the concrete hardens under normal atmospheric conditions [4].

Since CLC is a porous material with a homogeneous cellular structure, it possesses a number of attractive characteristics, such as good thermal and acoustic insulation, satisfactory workability, and self-flowing properties. Its good thermal and acoustic performance makes it a natural choice as a building construction material. Although

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its mechanical properties are low compared with those of normal concrete, CLC products are used in many applications, such as partition walls and load-bearing walls in low-rise residential buildings [5−6].

Fly ash (FA) is a by-product from the combustion of pulverized coal in power plants. More than 3.5 million tons of coal fly ash is produced in Thailand annually. Using FA as a replacement ingredient in cement is currently a common practice in Thailand because FA improves the properties of concrete and reduces its cost. The high content of amorphous silica, alumina (which comprises more than 70wt%), and fine spherical particles (15 μm in diameter on average) in FA are the primary reasons for its high pozzolanic index. Many researchers have already examined the influence of FA on the properties of concrete, such as compressive strength, sulfate resistance, and durability [7].

Natural zeolite (NZ), a volcanic or volcanogenic sediment material, has a three-dimensional structure, and it is classified as a hydrated aluminosilicate of alkali and alkaline earth cations with uniform pores, grooves, and pits. NZs possess special properties, such as ion exchange, molecular sieves, large surface areas, and catalytic activity, which make this material preferable for large-scale industrial applications[1]. Approximately 40 NZs have been identified over the last 200 years. The most common NZs are analcime, chabazite, clinoptilolite, mordenite, and phillipsite. Based on the recorded production and production estimates, the worldwide production of NZ is approximately 3-4 million tons per year[1].

The current research presents the test results and evaluations of incorporating FA and NZ into preformed foam CLC as a replacement for Portland cement. This information is essential for its wider application to other construction materials.

2. Experimental

2.1. Materials

Type-I Portland cement (OPC), foaming agent, water, FA, and NZ were the materials used. The specific gravities of OPC, FA, and NZ were measured in accordance with ASTM C 188-95(2003) [8], and their particle sizes were measured using laser particle size analysis. These data are provided in Table 1. A scanning electron microscopy (SEM) photo of an OPC particle is shown in Fig. 1(a). FA was obtained from a silo at the Mae Moh Power Plant in northern Thailand. Its SEM photo, which is shown in Fig. 1(b), reveals the spherical shape of the particles. NZ was a clinoptilolite ($(Na,K,Ca)_6(Si,Al)_{36}O_{72}\cdot 20H_2O$). An SEM photo of NZ, which is shown in Fig. 1(c), demonstrates its irregular and crushed-shape particles. Other researchers have also reported similar observations [9]. The chemical compositions of these three materials are listed in Table 2. The foaming agent was synthetic. Fig. 2 shows the particle size distributions obtained using the Malvern Mastersizer Instrument. The particle size of FA is similar to that of cement, whereas that of NZ is smaller.

Table 1. Physical properties of the material

Sample	Specific gravity	Median particle size, d_{50} / μm	Blaine fineness / ($cm^2 \cdot g^{-1}$)
OPC	3.15	14.12	3600
FA	2.02	14.52	4300
NZ	2.09	7.72	11300

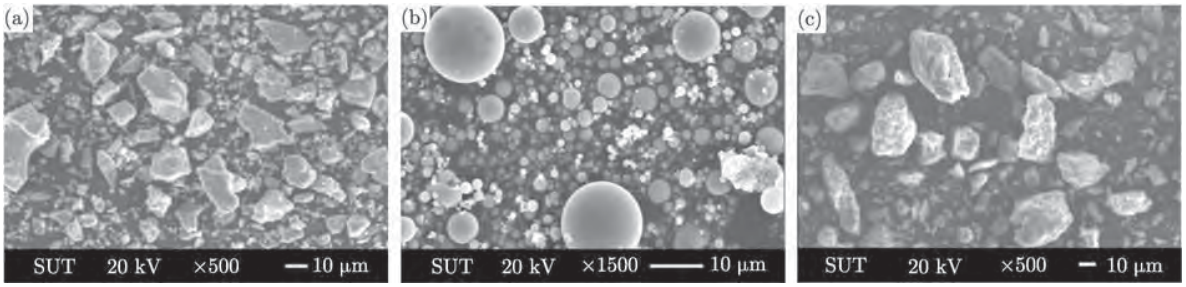


Fig. 1. SEM images of OPC (a), FA (b), and NZ (c).

Table 2. Chemical compositions of OPC, FA, and NZ **wt%**

Ingredient	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI	$SiO_2 + Al_2O_3 + Fe_2O_3$
OPC	19.85	4.49	3.56	66.96	1.36	—	0.34	2.46	0.98	—
FA	43.87	26.33	10.81	12.69	1.23	—	1.10	2.74	1.23	81.01
NZ	75.32	10.28	2.66	3.95	1.20	0.89	4.29	—	1.41	88.26

Note: LOI—loss on ignition.

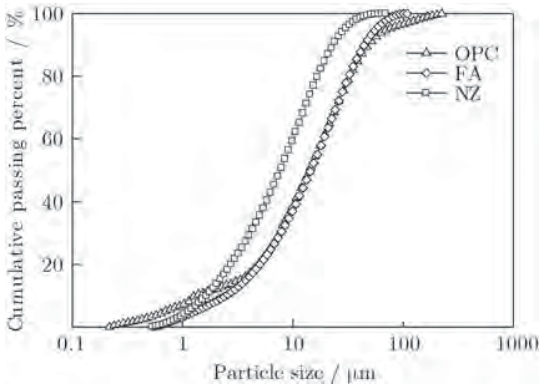


Fig. 2. Material particle size distribution.

2.2. Mix proportions

This experiment studied the effect of the filler contents on the density, setting time, water absorption, and compressive strength of CLC. The OPC was replaced with FA and NZ at levels of 0-30wt%. The mixes were labeled CON, FA10, FA20, FA30, NZ10, NZ20, and NZ30. For example, FA10 denotes the mix with 10wt% FA, and CON denotes the control mix (CLC with only OPC). The mass ratio of water to binder (W/B) of 0.5 was used for all mixtures. The foam required for a CLC density of 800-850 kg/m^3 was obtained per ASTM C 796-04[3]. The concrete mix proportions are provided in Table 3.

Table 3. Mix proportion of CLC

Mix No.	Symbol	Pozzolan replacement / wt%	Mix proportion / (kg·m^{-3})					W/B
			Binder			Foaming agent	Water	
			Cement	FA	NZ			
1	CON	0	665.0	—	—	0.772	332	0.5
2	FA10	10	598.5	66.5	—	0.759	332	0.5
3	FA20	20	532.0	133.0	—	0.746	332	0.5
4	FA30	30	465.5	199.5	—	0.733	332	0.5
5	NZ10	10	598.5	—	66.5	0.760	332	0.5
6	NZ20	20	532.0	—	133.0	0.748	332	0.5
7	NZ30	30	465.5	—	199.5	0.737	332	0.5

The foaming agent was diluted with water at a mass ratio of 1:40. Next, the liquid was pressurized with air at 6 kg/cm^2 and aerated to a density of 45 kg/m^3. OPC and FA (or NZ) were thoroughly mixed using a horizontal mixer. The foaming agent was added and mixed until a uniform paste was obtained. This process usually required approximately 3 min. The samples were poured into molds, and an external vibrator was applied to facilitate compaction. The CLCs were removed from the molds after 24 h, wrapped with a plastic film and placed in a moist room at (23±2)°C. A set of 100 mm×100 mm×100 mm specimens was used for the strength and porosity tests.

2.3. Compressive strength test

A compressive strength test was conducted at 3, 14, 28, and 60 d in accordance with BS 1881-116 [10]. The results are presented as the averages of three samples.

2.4. Concrete porosity determination

The pore-size measurements of the hardened CLC were determined using mercury intrusion porosimetry (MIP) with a pressure capacity of 228 MPa. The Washburn equation was used to determine pressure [11]. After curing for 3, 14, 28, and 60 d, the samples were obtained by carefully breaking the cube specimens with a chisel. The representative samples of 5 to 10-mm pieces, weighing between 2 and 3 g, were removed from the middle of each specimen. To stop the hydration reaction, the samples were submerged directly into liquid nitrogen for 5 min and vacuumed at a pressure of 0.5 Pa at –40°C for 48 h. This method has been previously used to stop the hydration reaction of cement paste [12-14]. A constant contact angle of 140° and a constant mercury surface tension of 480×10^{-3}J·m^{-2} were used to calculate the pore size.

2.5. X-ray diffraction (XRD)

Dried FA and NZ sample powders were sifted through a No. 100 sieve (150 μm openings). A sample of powder weighing approximately 1 g was used for XRD analysis. The XRD scans were performed for 2θ between 10° and 65° with an increment of 0.02°/step at a scan speed of 0.5 s/step. A quantitative XRD analysis determined the amorphous FA and NZ phases using Bruker's TOPAS software.

3. Results and discussion

3.1. Material properties

The chemical compositions of OPC, FA, and NZ are provided in Table 2. The main chemical component of FA is SiO_2, which accounts for 43.87wt% of its mass. As prescribed by ASTM C 618-03 [15], this sample is a Class F fly ash because the sum of SiO_2, Al_2O_3, and Fe_2O_3 is higher than 70wt%, and the LOI and SO_3 content do not exceed 6% and 5wt%, respectively. NZ has a high SiO_2 content of 75.32wt% and an LOI of 1.41%. The total content of SiO_2, Al_2O_3, and Fe_2O_3 in the NZ is 88.26wt%, which is more than the minimum requirement (70wt%) specified by

ASTM C 618-03 [15] for natural pozzolans.

The XRD patterns of FA and NZ shown in Fig. 3 indicate that the former powder consists primarily of crystalline phases of quartz; for NZ, the common zeolite mineral clinoptilolite is the major crystalline phase, and quartz is contained as a minor phase. Uzal and Turanlı [9] reported a similar result. A quantitative XRD analysis reveals that the contents of amorphous phases in FA and NZ are 78.8wt% and 20.5wt%, respectively. Moreover, the crystalline phase consists of 85wt% quartz and 15wt% mullite for FA and 22wt% quartz and 78wt% clinoptilolite for NZ.

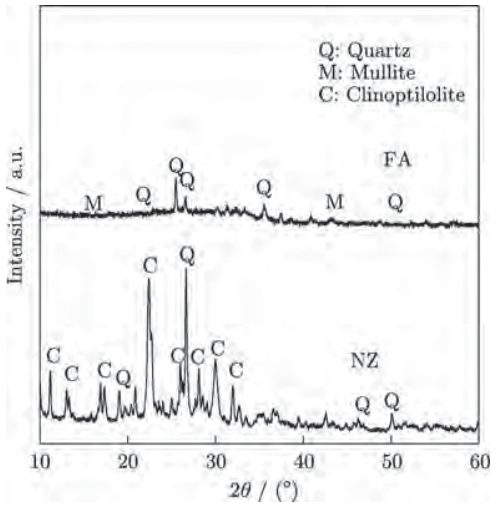


Fig. 3. XRD patterns of FA and NZ.

3.2. Setting time

The initial and final setting times of CLCs containing FA and NZ are presented in Fig. 4. It shows that the setting times prolong as the content of FA or NZ increases. The initial setting times of FA and NZ pastes increase from 5.2 to 14.45 h and from 5.2 to 12.15 h, respectively, whereas the final setting times increase from 13.1 to 23.5 h and from 13.1 to 19.95 h, respectively. The increase of pozzolan content reduces the cement content in the mix. As a result, a delay in the setting time of the cementitious system is due primary to a lower proportion of cement in the blended system. The setting times of the paste that contained NZ are slightly shorter than those of the paste contained FA because the former is a pozzolan with a Blaine fineness of 11300 cm^2/g, whereas the latter has a fineness of only 4300 cm^2/g. The fine pozzolan with a high surface area produces a greater pozzolanic reaction than the coarser pozzolan [16-17].

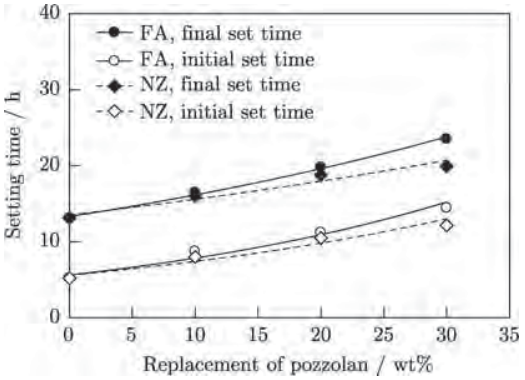


Fig. 4. Effect of FA and NZ on the setting time of CLC.

3.3. Compressive strength

Table 4 shows the compressive and relative strengths of CON. The compressive strengths of the control mix at 3, 14, 28, and 60 d are 1.81, 2.70, 3.05, and 3.15 MPa, respectively. The compressive strengths of the CLC increase with increasing the curing time due to the hydration reaction that increases the calcium silicate hydrate (C–S–H) product [18]. At 3 d the compressive strength of CLC containing 10wt% FA is slightly higher than that of the control mix at the same time point. This result is due to the proper amount of FA content, which affects the pozzolanic reaction rate and better dispersion and improves the compressive strength of the paste [7, 19-20]. The compressive strengths of CLC containing 20wt% or 30wt% FA are lower than that of the control mix. This result is due to the low OPC content that have been observed in other research [21]. In addition, the compressive strengths of FA30 at 14, 28, and 60 d are lower than those of the other mixes due to the greater amount of FA. FA is a pozzolan, and its pozzolanic reaction is slow compared with that of OPC; thus, the rate of strength development is also slow [19, 22].

Table 4. Compressive strength of CLCs containing OPC, FA, and NZ

Mix No.	Symbol	Compressive strength / MPa				Relative strength to CON / %			
		3 d	14 d	28 d	60 d	3 d	14 d	28 d	60 d
1	CON	1.81	2.70	3.05	3.15	100	100	100	100
2	FA10	1.95	3.17	3.45	3.65	108	117	113	116
3	FA20	1.65	2.75	3.10	3.30	91	102	102	105
4	FA30	1.27	2.15	2.42	2.58	70	80	79	82
5	NZ10	2.19	3.72	4.27	4.51	121	138	140	143
6	NZ20	1.92	3.18	3.66	3.91	106	118	120	124
7	NZ30	0.85	1.56	2.05	2.25	47	58	67	71

The compressive strengths of NZ30 at 3, 14, 28, and 60 d are 0.85, 1.56, 2.05, and 2.25 MPa, respectively. The strengths are weaker than those of the OPC due to the high NZ content and the slower pozzolanic reaction rate of zeolite, which do not significantly contribute to compressive strength [23]. The compressive strengths of NZ10 and NZ20 at 3, 14, 28, and 60 d are 2.19, 3.72, 4.27, and 4.51, and 1.92, 3.18, 3.66, and 3.91 MPa, respectively. These strengths are higher than those of CON at the same time point. The high SiO_2 content (75.32wt%) and NZ fineness (median particle size = 7.72 μm) improve the reaction with $Ca(OH)_2$ to produce an additional calcium silicate hydrate (C–S–H), which improves the compressive strength [1, 24−25].

At the replacement levels of 10wt% and 20wt%, the compressive strengths of CLC containing NZ are higher than those of CLC containing FA, as shown in Table 4. This finding is due to the high purity level (up to 90wt%) of NZ and the high SiO_2 content compared with those of FA. According to Ref. [25], the 28-d strength of zeolite concrete with a replacement level of 15wt% (the optimum) is also 23wt% higher than that of the control mix. As a result, the strength of hardened concrete is improved by incorporating a proper amount of zeolite [1, 16, 19, 26-27]. The optimum replacement level of NZ or FA is 10wt%. For a higher replacement level of 20wt%, the strengths of CLC are slightly reduced compared with those at the optimum replacement level of 10wt%; however, these strengths are still higher than those of the control mix. Replacing cement with FA or NZ affects the compressive strength because the compressive strength significantly increases with time but decreases with increasing the replacement level. Three factors can explain the increased compressive strength of CLC: hydration reaction, filler effect, and pozzolanic reaction. Hydration reaction is directly related to the cement amount in the mix. The filler effect involves the nucleation and packing effects, which depend on the material fineness. The nucleation effect occurs when small particles are dispersed into the cement paste and act as nucleation sites that enhance cement hydration, whereas the packing effect is the result of small particles that fill the voids of the paste [28-30]. Therefore, CLC with pozzolans of high fineness results in a more homogeneous and denser matrix, which increases the compressive strength of the paste.

3.4. Water absorption

The results of CLC water absorption at 28 d are presented in Fig. 5. The water absorption of CON is 30.0wt% at 28 d, whereas those of FA10, FA20, and FA30 are 30.6wt%, 32.5wt%, and 35.3wt%, respectively. The water absorption of CLC containing FA increases as the FA content increases. Kunhanandan Nambiar and Ramamurthy [31] reported similar results when they used Class F fly ash to replace sand at the sand-to-FA ratio of 0-100wt% to obtain foam concrete with the water absorption of 23wt%-30wt%.

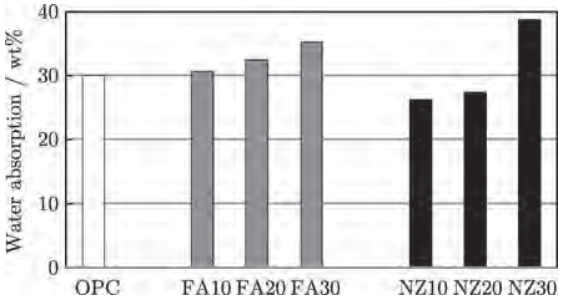


Fig. 5. Water absorption of CLC at 28 d.

The water absorptions of NZ10 and NZ20 are 26.3wt% and 27.3wt%, respectively. These figures are lower than those of CON. This finding is due to the amount of pore bubbles from the foam, which is slightly reduced with the addition of NZ. However, the water absorption of NZ30 is higher (38.8wt%). Other researchers have made similar observations regarding water absorption [25, 32]. This finding is related to the porosity results: a small increase in capillary pores in CLC hence causes a small increase of water absorption.

Fig. 5 shows that the water absorption of CLC containing NZ is more effective than CLC with FA at replacement levels of 0-20wt%. The water absorption of CLC containing 30wt% FA is slightly lower than that containing 30wt% NZ. It is observed that replacing cement with pozzolan in CLC results in the increase of large capillary pores. The result shows that large capillary pores of FA10 and FA20 are higher than those of NZ10, NZ20, and CON. Therefore, an increase of large capillary pores in CLC could influence their water absorption.

3.5. Microstructure of CLC

3.5.1. Porosity of CLC

The porosity results of all CLCs at 28 and 60 d are presented in Table 5 and Fig. 6. The porosity system consists of four types of pores: gel pores or small pores, less than 10 nm; medium capillary pores, 10 to 50 nm; large capillary pores, 50 to 10000 nm; and air void or extra large pores, larger than 10000 nm. Large capillary pores and extra large pores are influential on strength and permeability characteristics, whereas small pores and medium capillary pores are influential on drying shrinkage and creep [33−34]. The total porosities of the control mix, FA10, FA20, and FA30 at 28 d are 52.27%, 48.56%, 50.78%, and 59.32%, respectively. Incorporating 10wt% and 20wt% FA results in the CLCs with reduced total porosity. This result is due to the gradual filling of large pores from factors, such as the hydration reaction, the dispersing effect, the packing effect, and the pozzolanic reaction of FA particles. Small

and spherical FA particles fill air voids and decrease the porosity [28, 30]. At 30wt% FA, the total porosity significantly increases, primarily due to the packing effect of FA particles filling the air bubbles, which increases the capillary porosity of CLC. Note that the total porosity and capillary porosity of the CLCs increase, whereas the compressive strength and extra large pores decrease. Other investigations have reported similar findings [7]. The porosity of CLC containing FA at 60 d has a similar trend to that at 28 d.

Table 5. Porosity of CLCs containing OPC, FA, and NZ

Mix No.	Symbol	Porosity at 28 d / %					Porosity at 60 d / %				
		Small	Medium capillary	Large capillary	Extra large	Total	Small	Medium capillary	Large capillary	Extra large	Total
1	CON	0.05	2.84	26.72	22.66	52.27	0.05	2.15	26.93	22.51	51.64
2	FA10	0.28	1.94	38.62	7.72	48.56	0.35	1.86	36.80	7.71	46.72
3	FA20	0.19	2.93	40.51	7.15	50.78	0.20	2.42	40.37	7.56	50.55
4	FA30	0.24	4.39	47.70	6.99	59.32	0.25	3.96	47.67	6.73	58.61
5	NZ10	0.20	4.29	33.88	4.69	43.06	0.21	3.77	31.72	4.55	40.25
6	NZ20	0.38	4.72	34.37	5.34	44.81	0.31	4.40	34.11	5.13	43.95
7	NZ30	0.30	9.26	50.60	9.55	69.71	0.31	7.90	50.49	9.13	67.83

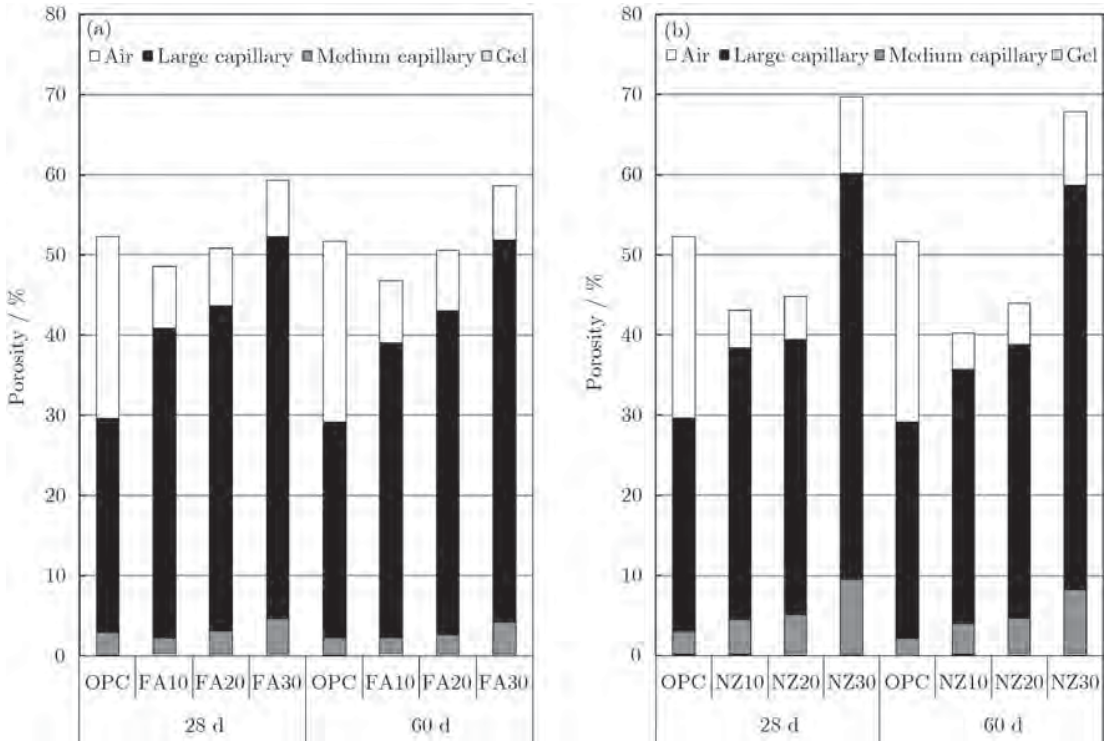


Fig. 6. CLC porosity with admixtures FA (a) and NZ (b).

As shown in Fig. 6, the total porosity of CLCs containing NZ10 and NZ20 are smaller than that of OPC concrete at all replacement levels and times. It is because NZ is more effective at reducing pore size due to a better dispersing effect, packing effect, and pozzolanic reaction of finer NZ particles. The small NZ particles fill the pores and decrease the porosity [9, 27].

Compared with FA, high-fineness NZ has a faster pozzolanic reaction and a better filler effect at reducing the voids of CLC. However, a considerable decrease in the total porosity of NZ10 occur 28 d later, primarily due to the decrease in large capillary pores. This decrease might be associated with the pore system becoming denser as a result of the additional formation and growth of the pozzolanic reaction products [9, 27].

The 10wt% incorporation of pozzolanic materials decreases the total porosity due to the filling effect and pore refinement. The total porosity of OPC concrete is 52.27%, whereas those of FA10 and NZ10 are 48.56% and 43.06%, respectively. The total porosity of NZ10 is reduced more than that of FA10 due to its finer particles. The increase in pozzolan content to 20% and 30% increases the total

porosity. The reduced OPC content and hydration products offset the filling effect. The extra large pores of CLCs containing pozzolans are reduced, whereas the small pores, medium capillary pores, and large capillary pores increase. The filling effect reduces extra large pores and increases small pores, medium capillary pores, and large capillary pores. All pores other than small pores increase significantly for 30% pozzolans. Again, this result is due to the reduced amounts of OPC and hydration products. Other investigations also reported similar findings [7]. The pores exhibit a similar trend at 60 d compared with that at 28 d.

As shown in Table 5 and Fig. 6, the incorporation of higher CLC replacement levels of both FA and NZ results in greater gel porosity compared with that of the control mix at all times. CLC with NZ exhibits increased gel porosity, which suggests that CLC with NZ is more effective than that with FA, and this is due to the better dispersion, packing effect and pozzolanic reaction in the blended cement paste. Other researchers have reported similar results [7, 16].

3.5.2. Effects of FA and NZ on the pore size distribution of CLC

The cumulative pore volumes of CLCs with FA and NZ are shown in Figs. 7 and 8. The cumulative pore volumes of the control mix at 28 and 60 d are 0.454 and 0.452 mL/g, respectively. These values decrease with curing time due to the hydration reactions and the increase of the C–S–H product [14, 23].

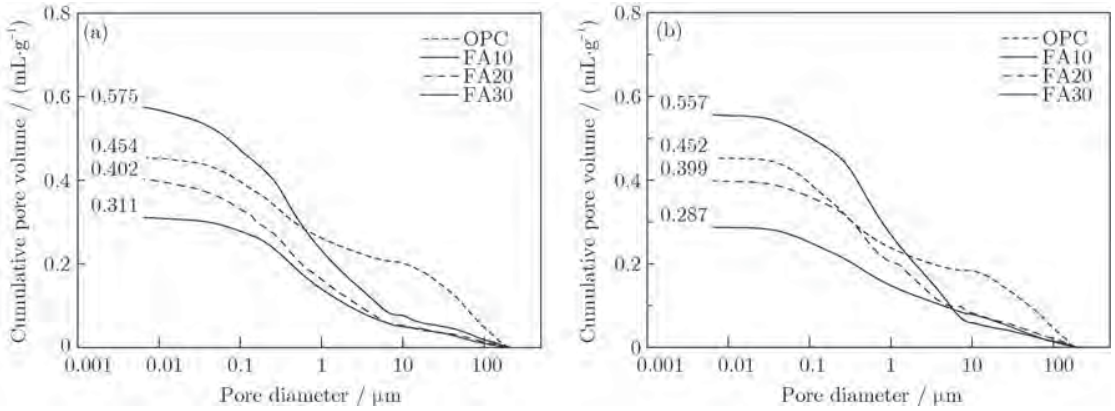


Fig. 7. Relationship of cumulative pore volume and pore diameter of CLC containing FA: (a) 28 d; (b) 60 d.

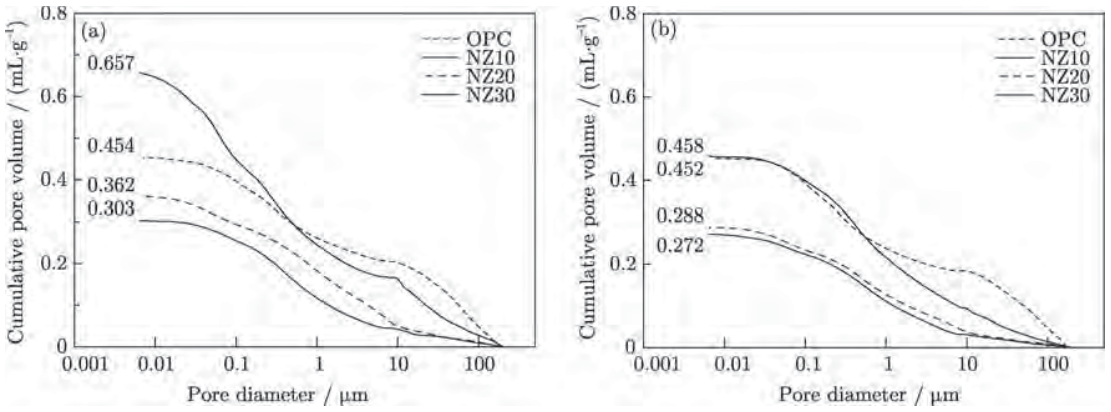


Fig. 8. Relationship of cumulative pore volume and pore diameter of CLC containing NZ: (a) 28 d; (b) 60 d.

As shown in Fig. 7, the cumulative pore volumes of CLC containing 10wt% FA are 0.311 mL/g at 28 d and 0.287 mL/g at 60 d. These figures are lower than those of the control mix and CLC containing 20wt% or 30wt% FA. As shown in Fig. 8, the cumulative pore volumes of CLC containing 10wt% NZ are 0.303 mL/g at 28 d and 0.272 mL/g at 60 d. FA and NZ are effective pozzolans with successful pozzolanic reactions. Incorporating a proper amount of pozzolan fills voids, reduces porosity, and increases the density of the paste [14, 16]. The SiO_2 and Al_2O_3 in pozzolanic materials react with $Ca(OH)_2$ to produce C–S–H and C–A–H, which results in a reduction of $Ca(OH)_2$ content by pozzolanic reaction [23, 27]. The results also reveal that the cumulative pore volumes of concretes containing NZ are smaller than those containing FA. This finding suggests that NZ is slightly more effective than

FA at reducing porosity.

3.5.3. SEM observations

The morphologies of the fractured surfaces of CLCs at 28 d are shown in Figs. 9 and 10. The pores of the control mix are clearly shaded circles of various sizes with relatively smooth surfaces. The pore sizes vary from less than 50 μm to 600 μm. Another researcher reported a similar observation [32].

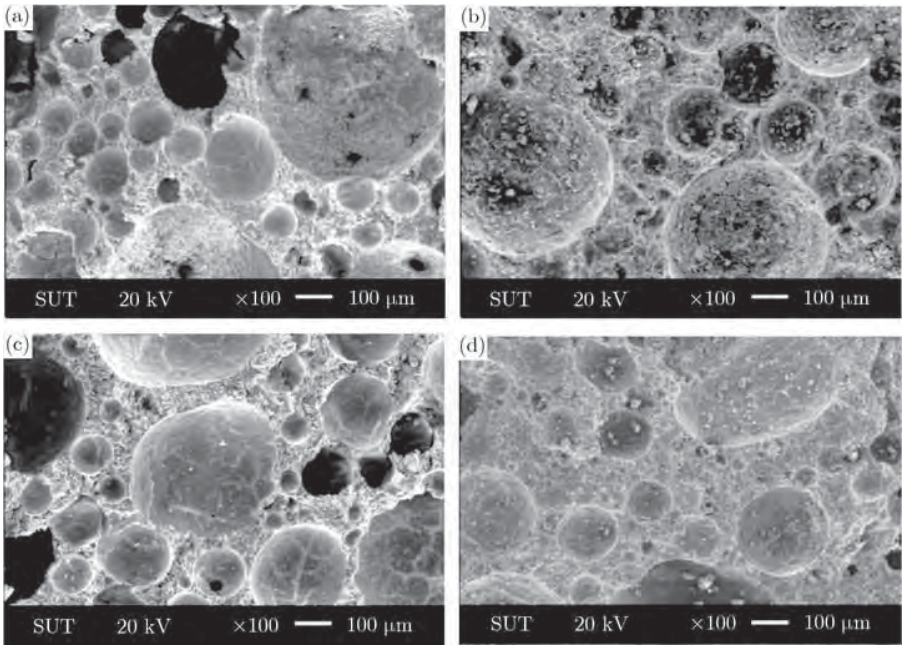


Fig. 9. SEM images of the fractured surfaces of CLCs containing FA at 28 d: (a) OPC; (b) FA10; (c) FA20; (d) FA30.

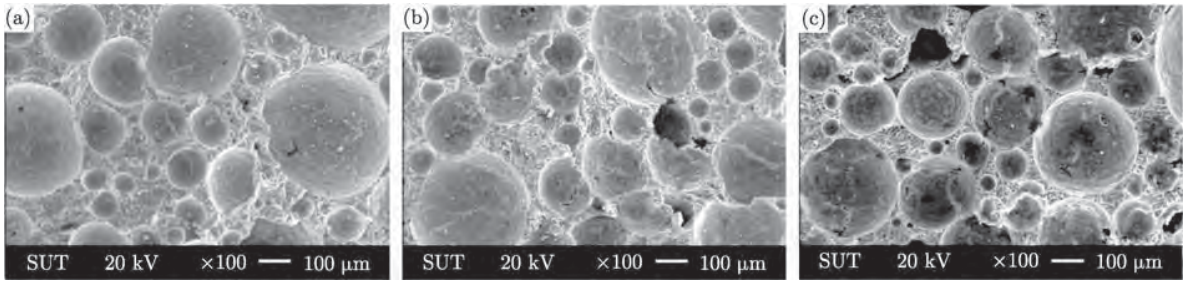


Fig. 10. SEM images of the fractured surfaces of CLCs containing NZ at 28 d: (a) NZ10; (b) NZ20; (c) NZ30.

Figs. 9(b)-9(d) display the SEM images of CLCs containing 10wt%, 20wt%, and 30wt% FA, respectively, which have completely different microstructures from the control mix (Fig. 9(a)). Clearly, the pores are more uniform than those of the control mix because FA facilitates the distribution of air voids by preventing them from merging and overlapping [35]. The pore sizes of these CLCs range from less than 50 μm to 400 μm. In addition, the pore size decreases as the FA replacement level increases [14]. Furthermore, some microcracks are detected at the pore surfaces (Figs. 9(c) and 9(d)). Drying shrinkage and mechanical stresses that occurred during sample preparation probably induce these features.

Figs. 10(a)-10(c) display the SEM images captured from CLCs containing 10wt%, 20wt%, and 30wt% NZ, respectively. Clearly, these pore sizes are slightly more uniform than those of CLCs containing FA. The pore sizes range from less than 50 μm to 300 μm. Fig. 10(a) shows that there are several closed pores, which demonstrates that CLC with 10wt% NZ have low water absorption [36]. In addition, the pore size decreases as the NZ replacement level increases (Fig. 10(c)).

SEM observations reveal that the pores of CLCs containing NZ are denser than those of CLCs containing FA at the same replacement level (excluding the 30wt% replacement level) and control mix. This effect is due to cement hydration and pozzolanic reactions [14, 26]. Numerous large pores are observed with 30wt% pozzolan re-

placement, which reflects the high total porosity and low strength of these CLCs, due primarily to their low OPC content and reduced hydration products.

4. Conclusions

CLCs with OPC partially replaced by FA or NZ with a density of approximately 800 kg/m^3 can be produced with relatively good compressive strength. NZ is slightly more reactive than FA and enhances the strength of CLC. The optimum replacement level for both FA and NZ is 10wt%, which, compared with CON, results in the 28-d compressive strength increasing by 113% and 140%, respectively. A replacement level of 20wt% results in decreased strength; however, these CLCs are still stronger than the control mix.

CLCs containing NZ set slightly faster than those containing FA. This finding is due to the high fineness of NZ, which also has a higher surface area and a greater pozzolanic reaction. The increase in pozzolans also prolongs the setting time of CLCs with NZ compared with the control mix due to the lower content of OPC.

The capillary porosity of CLCs containing FA and NZ increases as the replacement level of both types of pozzolans increases. Moreover, water absorption is primarily related to capillary porosity. The water absorption increases as the capillary porosity increases, which decreases the compressive strength.

The reduction of air voids in CLCs with density control is due to replacing OPC with pozzolans. The pozzolans cause a filler effect and refine the pore-size structure of the paste. This effect changes larger pores into smaller ones. Thus, the total porosity and cumulative pore volumes of CLCs containing FA and NZ are less than those of OPC.

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Dielectric Responses and Electrical Properties of $CaCu_3Ti_{4-x}V_xO_{12}$ Ceramics Prepared by a Simple Poly(ethylene glycol) Sol–Gel Route

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Nanocrystalline $CaCu_3Ti_{4-x}V_xO_{12}$ ($x = 0$, 0.025, and 0.05) powders with particle sizes of 100–200 nm were successfully synthesized using a poly(ethylene glycol) solution. All the ceramic samples exhibited the pure $CaCu_3Ti_4O_{12}$ phase. The grain size of $CaCu_3Ti_{4-x}V_xO_{12}$ ceramics increased slightly as V doping ion concentration increased; whereas, the dielectric permittivity of the ceramics decreased slightly. The nonlinear current–voltage properties of $CaCu_3Ti_4O_{12}$ ceramics were improved significantly by substitution of V ions. Impedance spectroscopy analysis and investigation of non-ohmic electrical properties revealed that the electrical resistance of the grain boundary and breakdown electric field strength were markedly increased by substitution of V ions; whereas, electrostatic potential barrier height at grain boundaries decreased slightly.
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1. Introduction

Recently, dielectric materials with high values of dielectric permittivity (ε') have been playing an important role in microelectronic devices such as multilayered ceramic capacitors (MLCCs). Many researchers have investigated the dielectric and electrical properties of perovskite oxides and related oxide ceramics to improve the dielectric properties of high-permittivity materials.[1–14] Among them, $CaCu_3Ti_4O_{12}$ (CCTO) and related oxides (such as $Na_{1/2}Bi_{1/2}Cu_3Ti_4O_{12}$, $Na_{1/2}La_{1/2}Cu_3Ti_4O_{12}$, $Na_{1/2}Y_{1/2}$-$Cu_3Ti_4O_{12}$, and $Y_{2/3}Cu_3Ti_4O_{12}$) have gained considerable interest both scientifically and technologically. Interestingly, these ceramics can exhibits values of ε' in the range of 10^3–10^5 at room temperature.[3,5,9,10,15–25]

To date, many investigations have been carried out to understand the physical mechanism(s) related to the apparent giant dielectric response in CCTO ceramics.[3,5,9,10,17,20] However, the origin of giant dielectric properties is still unclear. Both the intrinsic and extrinsic effects were proposed to underlie the unusually high ε' values of CCTO ceramics and single crystals. For the intrinsic effect, different models have been proposed to explain the giant dielectric response such as the mixed-valent structure model,[10,20] polaron relaxation model,[26] and nanoscale disorder model.[27,28] For the extrinsic effect, it is widely believed that the origin of the giant dielectric response in the CCTO ceramics is attributed to the internal barrier layer capacitor (IBLC) effect.[5,9,15–19,22,24] The giant dielectric response in CCTO is mainly caused by the polarization at grain boundary (GB) regions, which is well known as the "Maxwell–Wagner polarization".[5,29] Moreover, it was also found that this polarization can be introduced at other interfaces, both inside and outside the ceramics, such as internal domain boundaries (DBs)[30] and at the sample-electrode interface.[9,31,32]

It is interesting that CCTO and related oxide ceramics can also exhibit nonlinear current–voltage behavior.[5,16,17,19,22,24,33–36] This is because of the existence of intrinsic potential barriers at the GBs, i.e., the Schottky effect.[37,38] Therefore, it is possible that CCTO ceramics have the potential for varistor and gas sensor applications.[5]

To improve dielectric properties and to clarify the giant dielectric response in CCTO ceramics, substitution of metal ions into Ca^{2+}, Cu^{2+}, and Ti^{4+} sites for CCTO ceramics has been extensively investigated.[9,18,19,21,24,36,39–44] All doping ions have significant effects on ε', $\tan\delta$, electrical conductivity of GBs (σ_{gb}), as well as activation energy required for conduction at GBs and inside the grains. Moreover, doping ions also show a great effect on the nonlinear current density–electric field (J–E) characteristics of CCTO ceramics. For example, it was found that substitution of 2.0 wt % vanadium (V) can reduce the resistance of GB (R_{gb}) with a slight increase in the capacitance of GBs (C_{gb}).[45] Sen et al.[46] reported that ε' of CCTO ceramics was decreased by substitution of V ions. Ramajo et al.[36] found that addition of VO_2 into $CaCu_3Ti_4O_{12}/CaTiO_3$ composite ceramics can decrease ε', especially at high frequencies. A large decrease in ε' at high frequencies may be due to the effect of V doping on dielectric relaxation. It was also found that the nonlinear electrical properties of $CaCu_3Ti_4O_{12}/CaTiO_3$ ceramics can be improved significantly. According to the IBLC model,[29] the dielectric response in ceramics is closely related to the electrical response at GBs. Therefore, systematic investigation of the giant dielectric and electrical properties of CCTO-based ceramics is therefore important.

In general, the conventional solid state reaction method is selected to prepare CCTO using $CaCO_3$, CuO, and TiO_2 as the starting raw materials. This method requires high sintering temperatures and long reaction times to produce the pure CCTO phase. In contrast to the SSR method, synthesis of CCTO from chemical solutions usually offers the possibilities of close stoichiometric control and low-temperature chemical reactions.[15] Thus, preparation of CCTO ceramics using chemical solutions is therefore important.

In this work, the dielectric and electrical properties of $CaCu_3Ti_{4-x}V_xO_{12}$ ($x = 0$, 0.025, and 0.05) ceramics were

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systematically investigated at different temperatures. The phase formation and microstructure of the sintered ceramics were characterized. The effects of V doping ions on the giant dielectric properties and electrical response at GBs are discussed on the basis of the results of impedance spectroscopy analysis and measurement of current–voltage at various temperatures.

2. Experimental Procedure

A poly(ethylene glycol) (PEG) solution route was used to prepare $CaCu_3Ti_{4-x}V_xO_{12}$ powders, where $x = 0$, 0.025, and 0.05 (abbreviated as CCTO, CCTVO-1, and CCTVO-2 samples, respectively). The starting raw materials were $Ca(NO_3)_2 \cdot 4H_2O$ (99%, Sigma-Aldrich), $Cu(NO_3)_2 \cdot 4H_2O$ (99.5%, Carlo Erba), $C_{16}H_{28}O_6Ti$ (75 wt % in isopropanol, Sigma-Aldrich), ethanol, and PEG. Firstly, stoichiometric amounts of $Ca(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 4H_2O$ were dissolved in the solution of PEG (2.5 wt %) in ethanol with constant stirring at room temperature. Secondly, $C_{16}H_{28}O_6Ti$ solution was dropped slowly into the metal ion solution mentioned above with constant stirring. Immediately, a clean and transparent solution was obtained. Thirdly, the mixed solution was dried at 623 K for 30 min. The resulting dried porous precursors were ground and calcined at 1073 K for 3 h. The obtained $CaCu_3Ti_{4-x}V_xO_{12}$ powders were ground and pressed into pellets of 9.5 mm diameter and ~1–2 mm thickness by uniaxial compression at 200 MPa. Finally, these pellets were sintered in air at 1333 K for 1 h.

Scanning electron microscopy (SEM; LEO 1450VP) and X-ray diffraction (XRD; Philips PW3040) techniques were used to examine the microstructure and to characterize the phase formation of the sintered $CaCu_3Ti_{4-x}V_xO_{12}$ ceramics, respectively. Nanoparticles of $CaCu_3Ti_{4-x}V_xO_{12}$ powders were observed by transmission electron microscopy (TEM; FEI Tecnai G^2). Au electrodes were sputtered on the polished-face of each pellet at a current of 25 mA for 8 min using a Polaron SC500 sputter coating unit. The capacitance and dissipation factor (or $\tan\delta$) of the samples were measured using an Agilent 4294A Precision Impedance analyzer over the frequency range from 10^2 to 10^7 Hz at an oscillation voltage of 500 mV. The measurements were performed over the temperature range of 203–423 K. All temperature steps were kept constant with an accuracy of ±1 K. Current–voltage measurements were measured in the temperature range of 313–353 K using a high-voltage measurement unit (Keithley 247). The breakdown electric field (E_b) was obtained at the current density of 1 mA·cm^{-2}. Nonlinear coefficient (α) was calculated in the range of 1–10 mA·cm^{-2}.

The complex impedance Z^* was calculated from the relation,

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{1}{i\omega C_0 Z^*} = \frac{1}{i\omega C_0 (Z' - iZ'')}, \quad (1)$$

where ε' and ε'' are, respectively, the real (dielectric constant) and imaginary parts (dielectric loss) of the complex permittivity ε^*. Z' and Z'' are the real and imaginary parts of Z^*, respectively. ω is the angular frequency ($\omega = 2\pi f$) and $i = \sqrt{-1}$. $C_0 = \varepsilon_0 S/d$ is the empty cell capacitance, where S is the sample area, d is the sample thickness, and ε_0 is the permittivity of free space, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m.

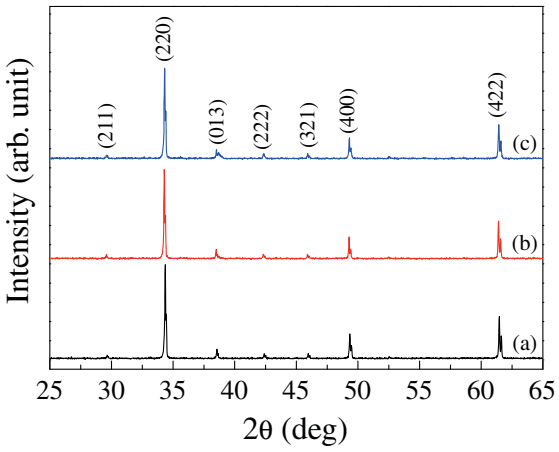


Fig. 1. (Color online) XRD patterns of (a) CCTO, (b) CCTVO-1, and (c) CCTVO-3 ceramic samples.

3. Results and Discussion

Figure 1 shows the XRD patterns of the CCTO and V-doped CCTO ceramics sintered at 1333 K for 1 h. All diffraction peaks for all of the samples confirm the formation of the $CaCu_3Ti_4O_{12}$ phase (JCPDS 75-2188) without any possible impurities such as CuO, TiO_2, or $CaTiO_3$. The lattice parameters (a) of the sintered ceramics were calculated by Cohen's least mean square method. The a values of the CCTO, CCTVO-1, and CCTVO-2 samples were found to be 7.389(9), 7.389(1), and 7.394(6) Å, respectively. These values are comparable to those reported in the literature[1,16] and JCPDS 75-2188 for 7.391 Å.

SEM images of the surface morphologies of the CCTO and V-doped CCTO ceramics are shown in Fig. 2. The microstructures of the CCTO ceramic sample consist of grains, GBs, and pores. The grain sizes of the CCTO ceramic sample are about 1–2 μm, as shown in Fig. 2(a). The mean grain size of the CCTVO-1 ceramic samples tends to increase slightly, as shown in Fig. 2(b). The largest grain of this sample was found to be ~5 μm in size. Figures 2(c) and 2(d) show the surface morphologies of the CCTVO-2 ceramic sample at different regions. The largest grain of the CCTVO-2 ceramic sample was found to be ~10 μm in size. These results mean that substitution of V ions can increase the sintering rate of CCTO ceramics. The grain growth mechanism in a ceramic is usually driven by GB mobility. For CCTO ceramics, the liquid phase sintering mechanism is likely to be the main factor for increasing the grain growth rate.[19] The presence of the liquid phase during heating and sintering processes can increase the diffusion rate of ions across GBs. For V-doped CCTO ceramics, it is likely that the related V phase may act as a liquid phase during heating and sintering processes. The effect of V doping on microstructural changes of ceramics is usually observed in a V-doped ZnO system. It is caused by the relatively low melting points of V and the related second phase.[47] Note that a large number of pores are observed in the microstructures of all ceramic samples, especially for the CCTO sample. The porosity of CCTO ceramics tends to

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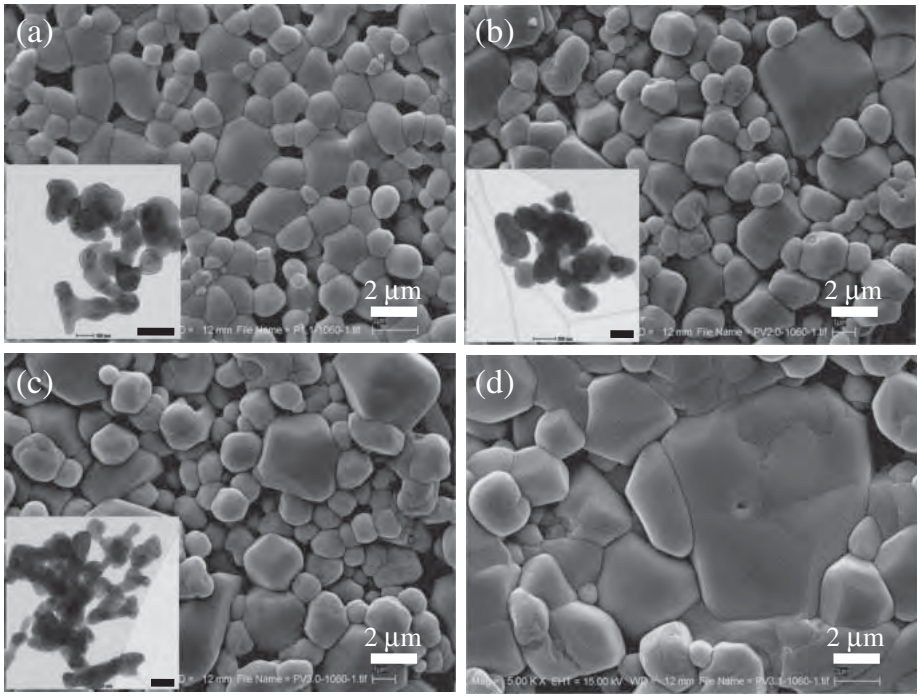


Fig. 2. SEM images of surface morphologies of (a) CCTO, (b) CCTVO-1, and (c, d) CCTVO-2 ceramic samples. Insets of figures (a–c) show their TEM images, revealing nanoparticles of the CCTO, CCTVO-1, and CCTVO-2 samples, respectively; each scale bar is 200 nm.

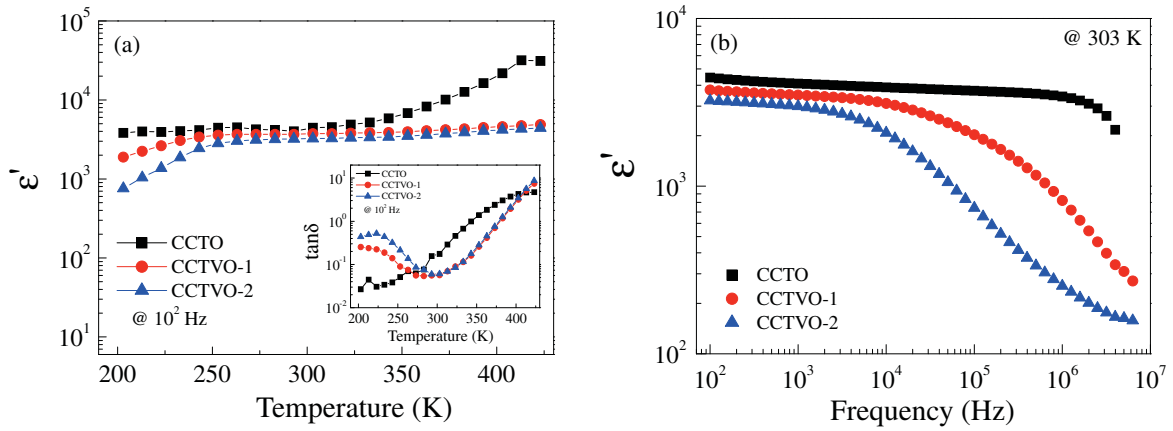


Fig. 3. (Color online) (a) ε' of CCTO and V-doped CCTO ceramic samples as a function of temperature; the inset shows the temperature dependence of $\tan\delta$ at a frequency of 10^2 Hz. (b) Frequency dependence of ε' at 303 K in CCTO and V-doped CCTO ceramic samples.

decrease with increasing V doping content. This result indicates that the CCTO ceramic sample sintered at 1333 K for 1 h has a low relative density. The insets of Figs. 2(a)–2(c) show the nanoparticles of the CCTO, CCTVO-1, and CCTVO-2 powders, respectively. The particle sizes of all samples are in the range of 100–200 nm.

Figure 3(a) shows the temperature dependence of ε' at 10^2 Hz for the CCTO and V-doped CCTO ceramics. Obviously, ε' in the temperature range of 203–423 K of CCTO ceramics decreases slightly with increasing V doping concentration. At high temperatures, ε' of the CCTO ceramic sample significantly increased compared with those observed in the CCTVO-1 and CCTVO-2 ceramic samples. The inset of Fig. 3(a) shows the temperature dependence of $\tan\delta$ at a frequency of 10^2 Hz. At a temperature of ~300 K, $\tan\delta$ was decreased by substitution of V ions. However, at low temperatures below 270 K, $\tan\delta$ increased with increasing V concentration. The apparent $\tan\delta$ peaks in the CCTVO-1 and CCTVO-2 samples at a low temperature are attributed to the dielectric relaxation process related to the decrease in their ε' with increasing temperature. Figure 3(b) shows the frequency dependence of ε' at 303 K for the CCTO and V-doped CCTO ceramic samples. Obviously, substitution of V into CCTO ceramics has a remarkable influence on the dielectric relaxation behavior. The step like decrease in ε' of V-doped CCTO ceramics shifts to a low-frequency range as V concentration increased. It is important to note that the relationship between the dielectric response and microstructure of V-doped CCTO ceramics is very unique. This is because the dielectric response in CCTO ceramics is usually enhanced as grain size increased or vice versa.[9,15,19,22–24,37,41,42] Recently,

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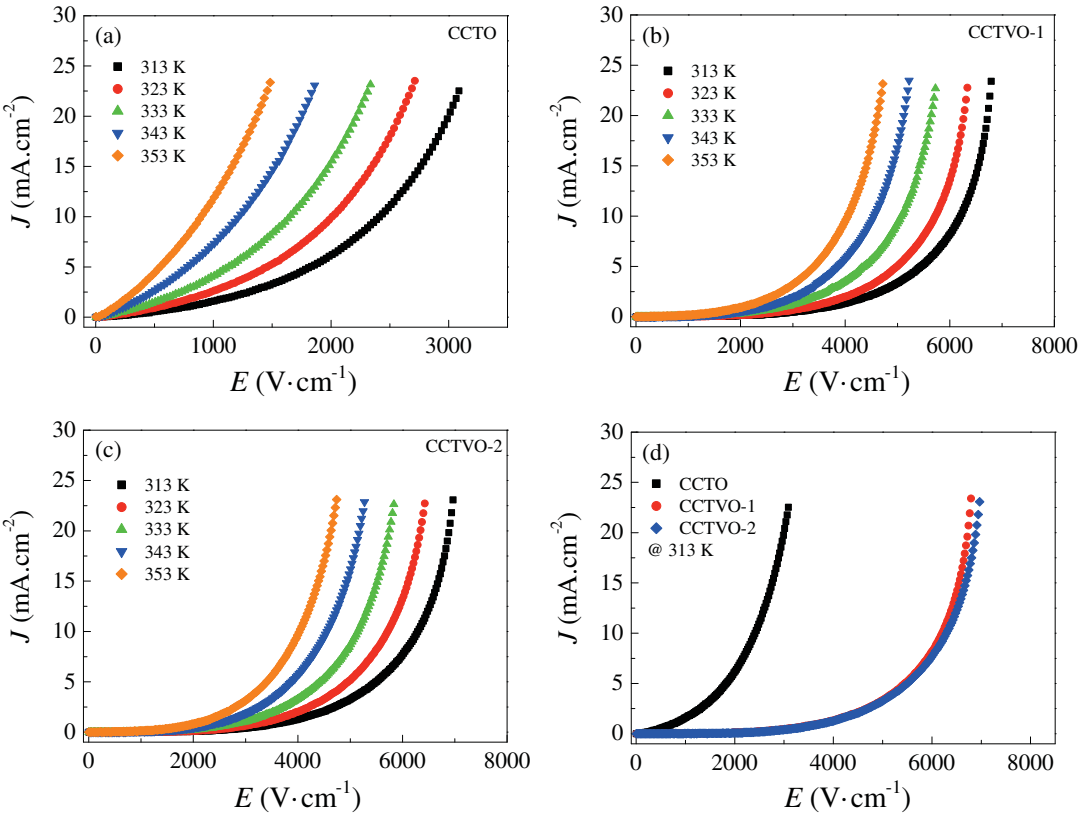


Fig. 4. (Color online) Temperature dependence of non-ohmic properties of (a) CCTO, (b) CCTVO-1, and (c) CCTVO-3 ceramic samples. (d) Non-ohmic characteristics (J vs E) of all samples at temperature of 313 K.

Schmidt et al.[48] have studied the effects of sintering temperature on the IBLC structure in CCTO ceramics. They found that the ε' of a CCTO ceramic is dependent on its C_{gb} and independent of mean grain size. Thus, the decrease in ε' observed in V-doped CCTO ceramics may be caused by the decrease in C_{gb}. Substitution of V ions to CCTO ceramics may have an effect on the electrical response of GBs. Investigation of electrical responses at GBs of CCTO ceramics is therefore important.

To study the physical nature of electrical transport at the GBs of CCTO ceramics, non-ohmic characteristics were investigated at various temperatures. The nonlinear J–E strength of the CCTO, CCTVO-1, and CCTVO-2 samples are shown in Figs. 4(a)–4(c), respectively. The J–E curves of all the samples show non-ohmic characteristics. It was observed that E_b decreases with increasing temperature, and non-ohmic J–E characteristic tends to become ohmic characteristic in nature as temperature increases. This behavior indicates the effect of temperature on the Schottky barrier.[38] It is likely that the electrical response of GBs in CCTO ceramics may be related to the existence of Schottky barriers at the GBs. Figure 4(d) shows the J–E curves of all samples at 313 K, showing the influence of V doping ions on the nonlinear electrical properties, indicating the effect of V on the intrinsic electrical properties of GBs. E_b of the CCTO ceramics was increased by substitution of V ions. The values of E_b were determined to be 781, 3731, and 3800 V·cm^{-1} for the CCTO, CCTVO-1, and CCTVO-2 ceramic samples, respectively, and those values of α were 2.00, 4.41, and 4.42, respectively. These results are similar to those of the VO_2-added $CaCu_3Ti_4O_{12}/CaTiO_3$ composite ceramics.[36] This means that substitution of V can change the intrinsic electrical properties of CCTO ceramics.

To understand the electrical properties of GBs, the total resistance of GBs is estimated by impedance spectroscopy, which is a powerful tool in separating the grain and the GB effects.[29] In general, the resistances of grains (R_g) and GB (R_{gb}) of CCTO ceramics can be calculated from the diameters of two semicircular arcs of the Z^* plot that appeared in the high- and low-frequency ranges, respectively.[29,48] At higher than room temperature, only the large semicircular arc in the low-frequency range is generally observed over the measured frequency range. R_g can be estimated from a nonzero intercept on the Z' axis at high frequencies.[29] We found that the large semicircular arcs of all the samples cannot be observed at room temperature. Thus, Z^* plots for CCTO and V-doped CCTO ceramics must be replotted in a high-temperature range. As shown in Fig. 5, the large semicircular arcs of all the samples can be observed at a temperature of 393 K. Substitution of V can increase the total R_{gb} of CCTO ceramics. It is likely that R_{gb} of the CCTVO-2 sample is larger than that of the CCTVO-1 sample. This result is consistent with the slight increase in E_b of the CCTVO-2 sample compared with the CCTVO-1 sample, as shown in Fig. 4(d).

To deepen the understanding on the intrinsic electrical properties of GBs, the potential barrier height existing at GBs for all ceramic samples should be calculated. The electrical response of GBs in CCTO polycrystalline ceramics is closely related to the existence of Schottky barriers at the GBs.[5,37,38]

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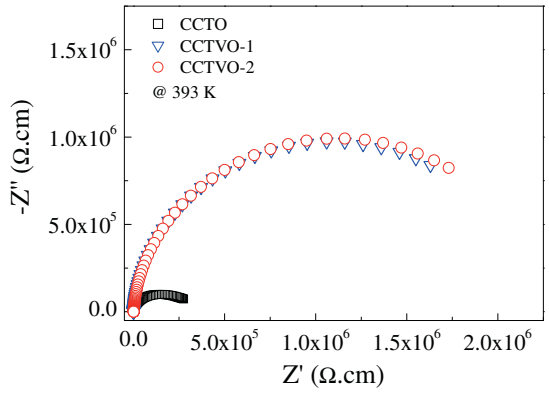


Fig. 5. (Color online) Impedance complex plane (Z^*) plots for CCTO and V-doped CCTO ceramics at temperature of 393 K.

Therefore, electrical conduction in the prebreakdown region is dominated by the Schottky emission. As a result, the relationship between J and E is as follows:[17,38,41,42)]

$$J = AT^2 \exp\left(\frac{\beta E^{1/2} - \Phi_B}{k_B T}\right), \quad (2)$$

$$\ln J = \frac{\beta E^{1/2}}{k_B T} + \left[\ln(AT^2) - \frac{\Phi_B}{k_B T}\right], \quad (3)$$

where Φ_B is the height of electrostatic potential barrier at the GBs, E is the electric field, β is a constant related to the potential barrier width, and A is the Richardson constant. To calculate Φ_B, the last term on the right hand side of Eq. (3) is expressed as

$$\ln J_0 = \ln(AT^2) - \frac{\Phi_B}{k_B T}. \quad (4)$$

Equation (3) is therefore expressed as

$$\ln J = J_0 + \frac{\beta E^{1/2}}{k_B T}. \quad (5)$$

From Eq. (5), $\ln J_0$ in the temperature range from 313 to 353 K of all samples can be calculated from the plots of $\ln J$ vs $E^{1/2}$ by the linear fitting of the slope. $\ln J_0$ can be obtained at $E = 0$. Figures 6(a) and 6(b) show the fitted linear relationship between $\ln J$ and $E^{1/2}$. Using the relationship in Eq. (4), the Φ_B values of the CCTO and V-doped CCTO ceramics were calculated from the slopes of the plots of $\ln J_0$ vs $1000/T$. As shown in Fig. 7, good linear fitting results are achieved and found to be 0.562, 0.551, and 0.437 eV for the CCTO, CCTVO-1, and CCTVO-2 ceramic samples, respectively. The overall electrical and dielectric properties of the V-doped CCTO ceramics are very similar to those observed in the La-doped CCTO ceramics.[42)] The ε' and Φ_B of CCTO ceramics decreased with increasing doping concentration (i.e., La or V); whereas, E_b increased. For the TiO_2/CCTO composite system,[17)] it was found that Φ_B is independent of the amount of TiO_2; on the other hand, R_{gb} increased slightly. The increase in R_{gb} of the TiO_2/CCTO ceramics was suggested to be caused by the increase in the thickness of GB. Note that Φ_B decreased after doping CCTO with V; whereas, the R_{gb} values of the CCTVO-1 and CCTVO-2 samples at 393 K are nearly the same. However, this behavior is difficult to describe well. The electrical resistance of GBs may not be dependent only on potential barrier height. Other factors may have an effect on electrical resistance such as segregations of impurities related to the liquid phase sintering process. However, the presence of a small amount of liquid films on the GBs is difficult to observe. This extrinsic factor may have an influence on the electrical properties of the CCTVO-1 and CCTVO-2 ceramic samples. According to previous works,[15,33,34,37,38,41,49)] the relationship between the Schottky effect at GBs and dielectric properties can be well explained and easy to understand. However, in some cases as well as the results presented in this work,[35,36,42)] this relationship is not easily established.

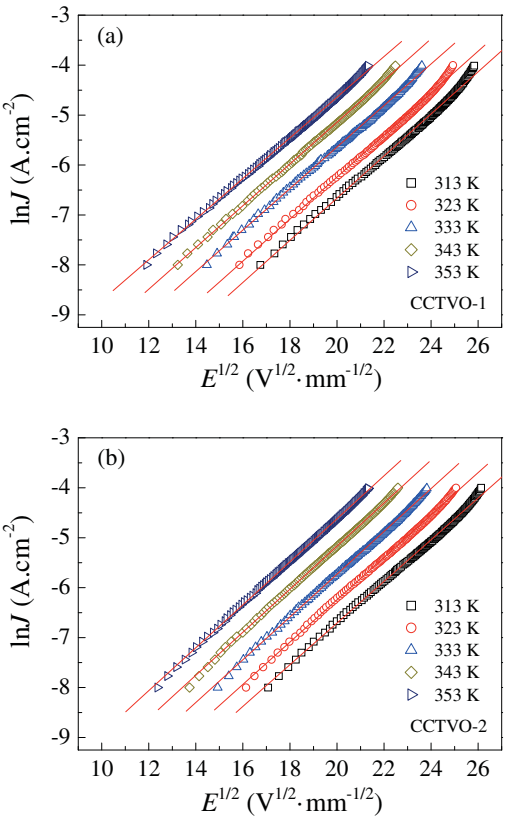


Fig. 6. (Color online) Plots of $\ln J$ vs $E^{1/2}$ for (a) CCTVO-1 and (b) CCTVO-2 ceramic samples.

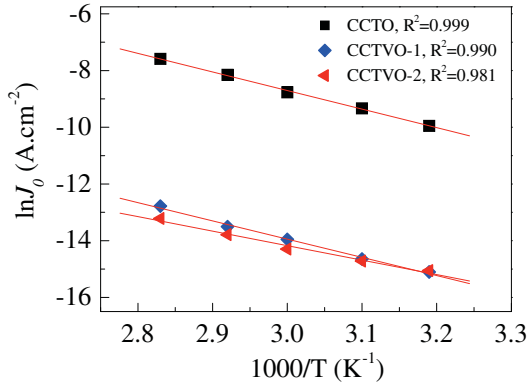


Fig. 7. (Color online) Plots of $\ln J_0$ vs $1000/T$ for $CaCu_3Ti_{4-x}V_xO_{12}$ ceramic samples; the solid lines are fitted results obtained using Eq. (4).

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4. Conclusions

In conclusion, we have successfully prepared nanocrystalline $CaCu_3Ti_{4-x}V_xO_{12}$ ($x = 0$, 0.025, and 0.05) powders with particle sizes of 100–200 nm. It was found that the grain size of CCTO ceramics increased slightly as V doping ion concentration increased. ε' decreased slightly as V concentration increased. Substitution of V can improve the non-ohmic properties of CCTO ceramics. By impedance spectroscopy analysis and investigation of non-ohmic properties at different temperatures, it was shown that R_{gb} and E_b were significantly increased by substitution of V ions, whereas, electrostatic potential barrier height at grain boundaries decreased slightly.

Acknowledgments

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Controlling ettringite formation in FBC fly ash geopolymer concrete

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ABSTRACT

Fluidized bed coal combstion (FBC) is extensively used in small self-generation power plants. The fly ash obtained from this FBC process contains high quantity of calcium and sulfate compounds which hinders its use in the construction industry. In addition, its reactivity is low and additional source material or additive is, therefore, needed to increase the reaction. This research studied the use of $Al(OH)_3$ and high concentrations of NaOH to control ettringite formation in the FBC fly ash geopolymer. Two replacement levels of 2.5 wt.% and 5.0 wt.% of $Al(OH)_3$ and three NaOH concentrations of 10, 12 and 15 M were used in the study. Results indicated that the NaOH concentration affected the ettringite formation and strength of the FBC geopolymer. No ettringite was formed at high NaOH concentration of 15 M which helped the dissolution of calcium sulfate and formed the additional calcium hydroxide. The subsequent pozzolanic reaction led to strength gain of the geopolymer. For 15 M NaOH, the addition of 2.5 wt.% $Al(OH)_3$ promoted the reaction and formed a dense matrix of alumino silicate compound. Relatively high 7-day compressive strength of 30 MPa was obtained.

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1. Introduction

Fluidized bed combustion (FBC) is an efficient and environmentally-friendly technique for coal combustion process. This FBC technology is growing particularly in small enterprises due to the reduction of SO_2 and NO_x gasses released in flue gas [1]. Generally, the bed is operated at 800–900 °C, the low temperature prohibited the formation of nitrogen oxides (NOx) from the combustion air. The FBC system also permits the removal of sulfur dioxide (SO_2) from the combustion of high-sulfur fuels by the addition of sulfur absorbents such as limestone in the bed. A wide range of fuels including high-ash or high-moisture content fuels could be handled and efficiently burnt using the FBC process. The fly ash from fluidized bed combustion (FBC) contains high amount of $CaSO_4$ and CaO due to the use of lime for the SO_2 capture. These compounds hindered the use of FBC fly ash in construction since concrete with high $CaSO_4$ is prone to unsoundness [2]. Substantial amount of FBC fly ash is, therefore, disposed at landfill sites and thus needed to be utilized.

Ettringite formation, after the concrete had hardened, can promote concrete deterioration [3]. Ettringite is basically a hydrated sulfate of calcium and aluminum ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) and exists in various forms, particularly as parallel needles of differing sizes in pores [4]. Ettringite is formed from the reaction between the anhydrite ($CaSO_4$) and residual dehydroxylated mineral (alumino-silicate) found in coal. This growth can lead to a deleterious effect on the mechanical properties of the material. For the FCB fly ash where sufficient $CaSO_4$ and alumino-silicate are present, its utilization as binder can lead to the formation of ettringite within the solidified matrix resulting in a significant structural problem. The needle-like crystals of ettringite growth exerts substantial internal stresses resulting in microcracking, swelling, and eventual failure [5]. However, in environments of high alkali hydroxide concentration, the formation of ettringite can be deterred [6].

Many researches indicate that the FBC-fly ash can be used as a source material for making geopolymer [7–9]. The geopolymer is an alumino-silicate compound prepared by incorporating high alkaline and sodium silicate solutions under low heat curing. This alumino-silicate cementitious compound possesses good mechanical properties viz., high compressive strength and stability at temperature up to 1400 °C [10].

Addition of alumina in geopolymer system resulted in increased aluminate ($Al(OH)_4^-$) species leading to a faster rate of condensation [11]. In the presence of sufficient quantity of calcium, calcium alumino-silicate hydrate (C–A–S–H) is formed [12,13]. FBC fly ash contains significant amount of calcium and sulfate, it is expected that addition of the alumina results in the formation of both C–A–S–H and ettringite. Formation of ettringite plays an important role in the FBC fly ash geopolymer system.

Since the calcium compounds ($CaSO_4$ and CaO) in FBC fly ash could result in the formation of ettringite in the geopolymer, this research attempted to control the formation of the ettringite by

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preparing the FBC-fly ash geopolymer with various NaOH concentrations and addition of $Al(OH)_3$. $Al(OH)_3$ is commercially available and when dissolved it produces strong alkali solution forming aluminate ion, $Al(OH)_4^-$. This ion can react with silica to form additional alumino-silicate compound, and it reacts with calcium compounds present in FBC fly ash to form calcium aluminate hydrate (C–A–H). This would result in the geopolymer formation with strength gain and good physical properties.

2. Experimental procedure

2.1. Materials

FBC-fly ash obtained from a small power plant in Thailand was used as a source material for geopolymer synthesis. Typical chemical composition of this FBC fly ash determined by X-ray fluorescence (XRF) is shown in Table 1. The major compounds were lime (CaO), quartz (SiO_2), alumina (Al_2O_3) and anhydrite ($CaSO_4$). The FBC-fly ash contained high CaO content of 42.2% due to the addition of lime to extract sulfate oxides. This fly ash had the particle size (D_{50}) of 24 μm with a specific gravity of 2.34. The FBC-fly ash reactivity was low and the glassy phase content was also low owing to the low burning temperature of 900 °C. Aluminum hydroxide ($Al(OH)_3$) was also used as the additional source of aluminum compound for making geopolymer. Sodium hydroxide (NaOH) pellets were dissolved with distilled water to provide the NaOH solutions of 10, 12 and 15 M concentrations. The sodium silicate solution (Na_2SiO_3) with 9% Na_2O and 30% SiO_2 by weight was used as the external source of SiO_2. River sand with specific gravity of 2.65 and fineness modulus of 2.8 was employed to prepare the mortar for strength test in accordance with ASTM C109.

2.2. Geopolymer preparation

The effect of NaOH concentration on the ettringite formation was studied by varying the NaOH concentration. For preliminary study, 15 M NaOH was selected to prepare the $Al(OH)_3$-FBC fly ash blend geopolymer as it was reported that there was no ettringite formation [5]. 2.5 wt.% and 5.0 wt.% $Al(OH)_3$ were incorporated to make the FBC fly ash geopolymer [14]. The Na_2SiO_3-to-NaOH mass ratio of 2 was used for the study. The NaOH and Na_2SiO_3 were thoroughly mixed together and then added to the powdery raw material. Owing to the high water absorption of the sample, the high powder-to-liquid mass ratio of 1.5 was used. The mix proportion is tabulated in Table 2. The mixture was continuously mixed in a pan mixer for 2 min before casting in 5-cm cubic acrylic mold and vibrated for 10 s to remove the air bubbles. The specimens were then covered with clingfilm and cured at 60 °C for 24 h.

For the geopolymer mortar strength test, sand was added to the paste mixture with the sand to powder ratio of 2:1 (by weight) and mixed for another 2 min. Casting and curing condition were similar to the paste preparation. Compressive strength test was performed at the ages of 7, 30 and 90 days. The results were reported as the average of three samples.

Table 1
Chemical composition and LOI of FBC fly ash.

Chemical composition	(wt.%)
SiO_2	21.0
Al_2O_3	8.1
Fe_2O_3	6.9
CaO	42.2
SiO_3	14.8
Other oxides	6.0
Loss on ignition (LOI)	1.0

2.3. Geopolymer testing

The geopolymer pastes were prepared for the XRD, TGA and SEM analyses. In addition, the degree of reaction was determined both on geopolymer and starting materials. This method was based on the dissolution of the powdery sample in 2 M HCl and 3 wt.% Na_2CO_3 [14–16]. 2 M HCl was used to dissolve CaO and MgO from the hydrated product, and 3 wt.% Na_2CO_3 was then employed to dissolve SiO_2, Al_2O_3, and Fe_2O_3. The remaining portion was the unreacted fly ash residue. The degree of reaction was calculated from the following equation:

$$\text{Degree of reaction} = \frac{m_{\text{sample}} - m_{\text{residue}}}{m_{\text{sample}}} \times 100 \quad (1)$$

where m_{sample} is the weight of powdery sample (g); m_{residue} the weight of dried residue (g).

The degree of reaction of the "blank" (raw materials before mixing with alkali solutions) was also determined. The degree of reaction of blank was then subtracted from those of geopolymers to obtain the corrected degree of reaction. The results were reported as an average of three samples.

3. Results and discussion

3.1. Morphological study of geopolymer pastes

The effect of NaOH concentration on ettringite formation was presented in XRD pattern as shown in Fig. 1. The XRD of FBC fly ash showed numerous sharp peaks of crystalline phases. Calcium and silica were the main compounds detected in the ash. Low reactive FBC fly ash could be converted to a more amorphous material by the geopolymerization process. The broad peaks and peak shift were found with the geopolymer pastes at 24–38° 2θ, indicating that the geopolymerization reaction resulted in the highly disorder material in the form of amorphous gel with some crystalline products [7,8]. This corresponded to the detection of aluminosilicate in the geopolymer matrix. New compounds of ettringite, calcium-silicate, and calcium-alumino-silicate were also formed. Ettringite was found quite readily in the sample with NaOH concentration of 10 M at 41° and 43° 2θ. Less ettringite was formed for the concentration of 12 M NaOH with the presence of peak at only 43° 2θ. For the highest concentration of 15 M NaOH, ettringite could not be detected and the peaks at 41° and 43° 2θ disappeared. It was previously reported that difficulty of ettringite formation was found in the presence of high alkali hydroxide concentration [6]. The high NaOH concentration could reduce the amount of gypsum in the FBC fly ash system resulting in the gypsum dissolution via the double decomposition reaction as shown in Eq. (2)[17].

$$CaSO_4 \cdot 2H_2O(s) + NaOH(aq) \rightarrow 4Ca(OH)_2(s) + Na_2SO_4(aq) \quad (2)$$

Sodium hydroxide, thus, promoted gypsum dissolution and the formation of calcium hydroxide. As gypsum dissolved in the NaOH solution, the concentration of both calcium and sulfate ions increased leading to the precipitation of calcium hydroxide ($Ksp = 7.9 \times 10^{-6}$). Therefore the amount of calcium hydroxide formed could limit the ettringite formations and thus allowing the formation of other phases [17].

From the result, 15 M NaOH was selected as the alkali solution to prepare the $Al(OH)_3$-FBC fly ash blend geopolymer. $Al(OH)_3$ was then incorporated to the FBC fly ash geopolymer. Two dosages of 2.5% and 5.0% of $Al(OH)_3$ by weight were blended with FBC fly ash and used as the source materials for making geopolymer. The results of XRD pattern of blend geopolymer pastes are shown in Fig. 1. The incorporation of $Al(OH)_3$ resulted in the formation of the alumino-silicate compound at 34° 2θ. At high $Al(OH)_3$ content

Table 2
Mix proportion of geopolymers (g).

Sample	% $Al(OH)_3$	Fly ash	$Al(OH)_3$	Na_2SiO_3	NaOH	NaOH concentration (M)
100FBC	0	40	–	40	20	10/12/15
2.5Al	2.5	39	1	40	20	15
5Al	5	38	2	40	20	15

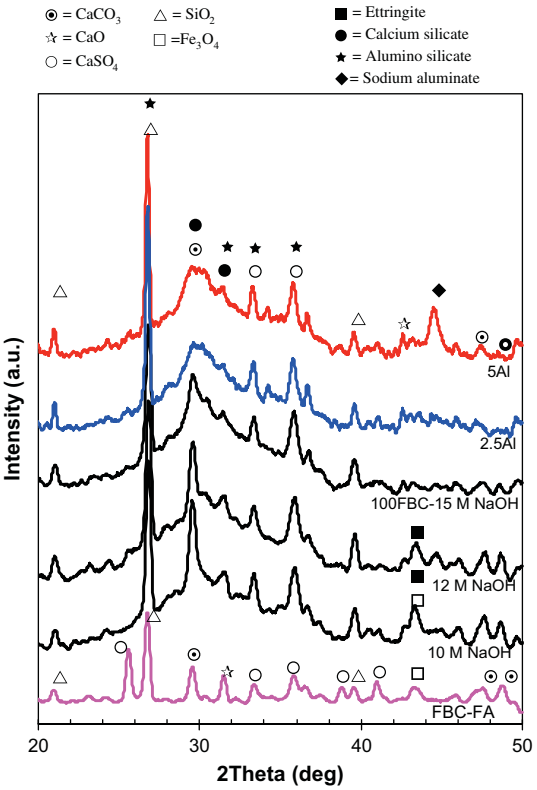


Fig. 1. XRD pattern of as-received FBC, FBC geopolymers and blend geopolymers prepared with 15 M NaOH.

of 5 wt.%, sodium-aluminate compound was detected in the composite with a prominent peak at 44.5° 2θ. With high alkaline concentration, this compound could subsequently convert to zeolite as an intermediate phase and could weaken the geopolymer.

3.2. Compressive strength of geopolymer mortars

The results of compressive strength of FBC fly ash geopolymer mortar are presented in Fig. 2. The 7-day strengths of FBC fly ash geopolymers were low at 7, 8 and 12 MPa for the mixes with 10, 12 and 15 M NaOH, respectively. This was due to the low reactive amorphous phase and high crystallinity of the as-received starting material. The compressive strength increased with the curing age owing to the high calcium content of FBC fly ash and the formation of calcium silicate hydrate (C–S–H) in the composite. In addition to alumino silicate compound, C–S–H was another significant factor enhancing the strength of FBC fly ash geopolymer. The leaching of minerals such as silicon and aluminum ions occurred when fly ash came into contact with NaOH and sodium silicate solutions [16] leading to the formation of calcium silicate and alumino-silicate gels. The calcium silicate hydrate (C–S–H) co-existed with the geopolymer products [18,19] and helped to develop the strength of geopolymer as a function of time. The increase in the NaOH concentration led to the higher strength gain since high NaOH concentration could better leach out the Si^{4+} and Al^{3+} ions

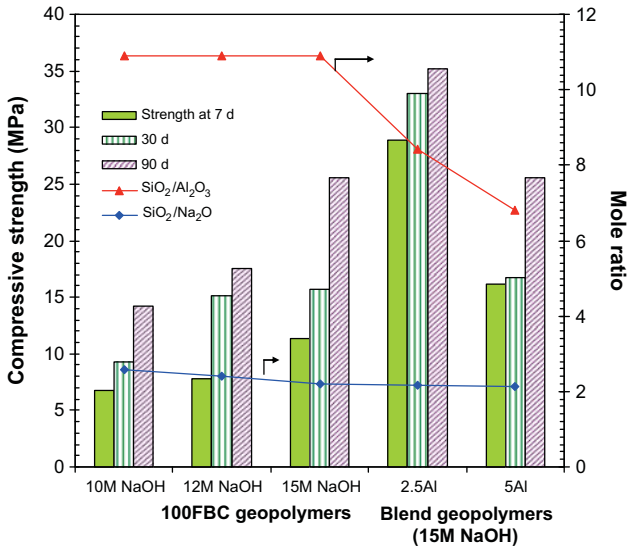


Fig. 2. Compressive strength of geopolymers.

resulting in the better formation of geopolymer gel [20]. The highest concentration of 15 M NaOH resulted with the geopolymer having a 90-day compressive strength of 26.0 MPa. In addition, the change in the NaOH concentration affected the SiO_2/Na_2O ratio. The increase in the NaOH concentration resulted in low SiO_2/Na_2O ratio and led to the formation of solid sodium silicate compound which was a weak compound and contributed to a relatively low strength matrix [14].

Compressive strengths of $Al(OH)_3$-FBC blend geopolymer prepared with 15 M NaOH are also presented in Fig. 2. Addition of 2.5 wt.% of $Al(OH)_3$ enhanced the strength of the geopolymer owing to the increase in the alumina which led to the reduction of the SiO_2/Al_2O_3 mole ratio. The higher Si/Al ratio gave geopolymer with a relatively low strength [21]. For the incorporation of 2.5 wt.% of $Al(OH)_3$, the strength of geopolymer at 90 days was thus increased to 36 MPa. The aluminum ion from $Al(OH)_3$ reacted with silicon ion to form the additional alumino-silicate gel. However, the incorporation of the high amount $Al(OH)_3$ of 5 wt.% resulted in the reduction of the strength of the geopolymer and the strengths were similar to the geopolymer without $Al(OH)_3$. The excess aluminum ion reacted with NaOH solution and formed the sodium aluminate compound as detected in the XRD pattern and it seems that this lowered the geopolymer strength.

3.3. Microstructural study

The results of microstructure study of FBC fly ash and geopolymers are shown in Fig. 3. The composite consisted of the unreacted fly ash particles, geopolymer matrix and other compounds. The needle-like ettringite was found in FBC fly ash geopolymer prepared with 12 M NaOH and less (Fig. 3a) and was in accordance with the XRD result. Ettringite was observed in crack and void of the geopolymer matrix. It could be converted to calcium aluminate monosulfate in the presence of moisture and high content of

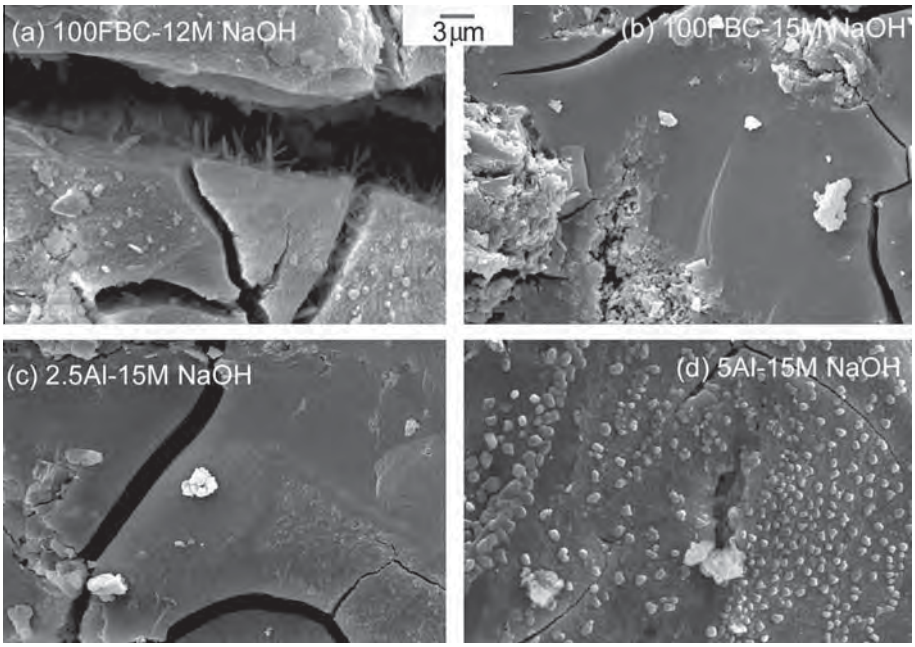


Fig. 3. SEM micrographs of geopolymer pastes at the age of 90 days.

calcium sulfate in the matrix. For the FBC fly ash geopolymer prepared with 15 M NaOH, no ettringite formation was observed (Fig. 3b). As mentioned, the high NaOH concentration helped the dissolution of calcium sulfate and formed calcium hydroxide. The pozzolanic reaction could subsequently carry out through the reaction between this calcium hydroxide and silica and alumina from the FBC fly ash particles resulting in more C–S–H in the matrix. With 2.5% $Al(OH)_3$, the prepared sample with 15 M NaOH also showed the dense and homogeneous matrix with no sign of ettringite formed in the cracks and voids (Fig. 3c). For the incorporation of 5 wt.% of $Al(OH)_3$ with 15 M NaOH, the matrix consisted of sodium silicate (Fig. 3d) and excess gibbsite ($Al(OH)_3$) with a small amount of cross linked geopolymer leading to a lower strength matrix [14]. Sodium aluminate zeolite could be found as indicated by the XRD peak at 44.5° 2θ.

3.4. Degree of reaction

Fig. 4 shows the degree of reaction of blend geopolymer pastes prepared with 15 M NaOH. The test was based on the dissolution of product, the remaining unreacted fly ash was determined. The FBC fly ash geopolymer has the degree of reaction of 21.9%. With $Al(OH)_3$ content of 2.5%, more products were formed in the composite leading to less unreacted material remaining in the sample. For the high dosage of 5% of $Al(OH)_3$, excess $Al(OH)_3$ was available and was difficult to be dissolved in chemical reagents. The degrees of reaction were 24.3% and 23.7% respectively for the samples with 2.5% and 5.0% $Al(OH)_3$. The high degree of reaction of the geopolymer with 2.5% $Al(OH)_3$ agreed with the results of strength in Fig. 4. The optimum $Al(OH)_3$ content was, therefore, 2.5% by weight of the powder and this mix gave a dense matrix with high degree of reaction and high strength.

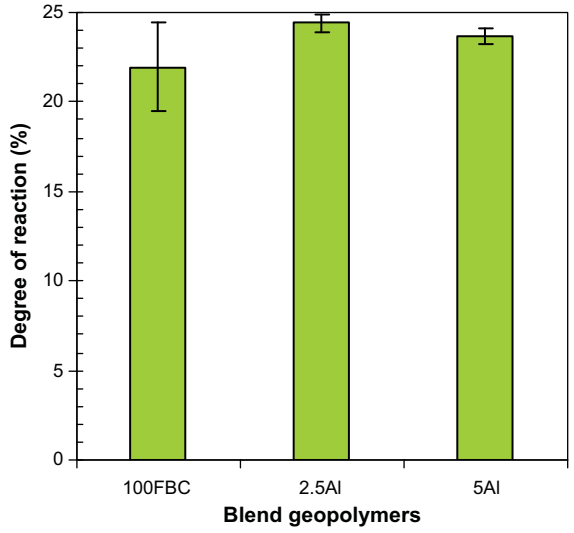


Fig. 4. Degree of reaction of geopolymer pastes at 90 days.

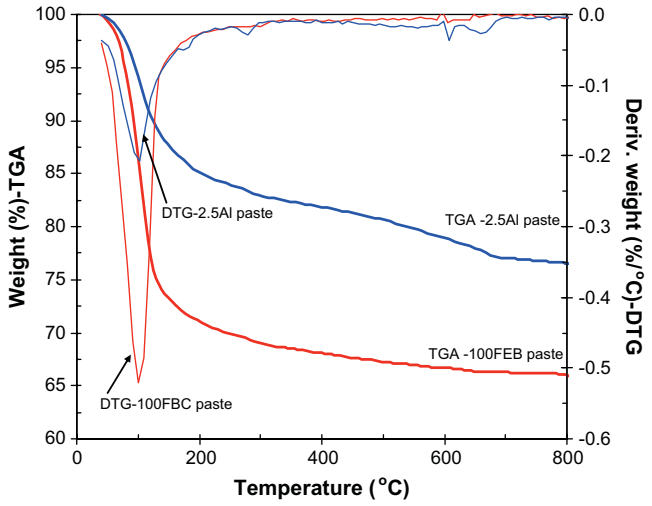


Fig. 5. TGA/DTG curves of geopolymer pastes at 90 days.

3.5. Thermal stability of geopolymers

Thermal stability of geopolymer pastes was measured by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG), results are shown in Fig. 5. TGA/DTG monitored the weight change during heating of specimen. FBC geopolymer showed higher weight loss than the 2.5Al blend geopolymer. This was due to the reaction between free lime in FBC fly ash and $Al(OH)_3$ in base condition forming the more binding materials (i.e. aluminosilicate and calcium aluminate compounds) in matrix. Weight loss was found at 100 °C owing to the evaporation of water. Two peaks at 300 and 580 °C, respectively, presented the starting and finishing dehydroxylation of $Al(OH)_3$. Less decomposition of $Ca(OH)_2$ at 400 °C indicated that calcium compound reacted with aluminate ion and resulted in more complex compounds, i.e. calcium aluminate and alumino silicate compounds.

4. Conclusions

Based on the results of this study, the following conclusions could be drawn.

The concentration of NaOH affected the ettringite formation in FBC fly ash geopolymer. For NaOH concentration of 10 M and 12 M NaOH, the ettringite was detected in cracks and voids of the geopolymer matrix. With NaOH concentration of 15 M, the dissolution of calcium sulfate was facilitated resulting in the formation of calcium hydroxide. This resulted in the pozzolanic reaction and led to strength gain of the geopolymer. The incorporation of 2.5 wt.% of $Al(OH)_3$ in FBC fly ash geopolymer promoted the reaction and provided dense and homogeneous matrix with the formation of additional alumino-silicate compound. However, the high dosage of 5 wt.% of $Al(OH)_3$ resulted in excess $Al(OH)_3$ and formed sodium aluminate which weakened the geopolymer. FBC fly ash utilization in geopolymer offers a new effective method to recycle FBC fly ash and an alternative cementitious material for non-structural member which does not require high strength products such as pavement, block and wall panel.

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Pressed lightweight concrete containing calcined diatomite aggregate

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HIGHLIGHTS

- Coarse diatomite aggregate calcined at 1000 °C contributed to high strength.
- Fine diatomite aggregate calcined at 600 °C also gave high strength.
- Pressed lightweight concrete gave 28-day compressive strengths of 7–12 MPa.
- Concretes with unit weight of 1000–1200 kg/m^3 were obtained.

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ABSTRACT

Diatomite in its natural form possesses low reactivity and is a weak material. Calcination rids of the burnable elements and enhances the properties of diatomite. This research studies the properties of pressed lightweight concrete containing calcined diatomite aggregate. The diatomite was crushed and classified as fine, medium and coarse aggregates and then calcined at 400–1000 °C for 4 h. The pressed lightweight concretes with 28-day compressive strength of 7.8–12.9 MPa, density of 1000–1200 kg/m^3, porosity of 58–61%, water absorption of 61–72% and thermal conductivity of 0.15–0.19 W/mK were obtained. The light weight and high strength blocks were obtained with the use coarse diatomite aggregate obtained from high calcined temperature of 1000 °C and the use of fine diatomite aggregate obtained from calcination temperature of 600 °C. At the high temperature of 1000 °C, the coarse aggregate was stable and strong and this contributed to the strength of the pressed lightweight concrete. At the calcination temperature of 600 °C, the fine diatiomite aggregate was reactive. Calcined diatomite is a suitable lightweight aggregate for making pressed lightweight concrete blocks.

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1. Introduction

Lightweight concrete is concrete with density less than normal concrete and not exceeds 1840 kg/m^3 [1].The production of lightweight aggregate concrete has been expanding. It includes no-fines concrete of low density of 400–1200 kg/m^3 for block production and of 1000–1840 kg/m^3 for structural concrete. The types of lightweight concrete are related to the availability of lightweight aggregate [2]. By the methods of production, lightweight concretes are classified into three types (a) lightweight concrete with porous lightweight aggregate of low apparent specific gravity (b) lightweight concrete with large voids within the concrete or mortar mass (c) lightweight concrete with no fine aggregate [3].The use of lightweight concrete blocks and structure lightweight concrete in construction can reduce the cost of construction as lightweight concrete reduce the dead load, cross sectional area, and amount of reinforcement of concrete structure.

Lightweight aggregate concrete (LWAC) has been the subject of investigations for many years [4,5]. They are mostly used for masonry wall as well as structural concrete because of the high strength to weight ratio, low coefficient of thermal conductivity and good sound insulation characteristic due to air voids in the lightweight aggregate [6]. Lightweight aggregate (LWA) are from either natural source such as perlite, diatomite, and pumice or from manufacturing such as expanded clay, expanded shale and sintered fly ash.

Diatoms were unicellular algae and probably the most widespread group of plants on the earth. There are more than twenty-five thousand species of diatoms with no two having the same morphology [7]. When the diatoms died, the tiny shells sunk, and over the centuries and formed thick layers. Eventually these deposits were fossilized and compressed into a soft, chalky rock that is now called diatomaceous earth [8]. Diatomaceous earth or diatomite is light in weight due to its cellular structure and high porosity [9] and possesses low thermal conductivity, but it is a rather soft material with low reactivity [10]. The uncalcined lightweight diatomite aggregate was used in making light weight

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concrete with reasonable strength of 2.5–8 MPa with unit weight of 900–1190 kg/m^3 [11]. Calcination of fine diatomite at 700 °C results in dehydroxylation of clay minerals and enhances its pozzolanic reactivity [9]. Thus, this research explores the use of diatomite in making lightweight aggregate by improving its properties with calcination at different temperatures. The effect of aggregate gradations on the properties of lightweight concrete was also studied. The pressed lightweight concrete blocks containing calcined diatomite should be suitable for use in masonry wall. In addition, the knowledge obtained should also be useful for the future study for its use in structural lightweight concrete as specified in ACI 213 [11].

2. Experimental program

2.1. Materials

Materials used in this research consisted of Type I Ordinary Portland Cement (OPC) and diatomite (DE) from Lampang province in the north of Thailand. Diatomite was crushed and calcined at 400, 600, 800, and 1000 °C for 4 h [9] and then classified as fine aggregate (FA), medium aggregate (MA) and coarse aggregate (CA) with particle sizes ranging between 0.001–1.18, 1.18–4.75, 4.75–12.5 mm, respectively as shown in Fig. 1. Chemical composition and mineralogical composition of as-received DE were determined using X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. The differential thermal analysis (DTA) and thermal gravitation analysis (TGA) were performed on DE to investigate its physical and chemical changes during heating. The physical properties of materials are shown in Table 1 and the chemical compositions of DE are shown in Table 2. The increase in fineness modulus resulted in increase in the water absorption and decrease in bulk density of DE. The water absorption of FA, MA, and CA were 61%, 102%, and 112% and bulk densities were 600, 425, and 417 kg/m^3, respectively. The sum of SiO_2, Al_2O_3, and Fe_2O_3 of diatomite aggregate increased with the increase in calcined temperature. This was due to the reduction in the loss on ignition (LOI) of DE with the increase in calcined temperature. The loss on ignition (LOI) of uncalcined DE (UC) was 9.1% which was below 10.0% as described in ASTM C 618 [12] for class N pozzolan. The LOIs of DE calcined at 400, 600, 800, and 1000 °C reduced to 7.0%, 4.5%, 1.0% and 0.60%, respectively. The reduction in the burnable elements improved the chemical composition of DE.

2.2. Mix proportion

2.2.1. Effect of calcined temperature

The FA, MA were calcined at 600 °C to obtain the pozzolanic property of DE [13] and CA was calcined at 400, 600, 800, and 1000 °C (CA400, CA600, CA800, and CA1000) to study the effect of the calcined temperatures on the coarse aggregate.



Fig. 1. Coarse, medium and fine DE aggregates.

Table 1
Physical properties of materials.

Materials	OPC	FA	MA	CA
Specific gravity	3.16	1.85	2.27	2.45
Median particle size (μm)	14.6	–	–	–
Particle size (mm)	–	0.001–1.18	1.18–4.75	4.75–12.5
Fineness modulus	–	1.33	4.02	5.75
Density (kg/m^3)	1440	600	425	417
Water absorption (%)	–	61	102	112

Table 2
Chemical composition of DE (by weight).

Chemical compositions (%)	Calcined temperature				
	Uncalcined	400 °C	600 °C	800 °C	1000 °C
SiO_2	74.30	76.09	78.40	78.29	79.86
Al_2O_3	8.07	7.98	8.18	9.43	9.01
Fe_2O_3	5.35	5.46	5.19	7.08	6.29
CaO	0.48	0.43	0.47	0.54	0.51
K_2O	1.76	1.89	1.99	2.21	2.28
TiO_2	0.11	0.43	0.51	0.51	0.56
Na_2O	0.15	0.13	0.12	0.17	0.16
P_2O_5	0.11	0.08	0.09	0.11	0.10
BaO	0.04	0.04	0.04	0.04	0.04
MgO	0.47	0.43	0.47	0.56	0.47
LOI	9.10	7.00	4.50	1.00	0.60

2.2.2. Effect of aggregate gradation

To study the effect of aggregate gradation, the FA and MA portions were varied and the CA portion was kept constant at 30%. The effect of the change in the small aggregate portion is larger than that of the large portion [14]. A total of three aggregate gradations with FA:MA:CA ratios of 0:70:30, 30:40:30, and 70:0:30 (0FA, 30FA, and 70FA) were used.

2.3. Details of mixing

All mixtures were made with water to cement ratio (W/C) of 2.0 by mass and diatomite to cement ratio (D/C) of 1.8 by mass. OPC and DE were firstly mixed until the mixture was homogenous which took approximately 1½ min. Afterward, water was added and the mixing was done for another 1½ min. The 50 × 50 × 50 mm cubes were made with a pressed machine with the pressure of 0.85 MPa. The pressing technique with small pressure was adopted as it simulated the manufacturing of concrete blocks without the need to use a large number of molds which requires assembling and cleaning of molds as well as demolding. The specimens were then covered with damp cloth and plastic sheet to prevent moisture loss in a controlled 25 °C room. At the age of 28 days, they were tested for density, compressive strength, water absorption and thermal conductivity. Samples of pressed lightweight concrete for testing are shown in Fig. 2.

2.4. Details of test

2.4.1. Density and compressive strength

The density was determined as described in ASTM C 138 [15]. The density was measured at the ages of 28 days using the compressive strength specimens. After the density determination, the cube specimens were tested to determine the compressive strength in accordance with ASTM C109 [16]. The reported compressive strengths were the average of three samples.

2.4.2. Porosity and water absorption

The cube specimens were tested for porosity and water absorption at the age of 28 days in accordance with ASTM C 642 [17]. The porosity was calculated using Eq. (1) and Eq. (2) was used for the calculation of water absorption.

$$\text{Porosity } (\%) = [(C - A)/(C - D)] * 100 \quad (1)$$

$$\text{Absorption } (\%) = [(B - A)/A] * 100 \quad (2)$$

where A = mass of oven – dry sample in air (g); B = mass of surface – dry sample in air after immersion (g), C = mass of surface – dry sample in air after immersion and boiling (g), and D = apparent mass of sample in water after immersion and boiling (g)

2.4.3. Thermal conductivity

The cube specimens were tested to determine the thermal conductivity at the age of 28 days in accordance with ASTM D 5930 [18].

3. Results and discussion

3.1. Scanning electron microscopy

The results of SEM of DE are shown in Fig. 3. The DE consisted of cylindrical shape particles approximately 10 μm in diameter and 30 μm in length with square cellular structure. The surface consisting of micro-pores made DE very porous and low in density [9,19].

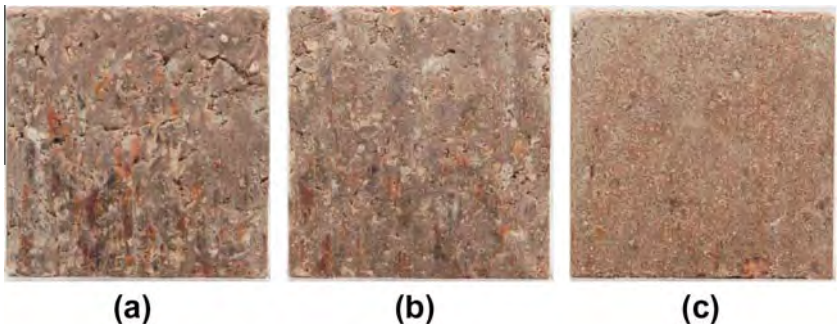


Fig. 2. Pressed lightweight concretes (a) 0FA, (b) 30FA, and (c) 70FA.

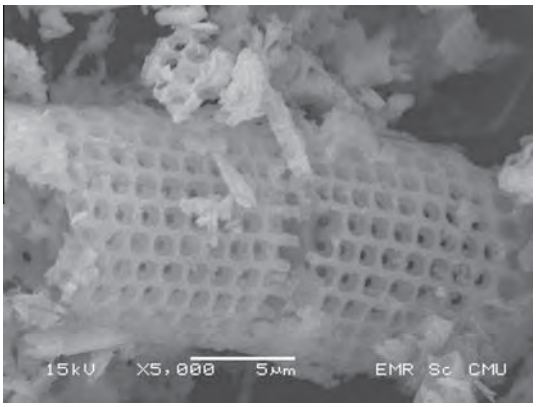


Fig. 3. SEM photomicrographs of diatomite.

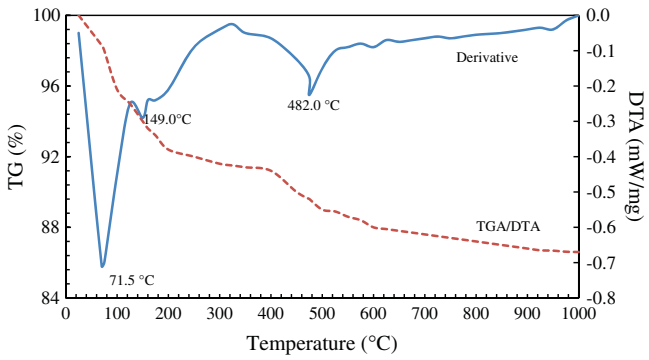


Fig. 4. DTA and TG curves of diatomite.

3.2. Differential thermal analysis (DTA) and thermal gravitation analysis (TGA)

The results of DTA and TGA of diatomite are shown in Fig. 4. The endothermic peaks associated with the loss of adsorbed water on particle surfaces of diatomite were observed at 71.5 °C and 149.0 °C. The other peak at 482.0 °C ascribed the dehydroxylation of clay minerals containing in DE [9]. This, therefore, indicated that the optimum calcined temperature for reactive diatomite should not be higher than 500 °C.

3.3. Mineralogical and morphological composition using XRD

The XRD results of DE are shown in Fig. 5. The DE contained mainly quartz, kaolinite and nontronite. Calcination at 400 °C reduced the peaks of kaolinite and nontronite. At higher temperature

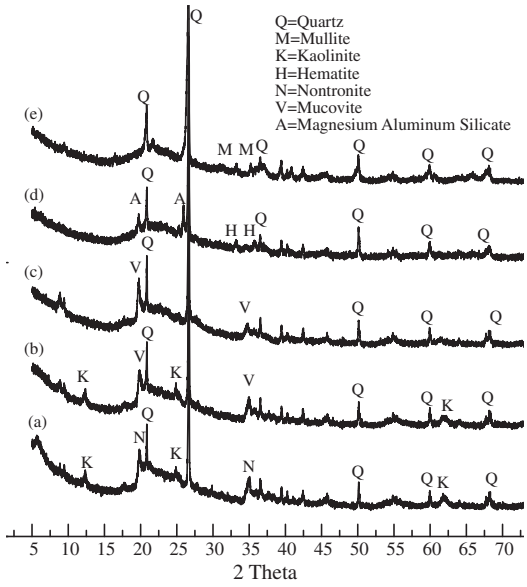


Fig. 5. XRD patterns of DE (a) UC, (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 1000 °C.

of 600 °C, kaolinite and nontronite peaks disappeared. This corresponded to the dehydroxylation of kaolinite. When clay mineral (kaolinite) was calcined at this temperature, it thus became active [13]. This was confirmed by the disappearance of main peaks of kaolinite at 12.5°, 24.8° and 61.8° 2θ. At 800 °C, small amounts of hematite and magnesium aluminum silicate were observed. At 1000 °C, the magnesium aluminum silicate peak disappeared as confirmed by the disappearance of main peaks at 19.8° and 25.8° 2θ. The peaks of mullite at 33.2° and 35.2° 2θ were observed at this high calcined temperature.

3.4. Compressive strength

The results of compressive strength of lightweight concrete containing calcined DE pressed cube are shown in Fig. 6. The compressive strength tended to increase slightly with the increasing calcination temperature of CA up to 800 °C and increased significantly when calcined at 1000 °C. For example, the 28-day compressive strengths of series 70FA mixes with 25, 400, 600, 800, and 1000 °C calcined CA were 8.1, 8.0, 8.6, 8.8, and 12.9 MPa, respectively. At calcination temperature below 500 °C (Fig. 4), the kaolinite (clay) in the uncalcined DE (UC) and CA400 was unstable and could swell when mixed with water [20]. A number of researches suggested the calcined temperatures between 600 and 800 °C as optimum calcined temperature for the pozzolanic property of DE

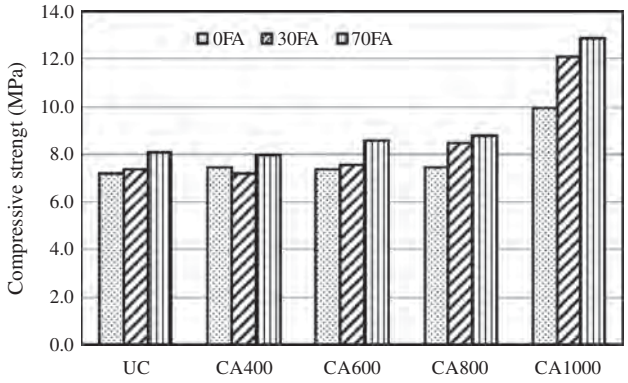


Fig. 6. Compressive strength at 28 days lightweight concrete.

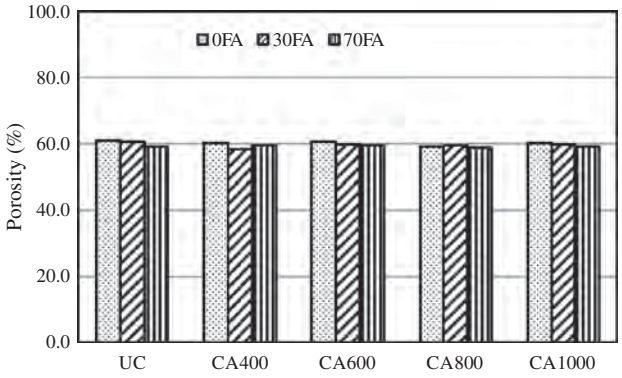


Fig. 8. Porosity at 28 days of lightweight concrete.

[9,19,21]. The CA1000 mix showed the highest compressive strength due to the appearance of mullite which was stable and strong mineral.

With regards to aggregate sizes, the mixes with a high amount of FA showed high compressive strength compared to those with the low amount of FA. For example, the 28-day compressive strengths of series 0FA, 30FA, and 70FA of CA1000 mixes were 10.0, 12.1, and 12.9 MPa, respectively. The use of FA aggregate with high surface area resulted in the better bonding of matrix and aggregate than that of CA and led to an increase in strength [22]. Furthermore, the FA was calcined at 600 °C and thus possessed pozzolanic property which also contributed to the strength development of the lightweight concrete.

3.5. Density

The results of the density of lightweight concretes with calcined diatomite are shown in Fig. 7. The increased in calcined temperature resulted in DE with a slightly reduced density compared with that of the uncalcined DE, due to the calcination of burnable elements [9]. For example, the density of lightweight concretes with UC, CA400, CA600, CA800, and CA1000 of 30FA series were 1313, 1219, 1169, 1222, and 1139 kg/m^3, respectively. The density also increased with the increasing amount of FA due to the relatively high densities of FA of 600 k/m^3 compared with the lower values of MA and CA of 425 and 417 k/m^3, respectively (Table 1). The densities of series 0FA, 30FA, and 70FA mixes with CA1000 were 1070, 1139, and 1238 kg/m^3, respectively. For 70FA series, the high amount of FA filled the space in the matrices and made concrete more compact and stronger than those using low amount of FA.

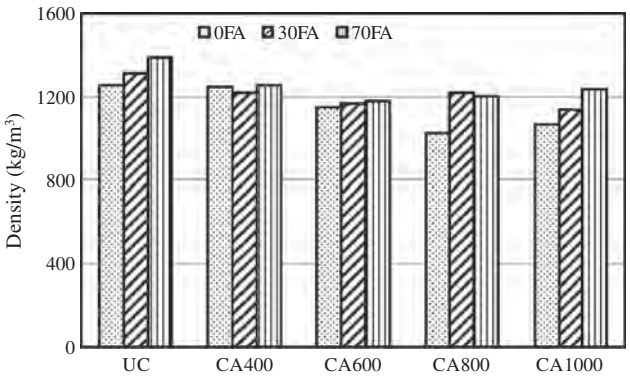


Fig. 7. Density of lightweight concrete at 28 days.

3.6. Porosity and water absorption

The results of porosity are shown in Fig. 8. The porosities at the age of 28 days were not very different and were between 59.0% and 61.2%. The results, however, indicated that the porosities slightly decreased with the increase in the amount of FA. For example, the porosities at 28 days of series 0FA, 30FA, and 70FA of CA1000 mixes were 60.30%, 60.12%, and 59.42%, respectively. The results of water absorption were similar to those of porosity as shown in Fig. 9. There was an indication that the water absorption values reduced with the increase in the amount of FA. The water absorption at 28 days of CA800 mixes of series 0FA, 30FA, and 70FA were 67.46, 66.73, and 66.06%, respectively. This was due to the increase in the surface area and reduction in the porosity of the concrete containing high amount of FA.

3.7. Thermal conductivity

The results of the thermal conductivity of lightweight concretes are shown in Fig. 10. The thermal conductivity slightly decreased with the increasing calcined temperature of DE. For example, the thermal conductivity of the concretes with UC, CA400, CA600, CA800, and CA1000 of series 0FA were 0.184, 0.157, 0.145, 0.130, and 0.151 W/mK, respectively. The reduction was due to the ridding of water molecule and other burnable minerals in aggregate with high calcination temperature [9]. In addition, the increase in calcined temperature of DE resulted in a decrease in density of pressed lightweight concrete and also a decrease in thermal conductivity. The reduction in the thermal conductivity is rather attractive thermal property on this lightweight concrete. For the calcinations at high temperatures of CA600, CA800, and CA1000 mixes, there was an indication that the thermal conductivity increased with the increasing amount of FA.

The thermal conductivity values of series 0FA, 30FA, and 70FA mixes with CA800 were 0.130, 0.148, and 0.159 W/mK, respectively. The thermal conductivity increased with the increasing of FA due to the increases in the filling of voids of small aggregate and the increase in the bonding of the small aggregate and the matrix due to increased surface area and pozzolanic property of the aggregate.

3.8. Relationship of compressive strength, thermal conductivity, density, and calcined temperature

The relationship between compressive strength and calcined temperature of lightweight concrete was presented by Eq. (3) and shown Fig. 11. The compressive strength increased with the increasing calcined temperature [9,19].

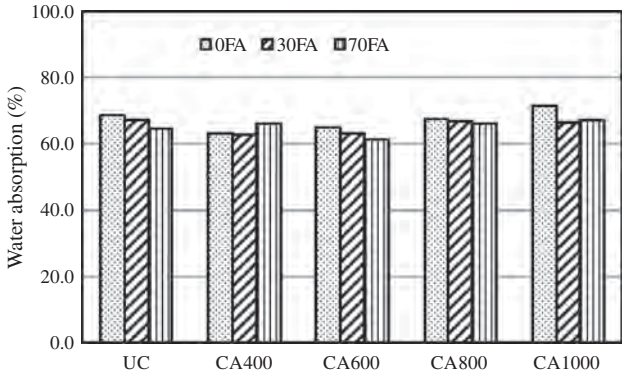


Fig. 9. Water absorption at 28 days of lightweight concrete.

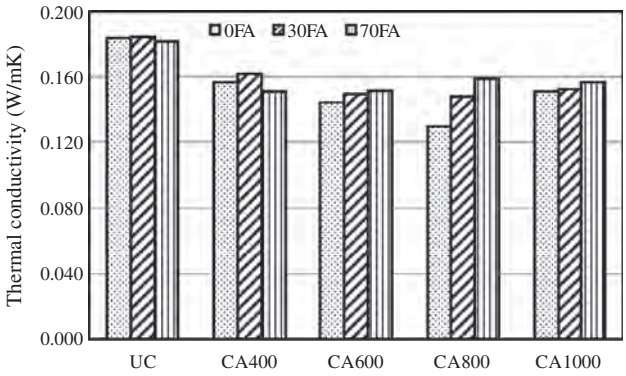


Fig. 10. Thermal conductivity at 28 days of lightweight concrete.

$$f_c' = (1 \times 10^{-0.5})T^2 - 0.0067T + 7.7068 \quad (3)$$

where f_c' is compressive strength (MPa) and T is the calcined temperature of DE (°C).

The relationship between density and thermal conductivity was linearly described by Eq. (4) and is shown in Fig. 12. The thermal conductivity increased with the increasing density [23,24] as the thermal conductivity depends on the density of concrete [25]. The increases in density of pressed lightweight concrete resulted in dense and packed structure and likewise an increase in the thermal conductivity. The values of thermal conductivity were between 0.130 and 0.184 W/mK with the corresponding densities between 1000 and 1200 kg/m^3 and were similar to the previously published results of 0.2–0.3 W/mK for low-strength lightweight DE concrete for thermal insulation [14].

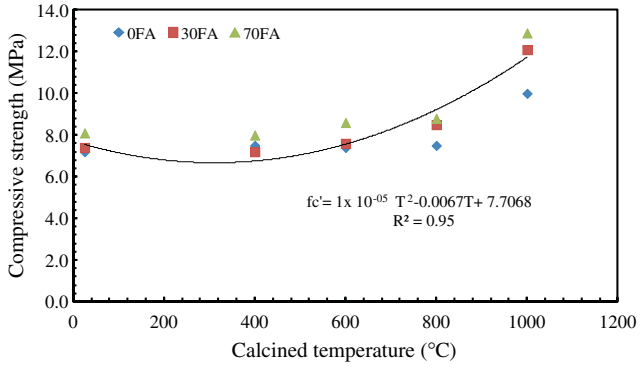


Fig. 11. Relationship of compressive strength and calcined temperature of lightweight concrete.

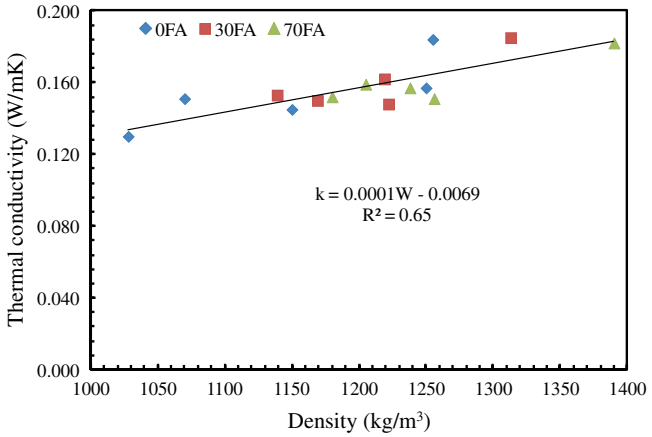


Fig. 12. Relationship between thermal conductivity and density of lightweight concrete.

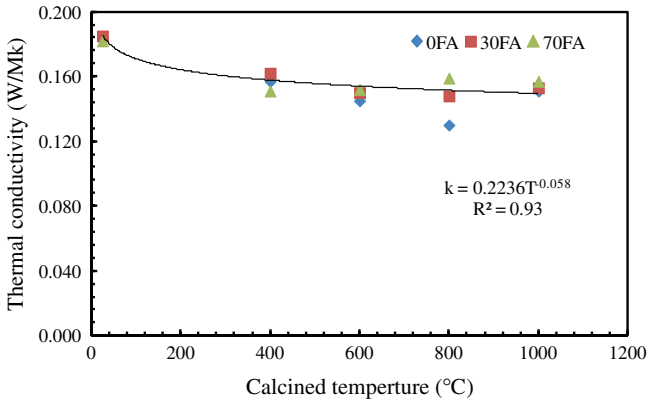


Fig. 13. Relationship between thermal conductivity and calcined temperature of DE.

$$k = 0.0001W - 0.0069 \quad (4)$$

where k is thermal conductivity (W/mK) and W is Density of lightweight concrete (kg/m^3).

In addition, the relationship of thermal conductivity and calcined temperature of DE was obtained from Eq. (5) and shown in Fig. 13.

$$k = 0.2236T^{-0.058} \quad (5)$$

where k is thermal conductivity (W/mK) and T is the calcined temperature of CA (°C).

It was demonstrated that DE could be used to make pressed lightweight concrete with densities of 1000–1200 kg/m^3 and reasonably high strengths of 7.8–12.9 MPa.

4. Conclusion

Based on the obtained data, the following conclusions can be draw.

(1) DTA and TG curves of DE indicated that the optimum calcined temperature for reactive diatomite should not be less than 500 °C which was consistent with XRD results of DE calcined at 600 °C where the kaolinite and nontronite peaks disappeared. At 1000 °C, the appearance of peak of mullite which was stable and strong indicated the strong aggregate.

(2) The use of calcined DE aggregate increased compressive strength, and reduced density, and thermal conductivity compared to those with uncalcined DE. The porosity and water absorption of concrete were less affected and the results of concrete with various calcined temperatures were similar.
(3) The calcined temperatures should be 600 °C for fine and medium aggregate to obtain the pozzolanic property; and 1000 °C for coarse aggregate to obtain good strength.
(4) The use of calcined DE is considered very attractive as the improvement in strength, density and thermal conductivity are very important.

Acknowledgement

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Strength, porosity, and chloride resistance of mortar using the combination of two kinds of pozzolanic materials

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Abstract: This article presents a study on the resistance to chloride penetration, corrosion, porosity, and strength of mortar containing fine fly ash (FA), ground rice husk-bark ash (RB), and ground bagasse ash (BA). Ordinary Portland cement (CT) was blended with a single pozzolan and two pozzolans. Strength, porosity, rapid chloride penetration, immersion, and corrosion tests were performed to characterize the mortar. Test results showed that the use of ternary blends of CT, FA, and RB or BA decreased the porosity of the mortar, as compared with binary blended mortar containing CT and RB or BA. The resistance to chloride penetration of the mortar improved substantially with partial replacement of CT with FA, RB, and BA. The use of ternary blends of CT, FA and RB or BA produced the mortars with good strength and resistance to chloride penetration. The resistance to chloride penetration was higher with an increase in the replacement level due to the reduced calcium hydroxide.

Keywords: mortar; pozzolanic materials; strength; porosity; chloride penetration; agricultural wastes

1. Introduction

Nowadays, researchers are interested in the properties of waste materials from industrial and agricultural production because the waste materials can substitute for some part of cement in order to reduce the amount of cement usage. Several attractive waste materials, such as fly ash, rice husk ash, palm oil fuel ash, and bagasse ash are considered for producing concrete [1-5]. These materials are pozzolanic materials containing silica and/or alumina compounds, which can develop additional pozzolanic reaction. Therefore, it is possible to have an appropriate mix proportion between cement and pozzolanic materials for producing good and strong concrete compared with normal concrete [6]. In addition, the pozzolanic materials can further contribute to the increase in durability of concrete.

In Thailand, industrial and agricultural by-products are used as fuel sources for the generation of power in industrial plants. Residues from the process are waste ashes, such as fly ash, rice husk-bark ash, bagasse ash, and palm oil fuel ash. These ashes cause unpleasant environment for nearby communities. This problem can be solved by adding value to the waste ashes and reuse them. Fly ash is the most used pozzolanic material in the construction industry. The other pozzolans are now receiving more attention, and the studies of the properties of these pozzolans are needed. The purpose of this research is to study and develop the waste ashes for use as pozzolans. The information is critical for the construction industry to accept and utilize these new pozzolans. Besides, the pollution and environmental problems will be alleviated.

2. Experimental

2.1. Materials

Portland cement type I (CT), fly ash (from Mae Moh power plant in Thailand), bagasse ash (from a sugar mill), rice husk-bark ash (from a small power plant), and type-F superplasticizer (SP) were the materials used in this research. Graded river sand passing through a standard sieve

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with the fineness modulus of 2.85 and the density of 2.65 g/cm^3 was used as a fine aggregate. Fine fly ash (FA) was obtained from the classification of original fly ash with 3% retained on the sieve No. 325 (opening 45 μm). Bagasse ash (BA) and rice husk-bark ash (RB) were ground by a ball mill until 3% weight retained on the sieve No. 325.

The physical properties of the pozzolans are given in Table 1. The Blaine finenesses of CT, BA, RB, and FA were 3600, 12500, 12000, and 5800 cm^2/g, respectively. The densities of CT, BA, RB, and FA were 3.14, 2.24, 2.25, and 2.46 g/cm^3, respectively. The median particle sizes of the material used from the finest to the coarsest are given as follows: FA 16 μm, RB 19.5 μm, BA 16.4 μm, and CT 16 μm. The chemical constituents of the pozzolans are given in Table 2. In addition, the SEM images of the materials are shown in Fig. 1.

Table 1. Physical properties of CT, FA, RB, and BA

Raw materials	Median particle size, d_{50} / μm	Retained on sieve No.325 / wt%	Density / (g·cm^{-3})	Blaine fineness / (cm^2·g^{-1})
CT	21	—	3.14	3600
FA	16	3	2.46	5800
RB	19.5	3	2.25	12000
BA	16.4	3	2.24	12500

Table 2. Compositions of CT, FA, RB, and BA **wt%**

Raw materials	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	LOI	SiO_2+ Al_2O_3+ Fe_2O_3
CT	54.98	25.1	5.5	5.9	3.4	0.5	4.7	0.9	—
FA	11.57	45.1	17.2	13.4	6.8	1.8	2.2	2.5	75.7
RB	5.5	76.3	1.6	1.5	0.01	3.9	0.9	8.24	79.4
BA	8.5	64.7	4.8	3.2	0.01	2	0.9	17.5	72.7

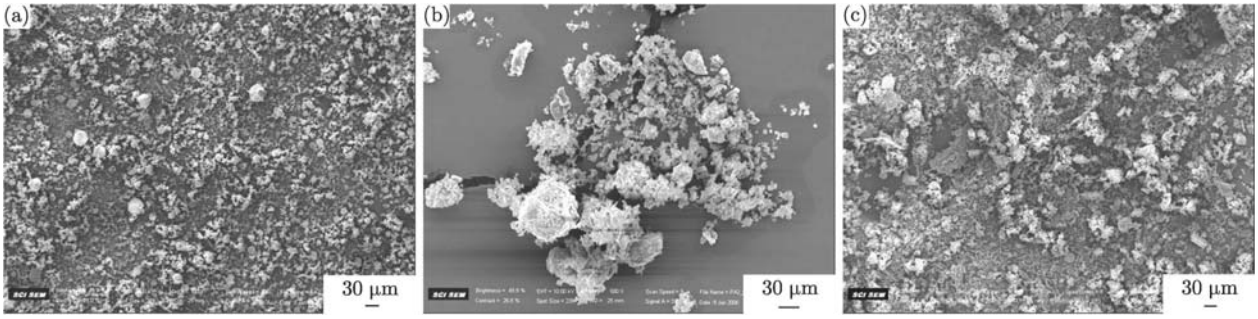


Fig. 1. SEM images of (a) fine FA, (b) ground rice husk-bark ash (RB), and (c) ground bagasse ash (BA).

2.2. Mix proportions and curing

Ordinary Portland cement (CT) was partially replaced with 0-40% of pozzolans. In addition to a single pozzolan, a blend of equal weight portion of FA and RB (FARB) and a blend of equal weight portion of FA and BA (FABA) were also used. Sand-to-binder ratios of 2.75 by weight and water to binder ratio (W/B) of 0.5 were used. SP was incorporated in order to obtain mortar mixes with a similar flow of 110% ± 5% in accordance with ASTM C109 [7]. The cast specimens were covered with polyurethane sheet and damped cloth and placed in a (23 ± 2)°C chamber. They were demolded at the age of 1 d and cured in water at (23 ± 20)°C. The mortar mix proportions are given in Table 3.

2.3. Compressive strength

The 50 mm cube specimens were prepared in accord-

Table 3. Mortar mix proportions

Mix symbol	CT	FA	RB	BA
CT	100	—	—	—
20FA	80	20	—	—
40FA	60	40	—	—
20RB	80	—	20	—
40RB	60	—	40	—
20BA	80	—	—	20
40BA	60	—	—	40
20FARB	80	10	10	—
40FARB	60	20	20	—
20FABA	80	10	—	10
40FABA	60	20	—	20

ance with ASTM C109 [7]. They were tested at the ages of 7, 28, and 90 d. The reported results are the average of three samples.

2.4. Porosity test

The porosity tests were tested at the ages of 7, 28, and 90 d in accordance with ASTM C39 [8] using cylindrical specimens with 100 mm in diameter and 200 mm in height. The cylindrical specimens were cured in water for 7, 28, and 90 d and were cut into 50 mm thick slices discarding the two ends. Then, they were dried at (100 ± 5)°C until their weights were constant. They were placed in the desiccators under vacuum for 3 h before they were immersed in the de-aired distilled water in order to obtain the saturated concrete samples. The porosity is calculated by the following equation:

$$p = \frac{W_a - W_d}{W_a - W_w} \times 100\% \quad (1)$$

where p is the effective porosity, W_a is the saturated specimen weight in air (g), W_d is the dried specimen weight after 24 h in the oven at (100 ± 5)°C (g), and W_w is the specimen weight in water (g). The reported results are the average of two samples.

2.5. Rapid test on resistance to chloride penetration

The ϕ 100 mm × 200 mm cylinders were prepared in accordance with ASTM C39 [8]. They were tested at the age of 28 d. After being cured in water until the age of 27 d, they were cut into 50 mm thick slices with the 50 mm ends discarded. The 50 mm slices were epoxy-coated around the cylinder.

2.5.1. Rapid chloride penetration test

The epoxy-coated specimens were conditioned and tested at the age of 28 d for rapid chloride penetration test (RCPT) in accordance with the method described in ASTM C1202 [9]. The reported results are the average of two samples.

2.5.2. Immersion test

To confirm the results, actual chloride penetration of mortar immersed in NaCl solution was performed. The test set-up was similar to that described in RTA T263 [10] with the exception that ϕ100 mm × 50 mm cylinder and 3% NaCl solution were used. Chloride penetration fronts into mortar specimens were determined using 0.1 mol/L $AgNO_3$ solution [11]. The ϕ100 mm × 50 mm slices were epoxy-coated at the top as well as around the cylindrical slice. The specimens were immersed at the age of 28 d and kept immersed for 30 d.

2.6. Accelerated corrosion test with impressed voltage

The mortar prisms of dimensions 40 mm × 40 mm × 160 mm with embedded steel of 9 mm in diameter and 195 mm in length were used for this test (anode). The steel was secured such that it protruded from the top surface of the prisms by 15.5 mm, thus provided a sufficient mortar cover of 15.5 mm at the bottom and the side of the prism, as shown in Fig. 2. The mortar prisms were subjected to the accelerated corrosion test with impressed voltage using a 5% NaCl solution and a constant voltage of 12 V dc (cathode). The condition of concrete was monitored visually at the interval of 4 h, and the time of initiation of first crack was recorded. This is used as a measurement of the specimen's relative resistance against chloride attack and reinforcement corrosion [12-13].



Fig. 2. Accelerated corrosion test with impressed voltage.

3. Results

3.1. SP requirement of mortar

The test result of the amount of SP required for the mortar component is shown in Table 4. The use of FA reduced the SP requirement as the FA particles were spherical and exerted the ball bearing effect to produce mortar with improved workability. The RB mortar required more SP than CT mortar because of the high fineness and porosity of RB. The SP required for CT, 20RB and 40RB mortars were 0.22%, 0.28%, and 2.5%. Similar increases in the water requirement and/or SP content of RB mortars were reported [14-15]. The increase in the SP requirement was partly due to the high loss of ignition of 8.24% for RB. For the BA, the amount of SP required further increased to 1.2% for the 20BA mortar and 3.8% for the 40BA mortar. The increase in SP requirement was due to the increase in loss on ignition (LOI) as the loss on ignition (LOI) of BA was rather high at 17.5%. For the ternary blended system (TBS), the SP requirements were intermediate between those of single pozzolan mortar (binary blended system, BBS). The SP requirements of FA + RB mortars were between those of FA and RB mortars, and the SP requirements of FA + BA mortars were between those of FA and

Table 4. Compressive strength of mortars

Mix	SP / %	Compressive strength / MPa — Normalized / %		
		7 d	28 d	90 d
CT	0.22	42.9 — 100	45.3 — 100	48.8 — 100
20FA	0.14	37.6 — 88	41.9 — 92	47.4 — 97
40FA	0.10	36.0 — 84	40.7 — 90	46.5 — 95
20RB	0.28	36.6 — 85	40.4 — 89	44.8 — 92
40RB	2.50	35.3 — 82	39.5 — 87	43.5 — 89
20BA	1.20	35.5 — 83	38.9 — 86	42.9 — 88
40BA	3.80	32.2 — 75	38.1 — 84	41.6 — 85
20FARB	0.24	38.1 — 89	41.4 — 91	46.3 — 95
40FARB	1.40	37.6 — 88	40.7 — 90	45.5 — 90
20FABA	0.72	36.1 — 84	41.0 — 91	46.1 — 94
40FABA	2.10	35.2 — 88	39.7 — 91	45.5 — 93

BA mortars.

3.2. Compressive strength

The results of compressive strengths and their percentages are shown in Table 4. The strength of the CT mortar at 7, 28, and 90 d were 42.9, 45.3, and 48.8 MPa, respectively. The strength of FA, RB, and BA mortars tested at 7 d were 83%-88% of that of CT mortar at the same age. At 28 and 90 d, they were 86%-92% and 88%-97%, respectively. The slight increase in the percentage strength was due to the pozzolanic reaction, which contributed to the strength development at the later age. The FA, RB, and BA could be used as pozzolanic materials because their strength indices or strength percentages were higher than 75% as required by ASTM C618 [16].

For the ternary blended mortars (two pozzolans), the test results showed good trend of strength development in comparison with the binary blended (single pozzolan). For example, the normalized 7-d strength of 40FARB mortar was 88%, higher than 84% of 40FA mortar and 82% of 40RB mortar. The normalized 7-d strength of 40FABA mortar was 84%, higher than 75% of 40RB mortar. The use of the ternary blended system (TBS) improved the strength development of mortar through the synergic effect of two pozzolans [17-19].

3.3. Porosity

The porosity percentage in this topic was examined by the division basis of a vacuum pump, as in previous researches [3, 13]. The values of porosity at 7, 28, and 90 d were calculated by Eq. (1), as shown in Fig. 3. The porosity reduced with curing time, which was as expected due to the addition hydration and pozolanic reaction. The incorporation of pozzolans increased the porosity of mortars, and the increase was more with the increase in the replacement level. At the same replacement level, the increase in porosity was the largest with the use of BA, and this was followed by RB and FA. The incorporation of fly ash increased the total porosity of the paste with pore refinement [20]. Similar increase in the porosity of pastes with the use of pozzolans was also reported in Refs. [3, 13]. The RB and BA were very fine pozzolans with some pores remained in the particles [1, 3]. Their uses, therefore, resulted in the increase in the porosity of mortars. The large increase in porosity of BA mortar was due to the large content of loss on ignition (LOI), which consisted of numerous pores in the remainder of the unburnt or not completely burnt portions.

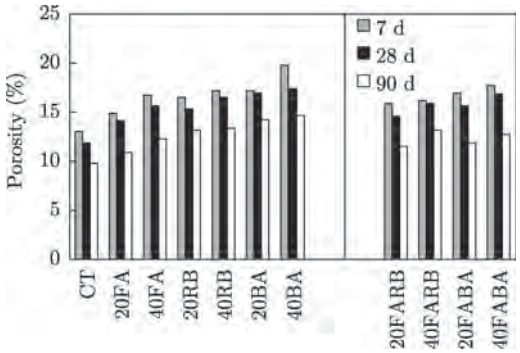


Fig. 3. Porosity of mortars.

For the ternary blended system or TBS (two pozzolans), the porosity of mortars also increased compared with the control mortar. However, the porosity of TBS mortars was significantly lower than that of the corresponding mortar mixed with a single pozzolan (RB or BA) especially at the later age of 90 d. For example, the porosity of 20FARB at 90 d was 11.25%, as compared with 10.5% of 20FA mortar and 13.0% of 20RB mortar. Also, the porosity of 20FABA at 90 d was 11.5%, as compared with 14.0% of 20BA. The reduction in porosity was a result of the FA inclusion and its synergy effect with the other pozzolan. The use of TBS slightly increased the porosity of mortars and possibly led to the strength reduction [20-21]. Khatib and Mangat [22] reported that if the porosity is increased, the strength will be generally decreased. However, the increase in porosity was accompanied with pore refinement, which could offset the strength reduction and enhance the durability of the mortar. The porosities in this

study were in the range of 9.8%-19.8%, and the strengths were between 32.2 and 48.8 MPa.

3.4. Chloride resistance

Three kinds of test methods for resistance to chloride were studied to compare and reinforce the finding.

3.4.1. Rapid chloride penetration test (RCPT)

The rapid chloride penetration test (RCPT) as per ASTM C1202 [9] was conducted for the mortar samples at the age of 28 d. Fig. 4 shows the test specimens' preparation and the test device installation. Normally, the test used electric current and may cause the heat problem especially with mortar specimens with rather high coulomb passed [23]. In this research, the mortar strengths were reasonably high (32.2-42.9 MPa), and the developed heat was acceptable.

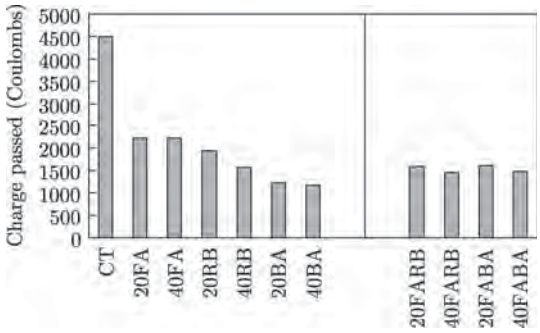


Fig. 4. Rapid chloride penetration test (RCPT) results.

The test results of RCPT are shown in Fig. 4. The chloride penetration was significantly reduced when the pozzolanic materials were used to partially substitute Portland cement. Similar finding was also reported by other researchers [3, 19, 23]. The main composition of RB and BA was SiO_2 [15, 24]. The product derived from the pozzolanic reaction between $Ca(OH)_2$and SiO_2 was calcium silicate hydrate (CSH) [25], which reduced the total $Ca(OH)_2$ in the system and increased the mortar durability. The chloride penetration of CT mortar was 4500 C. The chloride penetration of 20FA and 40FA mortar reduced to 2235 and 2230 C. The incorporation of pozzolans, such as fly ash, reduced the $Ca(OH)_2$ in the system and enhanced the resistance to chloride penetration [23, 26-27]. The use of 20% and 40% RB reduced the chloride penetration of mortars compared with those FA mortars. The chloride penetrations of 20RB and 40RB mortars were 1950 and 1560 C. The chloride penetrations of 20BA and 40BA mortars were the lowest at 1230 and 1180 C. The increases in the resistance to chloride penetration were due to low calcium oxide and high SiO_2 contents of both RB and BA, resulting in increased CSH and reduced calcium in the system. The incorporation of pozzolans resulted in CSH gel with reduced calcium to silicate ratio (C/S ratio) and increased the durability of mortar [28].

For the ternary blended system (TBS), the results, as shown in Fig. 4, indicated that the chloride penetrations of the TBS mortars were also significantly reduced, as compared with that of the CT mortar. The chloride penetrations of the TBS mortars were only 1460-1620 C, which were lower than those of FA mortars and the 20RB mortar.

3.4.2. Immersion test

The results of the chloride depth test are shown in Fig. 5. The results conformed with the RCPT ones and the difference was the order of magnitude. The chloride depth of CT mortar was 18.5 mm and reduced to 17.5 and 16.0 mm with the incorporation of 20% and 40% of FA. The chloride depths of 20RB and 40RB mortars were 17.5 and 15.5 mm and were comparable to those of FA mortars. The incorporation of BA significantly reduced the chloride depth of the mortars and suggested that the most effective pozzolanic material for the chloride resistance was BA.

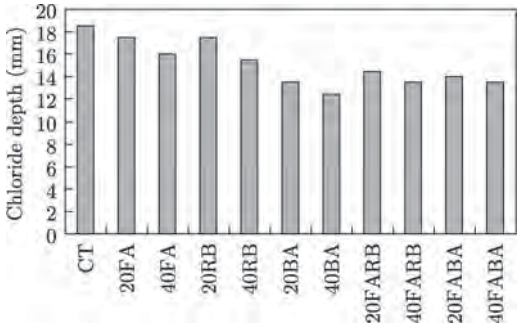


Fig. 5. Chloride depth by immersion test.

For the ternary blended system (TBS), the chloride depths were generally reduced compared with the binary blended system (BBS) mortars. The chloride depths of the TBS mortars were 13.5-14.5 mm, which were only slightly higher than the lowest values of BA mortars of 12.5-13.5 mm. This again confirmed the synergy effect of the fine pozzolans in the ternary system [17, 23].

3.5. Time to the first crack

The test results of time to the first crack of mortars are shown in the Fig. 6. The time to the first crack of CT mortar was 72 h and increased with the incorporation and amount of pozzolan. The times to the first crack of 20FA and 40FA increased slightly to 84 and 90 h compared with that of the control mortar. The times to the first crack of 20RB and 40RB increased further to 98 and 110 h. The times to the first crack of 20BA and 40BA mortars were the highest at 122 and 130 h. The results clearly showed that the incorporation of pozzolans effectively increased the resistance to chloride attack as indicated by the in-

creased time to the first crack. For the binary blended system (BBS), the incorporation of BA was most effective and followed in turn by RB and FA.

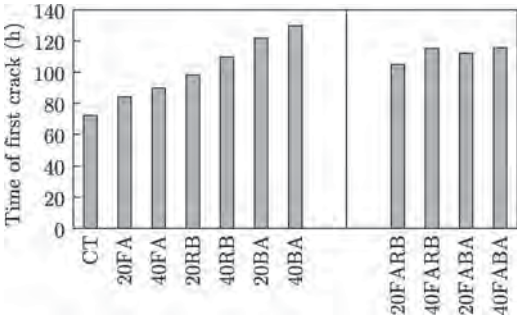


Fig. 6. Time of the first crack of mortars.

For the ternary blended system (TBS), the times to the first crack of the TBS mortars were significantly longer than that of the CT mortars. The times to the first crack of 20FARB, 20FABA, 40FARB, and 40 FABA mortars were 105-116 h compared with 72 h of the CT mortar. The times to the first crack of 20FARB and 40FARB mortars were relatively high and comparable to those of 20RB and 40RB mortars. The times to the first crack of 20FABA and 40 FABA were slightly lower than those of 20BA and 40 BA. The pozzolanic reaction enhanced the durability of pastes through the reduction in pore size and the cavities [29]. The small particles of pozzolan also acted as the nucleation sites for accelerating the hydration reaction in the cement plate [30]. The results confirmed the synergic effect of the two pozzolans system [17]. Fig. 7 shows the mortar prism after the test of time to the first crack.

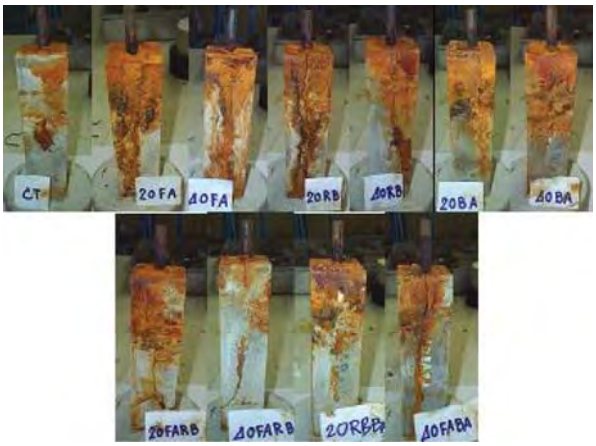


Fig. 7. Samples after the test of time to the first crack.

All test results confirm the finding that the waste ashes derived from the industrial and agricultural production, namely, fly ash, rice husk-bark ash, and bagasse ash are effective pozzolanic materials and suitable for use as supplementary cementitious materials. The use of the ternary blended system (TBS) with FA blended with RB or BA is very attractive. The results suggested a better performance of the ternary blend compared with the binary blend considering strength, porosity, and resistance to chloride penetration.

In summary, the use of the ternary blended system (TBS) improved the strength development of mortars through the synergic effect of two pozzolans. This is due to the better dispersion and filler effect of the finer fly ash despite the higher pozzolanic activity. This makes the mortar denser and, hence, better resistant to the ingression of chloride. The incorporation of fly ash adds additional dispersing effect of cement grains as well as the other fine pozzolan particles. The use of fly ash reduced the SP requirement as the fly ash particles were spherical and exerted the ball bearing effect to produce mortars with improved durability. In addition, the high SiO_2 contents of both rice husk-bark ash and bagasse ash result in increased CSH and reduced $Ca(OH)_2$ in the system. The product derived from the pozzolanic reaction between $Ca(OH)_2$and SiO_2 was CSH, which reduced the total $Ca(OH)_2$ in the system and increased the mortar durability.

4. Conclusions

From the test, it can be concluded that FA, RB, and BA can be used as pozzolans to replace part of Portland cement in making mortars with relatively high strength and good resistance to chloride penetration. Test results also indicate that the use of the blend of pozzolans in the equal portion of BA and FA, and RB and FA also effectively improves the mortar in terms of strength and resistance to chloride penetration. The improvement is due to the dispersing effect of fly ash and the synergic effect of the blend of fine pozzolans.

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Investigation on the Dielectric Properties of 0–3 Lead Zirconate Titanate-Geopolymer Composites

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Lead zirconate titanate (PZT)-fly ash geopolymer pastes composites of 0–3 connectivity were fabricated using 30–50% by volume. The mineralogical compositions of fly ash geopolymer materials were investigated using X-ray diffraction (XRD). The 10 mol sodium hydroxide solution and sodium silicate solution at a sodium silicate-to-sodium hydroxide ratio of 0.67 were used to prepare geopolymer pastes. The pastes were cured at 60°C for 2 days. The results showed that the dielectric constant of PZT-fly ash geopolymer pastes composites decreased with increasing PZT content at 1 KHz. The dielectric properties of PZT-fly ash geopolymer pastes composites were also found to depend on the frequency.

Keywords Dielectric properties; PZT; fly ash geopolymer; composite

1. Introduction

The use of a structural material for electronics enables a structure to provide electronic functions, thereby making the structure multifunctional and smart [1]. Ferroelectric materials are the active components in a wide variety of piezoelectric devices used in the biomedical, military, aerospace and electronics industries [2]. An important piezoelectric material is lead zirconate titanate (PZT) due to its advantageous properties and well-characterized behavior [3]. Cement-based piezoelectric composite has good compatibility with civil engineering's main structural material [4]. The advantage of using composites such as the cement-based piezoelectric composites are a better match to the host, concrete, than normal piezoelectric ceramic or other types of piezoelectric composites. In 2002, PZT-cement composites of 0–3 connectivity were fabricated using the mixture and spread normally [5]. PZT-cement composites are able to solve problems that cannot be matched.

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Current global warming and climate change affecting the world is one of the most important issues that were raised. CO_2 release from industries is the main cause of global warming. Cement industry is a major contributor to CO_2 emissions and therefore should be improved by the reduction of the consumption of Portland cement. In the past few years, cement mixed with cement or pozzolanic materials are widely used in cement and concrete construction by replacing part of the cement. Because fly ash (FA) has been widely used to replace cement with silica fume (SF) and other natural pozzolanic materials require less water or can be used to great success [6]. On one hand, fly ash has been recognized as an important construction material since it benefits the environment and the interests of the engineering [7].

Fly ash is the fine portion of coal combustion by-products produced at power-generating stations and collected from flue gases by electrostatic precipitators [8]. In Thailand, the annual output of lignite fly ash from Mae Moh Power Station is around 3.0 million tons. Approximately 1.8 million tons are used as pozzolanic materials in the concrete industry. The level of fly ash replacement is normally restricted to less than 30% of Portland cement. Around 1.2 million tons are left over and discarded at landfill sites [9]. This lignite fly ash contains a reasonable amount of silica and alumina and can be used as a source material for making geopolymers [9–11]. Other materials containing high amount of silica and/or alumina such as metakaolin [12], bottom ash [13], and rice husk ash [14] are also suitable for being used as source materials for making geopolymers.

Aluminosilicate inorganic polymers, also called geopolymers [15]. The materials formed under high alkali conditions from aluminosilicate solid and alkali silicate solutions [15]. The geopolymer is a type of cross-linked long-chain inorganic polymer material between tetrahedral $[AlO_4]$ and $[SiO_4]$ units, built in three-dimensional structures. The linkages of $[AlO_4]$ and $[SiO_4]$ units require charge balancing from alkali ions such as Li^+, Na^+, and K^+. The mechanism of the existence of alkali ions in the molecular structure of geopolymer materials is not clearly understood at present. Usually, the accustomed viewpoint is that alkali metal ions play a charge-balancing role or are actively bonded to the matrix. Hence, the typical geopolymer composition is usually expressed as $nM_2O{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$ (M is an alkali metal element such as Li, Na, or K) [16]. Geopolymer fabrication is one of the efficient methods to form the fast inorganic ionic conductor owing to free sintering and low cost. Hydroxide and water molecules in a geopolymer material are the most important factor influencing the dielectric property and their electrical conductivity at room temperature [16]. Free alkali metal ions are also expected to play an important role in the electrical properties of geopolymer materials. Therefore, this investigation aimed at studying the dielectric properties in a frequency range of 1–100 kHz of PZT-fly ash geopolymer pastes composites.

2. Experimental

Lignite high calcium fly ash from Mae Moh Power Plant in the North of Thailand was used for this study. Its particle size distribution, chemical and mineralogical compositions were investigated. Sodium silicate to sodium hydroxide ratio of 0.67 and 10 mol NaOH solution were used as alkali solutions.

Lead zirconate titanate, $Pb(Zr_{0.52}Ti_{0.48})O_3$. PZT solid solutions were pressed with an applied pressure using uniaxial press and sintered at 1200°C for 2 h. PZT ceramic median particles size of 425 μm were used in this investigation [17].

The compositions of fly ash geopolymer pastes representing as SiO_2/Al_2O_3, Na_2O/SiO_2, Na_2O/Al_2O_3, and H_2O/Na_2O ratios are shown in the ratio of liquid alkali

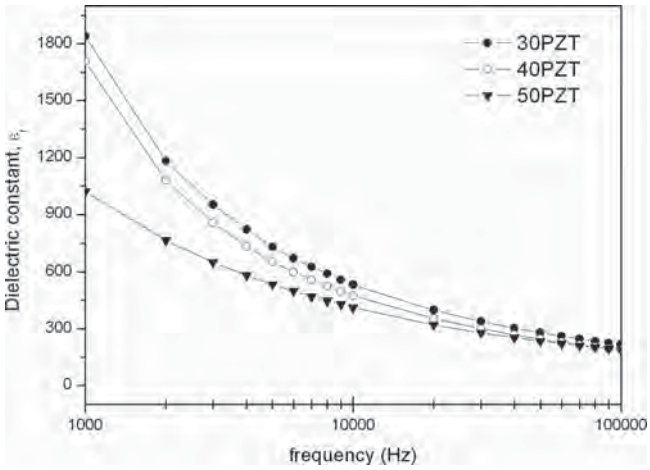


Figure 1. Dielectric constant of PZT-FA geopolymer composites at frequency for 1–100 kHz.

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solution to fly ash(L/A) of 0.4. The 0–3 composites were produced by first mixing fly ash (FA) and PZT ceramic using PZT at 30%, 40% and 50% by vol. The NaOH solution was then added to the mixture and mixed for 5 min and the sodium silicate solution was added to the mixture and mixed for another 5 min and the sodium silicate to sodium hydroxide ratio of 0.67 were used. After mixing, the alkali activated fly ash paste was cast in a 15-mm-diameter and 2-mm-thick plastic mould. The cast samples were left standing in the 25°C control room for 1 h. It was then sealed to avoid the loss of water and put to cure in a controlled chamber at 60°C for 48 h. The surfaces of the specimens were coated with silver paint for dielectric property measurements.

The mineralogical and phase compositions of fly ashes and geopolymer specimens were investigated using X-ray diffraction (Philips PW 1792) using Ni-filtered Cuk radiation. Thereafter, the composites were coated silver paint. The capacitance and dielectric loss tangent were measured with a LCZ-meter (Hewlett Packard, model 4276A) under stress free at room temperature (25°C) with frequency of 100–100000 Hz. The dielectric constant was then calculated from a parallel plate capacitor equation, e.g. $\varepsilon_r = Cd/\varepsilon_0 A$, where C is the capacitance of the sample, d and A are the thickness and the area of the electrode, respectively, and ε_0 is the dielectric permittivity of vacuum [18].

3. Results and Discussion

The dielectric properties, e.g. dielectric constant, ε_r and dielectric loss, tanδ, of the PZT-FA geopolymer composites (PZT-FA geopolymer 30/70, 40/60 and 50/50 vol%) were measured and plotted versus the frequency at room temperature, as shown in Figures 1 and 2, it can be seen that the dielectric constant and the dielectric loss decreases sharply with increasing frequency. The dielectric constant values of the composites are significantly higher at low frequency. With increasing frequency, some polarizations, especially interfacial polarizations cannot follow the change of electric field because of the long time for the construction of space charge polarization. Therefore, the dielectric constant of the composites is lower at high frequency [19]. Dielectric constant, ε_r value of 30% PZT composite is 1840 at 1 kHz

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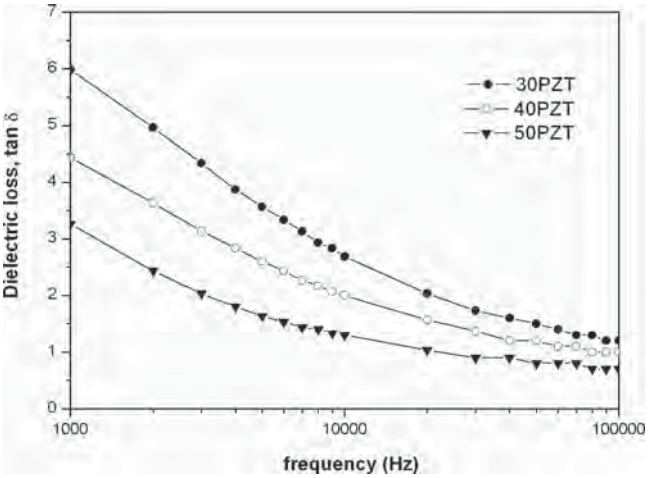


Figure 2. Dielectric loss of PZT-FA geopolymer composites at frequency for 1–100 Hz.

and 188 at 100 kHz (Fig. 1). Dielectric loss, *tanδ* value of 30% PZT composite is 5.9 at 1 kHz and 1.2 at 100 kHz (Fig. 2).

The variation of dielectric properties, e.g. the dielectric constant, ε_r and dielectric loss, *tanδ* as a function of content of PZT has been studied at the frequency of 1 kHz and the results are plotted in Figure 3, it can be seen that there is roughly nonlinear decrease of the dielectric constant values of the composites as a function of the PZT content where ε_r value of 1834.2 (30% PZT), 1706.2 (40% PZT) and 1017.6 (50% PZT). From the previous studies the dielectric constants at 1 kHz of geopolymer pastes and PZT are found to be $\approx 1 \times 10^5$ and $\approx 1 \times 10^3$, respectively [4, 20]. The dielectric loss was found to reduce with increasing PZT content where *tanδ* value = 5.9, 4.3 and 3.2 for 30%, 40% and 50% PZT, respectively.

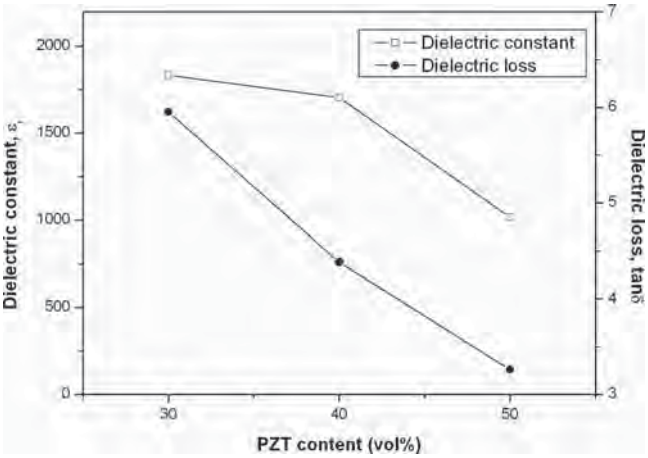


Figure 3. Effect of PZT content on dielectric constant and dielectric loss of PZT-FA geopolymer composites at frequency for 1 kHz.

4. Conclusion

0–3 PZT-FA geopolymer composites (PZT percentages of 30, 40, and 50 by volume) were prepared using PZT ceramic and FA geopolymer paste. Both the ε_r and *tanδ* decreases with increasing frequencies from 1–100 kHz. At 1 kHz, ε_r value can be seen to decrease from 1834.2 to 1017.6 (30% to 50% PZT) and tanδ value reduced from 5.9 to 3.2 (30% to 50% PZT). The dielectric constant decreases with increasing content of PZT in PZT-FA geopolymer composites system.

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Thermogravimetry of ternary cement blends

Effect of different curing methods

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Abstract This study reports the microstructure characteristic and compressive strength of multi-blended cement under different curing methods. Fly ash, ground bottom ash, and undensified silica fume were used to replace part of cement at 50 % by mass. Mortar and paste specimens were cured in air at ambient temperature, water at 25, 40, and 60 °C and sealed with plastic sheeting for 28 days. In addition, these specimens were cured in an autoclave for 6, 9, and 12 h. Results indicated that the compressive strength of multi-blended mixes containing silica fume 10 % by mass cured with plastic sealed and cured in water at 25 and 40 °C was similar to or higher than the corresponding Portland cement control at 28 day. Moreover, the mixes containing silica fume 10 % by mass cured in water at 60 °C had higher compressive strength than Portland cement control. X-ray diffraction and thermogravimetry results confirmed that there was increased pozzolanic reaction with increasing silica fume content which relates to the increasing in strength. For autoclaved curing, the compressive strength of multi-blended cement specimens with silica fume (total of 50 % replacement) was noticeably higher than control Portland cement mix and was highest when autoclaving time was 9 h. X-ray diffraction results showed the pattern of 0.9, 1.1, and 1.4 nm tobermorite crystalline phases as the main product of this curing. Thermogravimetry results showed dehydration of 1.4 nm tobermorite and 1.1 nm tobermorite at about 80–90 and 135–150 °C, respectively. Tobermorite (also shown by scanning electron microscope) thereby as a result lead to significant compressive strength improvement in the short time of autoclaved curing.

Keywords Blended cement · Fly ash · Bottom ash · Silica fume · Microstructure · Compressive strength

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Introduction

The production of Portland cement is one of major contributor to CO_2 emission which implicated to global warming and climate change hence it should be improved and reduced. The reduction of cement consumption by mean of using Portland cement replacement materials has been widely investigated. Pozzolanic materials such as fly ash (FA), granulated blast furnace slag (GGBS), silica fume (SF), and other natural pozzolan materials are widely used to replace part of Portland cement as blended cement. Many researchers have studied high-volume fly ash (HVFA) as a Portland cement replacement (binary blended cement) in mortar or concrete but only a few studies have been carried out to determine properties of multi-blended cement at high level (volume) content. In commercial practice, the dosage of FA is limited to 15–20 % by mass of the total cementitious material while HVFA generally has 50 % or more of FA by mass of the cementitious material [1]. However, the strengths of HVFA concrete are lower than that of only Portland cement concrete (PC) at early age [2–6].

SF is widely used as a pozzolanic materials in blended cement or as a mineral admixture in high strength concrete (HSC) due to its high reactivity thus can give strength at early age compared with FA or other mineral admixtures.

SF particle is the nano size range (≈100 nm) and contained more than 85 % of SiO_2 in amorphous form. Previous studies [7–10] reported that the utilization of nano size range material as cement replacement or admixture materials have been found to improve physical and mechanical properties of Portland cement, especially blended cement with pozzolanic materials. However, the usage of SF is limited due to its tendency to agglomerate and the high water demand [11]. Thus, mix designs involving high-volume SF also use high level water reducers or superplasticizers. The incorporations of FA and SF have been found to offer enhanced properties of blended cement concrete than FA or SF concrete alone. Nassif et al. [12] studied the effect of pozzolanic materials and curing methods on the elastic modulus of high performance concrete (HPC) using FA, SF, and GGBS as pozzolanic materials in blended cement. It is found that concrete incorporating FA and SF can improve slump of concrete when compared to concrete containing SF only. Guneyisi et al. [13] reported that the compressive strength of ternary (PC + FA + SF) blended cement was higher than that of binary (PC + FA) blended cement at the same replacement level. In addition, Barbhuiya et al. [14] investigated the properties of FA concrete modified with hydrated lime and SF. The FA concrete incorporating SF improved the early strength of concrete. Nochaiya et al. [15] studied the utilization of FA with SF and properties of Portland cement–fly ash–silica fume concrete. It is also reported that the utilization of SF with FA was found to increase the compressive strength of concrete at early ages (pre 28 days).

Bottom ash (BA) is another by-product of thermoelectric power plants occurring at the same time as FA. It consists of chemical composition similar to FA. However, the utilization of BA in the substitution of Portland cement is limited due to its high particle size and porous particle, compared to FA. However, BA can be used to replace part of cement by reducing the particle size. Cheriaf et al. [16] studied the pozzolanic properties of BA by varying the time of grinding. It was found that the pozzolanic activity of BA increased with increased time of grinding and strength can be improved. Wongkeo and Chaipanich [17] studied the use of ground BA and SF to produce the bottom ash lightweight concrete (BLWC). It was found that the properties of BLWC improved when SF was added to the mix.

Curing of cement, mortar or concrete specimens is very important for their strength and durability development. Curing is a process to keep their specimens saturated or to prevent loss of moisture that is essential for the hydration of cement. The rate and degree of hydration, strength gain, and other properties depend on the curing process. Nowadays, curing is more important for concrete that contains mineral admixtures than for normal concrete [18]. Curing at ambient temperature can be divided into two groups: (1) water curing and (2) sealed curing. Water curing is better than sealed curing, particularly important when using low w/c ratio concrete (w/c < 0.40) [19]. In addition, the rate of hydration of cement increased with increasing curing temperature, especially at lower degree of hydration [20]. In practice, concrete is mostly cured by covering it with wet burlap, waterproof paper, or plastic sheeting. Autoclaved is synonymous of high-pressure steam curing. The curing temperature of this curing exceeds 100 °C. Normally, the range of curing temperature used in autoclaving is 160–210 °C (320–410 °F) at steam pressure of 6–20 atm [19]. The chemistry of hydration changes under these conditions have substantially different properties from products cured below 100 °C. In the absence of reactive silica (PC only) the α-C_2SH phase is formed whereas tobermorite ($C_5S_6H_5$) phase is formed on continued heating in the presence of reactive silica [21]. The change of hydration product has lead to strength gain and properties development in the short time of curing. Thus, the used of suitable curing method can improve strength and properties of blended cement at early age.

This paper reports the effect of curing methods on the compressive strength and characteristic of blends cement mortar containing FA, ground bottom ash (BA), and SF. Curing methods such as air cured at ambient temperature, sealed cured with plastic sheeting, water cured at 25, 40, and 60 °C, and high-pressure steam curing (autoclaved) were used in this study.

Experimental

Materials

Ordinary Portland cement type 1 (PC) was used in the binder phase of this study. FA and BA obtained from Mae Moh power plant in Lampang, Thailand and undensified SF grade 920-U produced by Elkem were used as supplementary materials. The chemical compositions and physical properties of raw materials (PC, FA, BA, and SF powder) are given in Table 1. River sand with specific gravity of 2.65 was used as fine aggregate of mortar. Napthalene based superplasticizer from Sika (Thailand) Limited was used in this study.

Samples preparation and test methods

The selective dissolution method with 1 % HF (hydrofluoric acid) solution was used to determine the amorphous

Table 1 Chemical compositions and physical properties of materials used in this research

	PC	FA	BA	SF
Chemical composition/%				
SiO_2	20.64	45.37	47.592	93.549
Al_2O_3	4.848	20.65	19.1	0.556
CaO	63.62	10.43	10.16	1.128
Fe_2O_3	3.17	12.31	14.34	0.172
MgO	1.137	2.127	1.477	0.747
Na_2O	0.51	1.331	1.084	0.137
K_2O	0.812	1.496	1.213	1.047
P_2O_5	0.32	0.245	0.164	0.531
TiO_2	0.213	0.517	0.311	0.002
SO_3	2.753	2.526	2.436	1.006
Loss on ignition	2.076	3.002	2.124	1.16
Specific gravity	3.15	2.10	2.70	2.20
Average particle size/μm	8.31	5.22	7.81	0.1

phase of FA, BA, and SF powder. The procedure was followed and applied by Fernandez-Jimenez et al. [22]. 1 g of each powder was added to a plastic beaker containing 100 mL of 1 % HF. The mix was stirred using magnetic stirrer for 6 h at ambient temperature and then filtered using filter paper. The filter paper and the insoluble residue was oven-dried at 105 °C for 24 h. The amorphous phase was determined by subtracting the final from the initial mass.

In this study, FA, BA, and SF were used to replace part of PC. The replacement levels of FA were 30, 40, 45, and 50 % while those of BA were 10, 15, and 20 % by mass of binder. SF was used to replace PC at 5 and 10 % by mass. The mix proportions and mix design are summarized in Table 2. The seven mortar mixes were designed having a constant water/binder ratio of 0.485 and flow of mortar of 110 ± 5 mm. The mortar mixes were mixed and then cast into 50 × 50 × 50 mm molds

Table 3 Percentage of insoluble and soluble phase of pozolanic materials after treated with 1 % HF solution

Raw materials	Insoluble residue/%	Soluble phase/%
FA	37.00	63.00
BA	47.36	52.64
SF	25.94	74.06

and compacted using a vibrating table. The mortar specimens were stored in molds for 24 h and then demolded. All the mortar specimens were cured in air at ambient temperature (at 26–30 °C and relative humidity 50–65), water at 25, 40, and 60 °C and sealed with plastic sheeting for 28 days. For autoclaved curing, the mortar specimens were autoclaved at 130 °C and under pressure 20 psi for 6, 9, and 12 h. After the end of autoclaved curing periods for 6, 9, and 12 h, all of the samples were left in a autoclaved chamber for cooling period of 12 h before compressive strength, XRD, and TG tests. The compressive strength was tested using tecnotest compression testing machines. Moreover, the identification phases of the samples was investigated using X-ray diffractometer (XRD; PHILIPS X'Pert MPD) and thermogravimetry using the Mettler Toledo TG/SDTA 851e (inert atmosphere 180 with N_2 flow of 30 mL min^{-1}, heating rate 10 °C min^{-1}, analysis range 30–800 °C). For XRD and TG testing, samples were immersed in acetone after reaching the required curing age to stop hydration process before characterization tests. For autoclaved curing, the samples were immersed in acetone after the end of cooling period for 12 h. The 28 days of hydration were selected to identify phases using XRD and TG technique. This is due to the hydration process that would have mostly occurred by 28 days and the standard test age used to determine the relative strength of concrete in practice.

Table 2 Mix proportion of blended cement mortar

Materials	Mix						
	100PC	50FA	45FA5SF	40FA10SF	30FA 20BA	30FA15BA5SF	30FA10BA10SF
OPC/kg m^{-3}	538	269	269	269	269	269	269
FA/kg m^{-3}	–	269	242	215	161	161	161
SF/kg m^{-3}	–	–	27	54	–	27	54
BA/kg m^{-3}	–	–	–	–	108	81	54
Aggregate/kg m^{-3}	1,480	1,420	1,420	1,420	1,436	1,430	1,428
Water/kg m^{-3}	261	261	261	261	261	261	261
SP/%	0.8	–	0.4	0.8	0.4	0.6	1.1
CaO/SiO_2 ratio	3.08	1.12	1.03	0.95	1.11	1.02	0.97
$CaO/(SiO_2 + Al_2O_3)$ ratio	2.50	0.81	0.78	0.74	0.81	0.77	0.76

Results and discussion

Characterization of raw materials

The main constituents of FA and BA powder are SiO_2 and Al_2O_3 while more than 90 % of SiO_2 is presented in SF powder (as shown in Table 1). It is worthwhile to point out that more than 10 % of CaO is presented in FA and BA powder. Table 3 shows the percentage of insoluble and soluble phase of FA, BA, and SF powder after treated with 1 % HF solution. The insoluble residue of all samples refers to crystalline phase while the amorphous phase (soluble phase) was dissolved in HF solution. The main chemical compositions of soluble phase are SiO_2 and Al_2O_3. The results showed the amorphous phase of FA, BA, and SF powder of 63, 52.64, and 74.06 %, respectively. It is found that FA powder has more amorphous phase than BA powder. Thus, it can be expected that FA powder is more reactive than BA powder. X-ray diffraction was used to determine crystalline phase of powder sample. The crystalline phase of FA powder consists of anhydrite, magnetite, gehlenite, lime, quartz, and chabazite while BA powder contains of augite, magnetite, and anorthite as main crystalline compounds, with hematite, gehlenite, quartz, corundum, and chabazite as minor constituents (as shown in Fig. 1). BA powder can be seen to contain more crystalline phases than FA powder which relates to amorphous phase determination by the selective dissolution method.

X-ray diffraction analysis

The XRD analyses of 28 day hydration blended cement pastes are shown in Fig. 2. The XRD patterns of all specimens cured in water at 25 and 60 °C (Fig. 2a, b) indicated the main peaks of calcium hydroxide ($Ca(OH)_2$), ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$), and C–S–H ($Ca_2SiO_4H_2O$) phase which is the main hydration product. In addition, small unhydrated peaks of Alite (Ca_3SiO_5:C_3S) and Belite (Ca_2SiO_4:C_2S) phases (originated from Portland cement) and calcite ($CaCO_3$) are also detected. The hydration process may be determined using XRD by determining the amount of $Ca(OH)_2$ or unreacted cement constituents [23]. However, some C–S–H crystalline phase can be detected by XRD which can also give an indication of the hydration process. From the results, it is found that the C–S–H phase of samples cured in water at 25 °C cannot be detected in XRD patterns. This is due to the C–S–H gel is mostly formed in the poorly crystalline form or amorphous

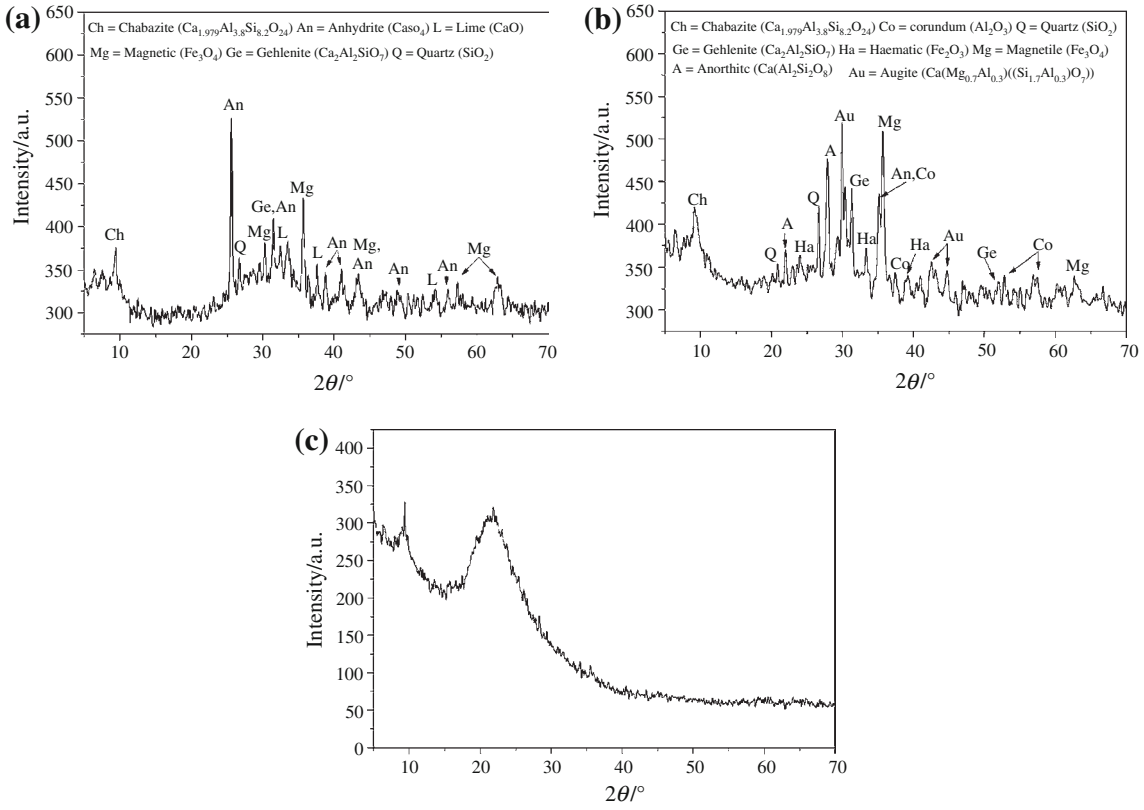


Fig. 1 XRD patterns of pozzolanic materials **a** FA, **b** BA, and **c** SF. The peaks are labeled: *Ch* chabazite ($Ca_{1.979}Al_{3.8}Si_{8.2}O_{24}$), *An* anhydrite ($CaSO_4$), *L* lime (CaO), *Ge* gehlenite ($Ca_2Al_2SiO_7$) *Q* quartz (SiO_2), *Mg* magnetite (Fe_3O_4), *Ha* haematite (Fe_2O_3), *Co* corundum (Al_2O_3), *A* anorthite ($CaAl_2Si_2O_8$), and *Au* augite ($Ca(Mg_{0.7}Al_{0.3})((Si_{1.7}Al_{0.3})O_7)$)

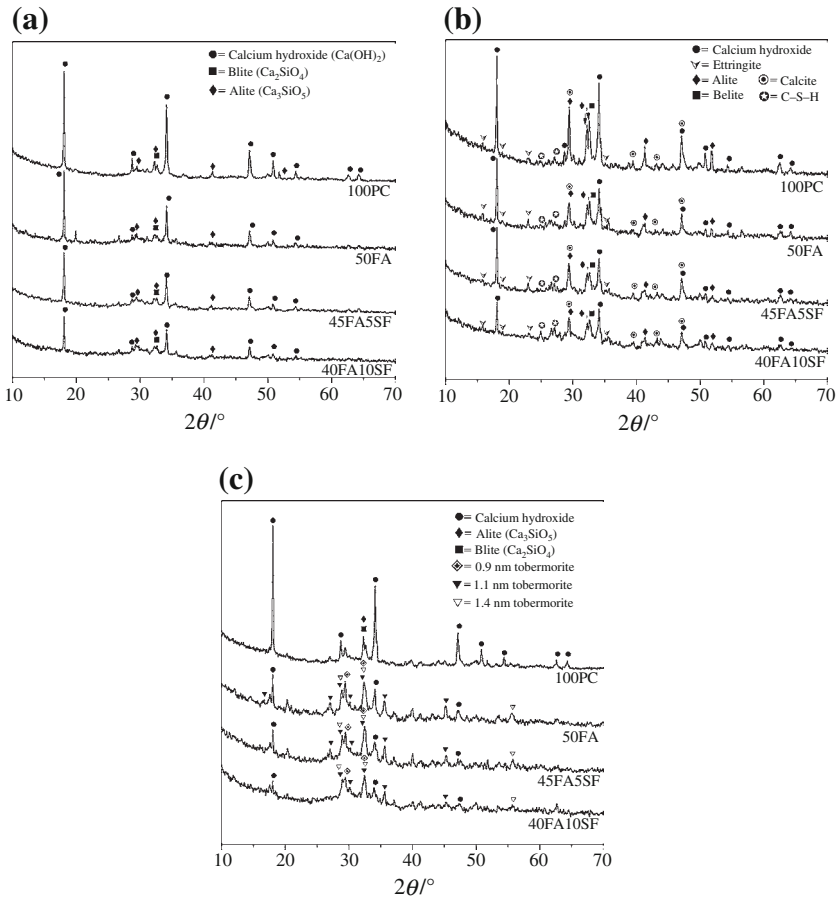


Fig. 2 XRD patterns of blended cement **a** water curing at 25 °C, **b** water curing at 60 °C, and **c** autoclaved curing for 6 h

disordered structures at room temperature, but the stable and highly crystalline C–S–H gel will be formed when heated [24–26]. Thus, the C–S–H gel in samples cured at 25 °C is not detected in XRD, but can be detected in the samples cured at 60 °C. In this study, it is found that the intensity of $Ca(OH)_2$ peak of the mix containing pozzolanic materials (50FA, 45FA5SF, and 40FA10SF mixes) was lower than that of the PC control. Moreover, the intensity of $Ca(OH)_2$ peak can be seen to decrease with increased SF substitution. The unhydrated peaks of C_3S and C_2S phases also decreased due to the dilution effect. The reduction of intensity of $Ca(OH)_2$ peak is accompanied by an increase in intensity of C–S–H phase due to increasing pozzolanic reaction and C–S–H is seen to increase with increased SF substitution. The intensity of C–S–H phase of specimen cured in water at 60 °C is higher than that of specimen cured in water at 25 °C. This indicates that the pozzolanic reaction was improved with an increased in curing temperature, especially for mixes containing SF.

For specimen cured by autoclaved method for 6 h (Fig. 2c), the XRD patterns of all specimens show the main peaks of $Ca(OH)_2$ phase and peaks of C_3S and C_2S phases similar to the specimens cured in water at 25 and 60 °C. However, blended cement specimens showed the XRD patterns of 0.9 nm tobermorite ($Ca_5Si_6O_{16}(OH)_2$), 1.1 nm tobermorite ($Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$), and 1.4 nm tobermorite ($Ca_5Si_6O_{16}(OH)_2{\cdot}8H_2O$) which exhibits the same basal spacing as the 1.1 nm tobermorite. Normally, tobermorite in autoclaved cement has only been found as the 1.1 nm tobermorite phase. Substitution of a part of the Si atoms in SiO_4 tetrahedral with Al is observed in synthetic 1.1 nm tobermorite. The 1.4 nm tobermorite shows only a minor degree of Al substitution [27]. This reason may lead to 0.9 nm tobermorite formation. Thus, the Al_2O_3 content which is the composition of pozzolanic material and CaO/(Al_2O_3 + SiO_2) ratio has an effect on the formation of tobermorite. The consistency of tobermorite formation of 1.1 nm thus shows that pozzolanic reaction of blended cement is improved under autoclaved curing.

Thermogravimetry

Thermogravimetry (TG) of 28 day hydrated cement pastes are shown in Fig. 3. The results are plotted as derivative thermogravimetric (DTG) curves in order to identify the detected phases (Fig. 4). For normal hydration, the first major mass loss located below 200 °C is the result of dehydration reactions of several hydrates such as C–S–H,

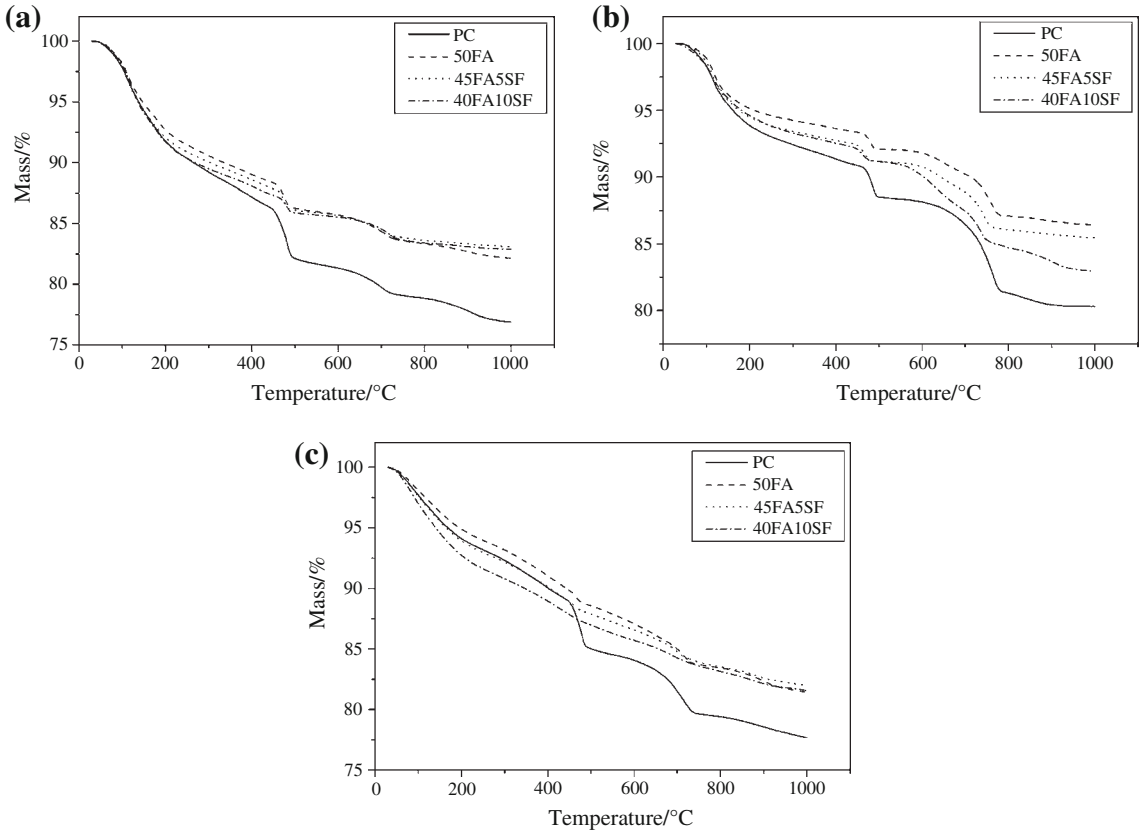


Fig. 3 TG curves of blended cement pastes **a** water curing at 25 °C, **b** water curing at 60 °C, and **c** autoclaved curing for 6 h

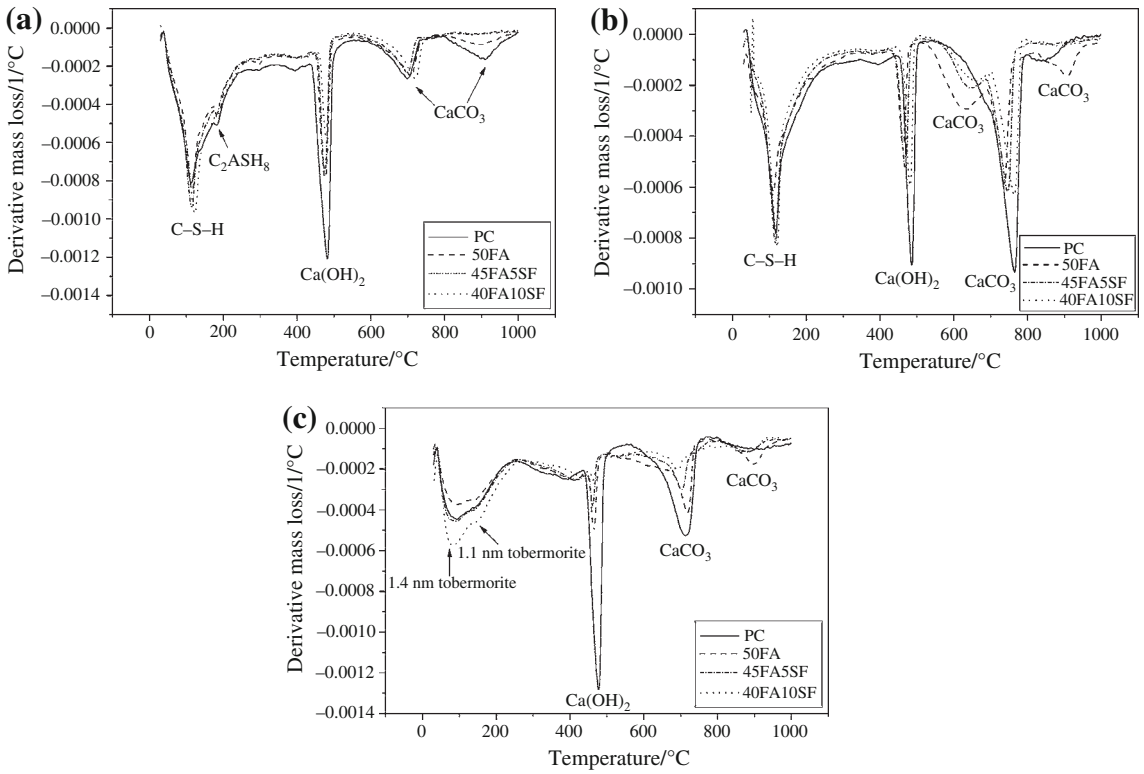


Fig. 4 DTG curves of blended cement pastes **a** water curing at 25 °C, **b** water curing at 60 °C, and **c** autoclaved curing for 6 h

ettringite (AFt) monosulfoaluminate (AFm), and gehlenite (C_2ASH_8) [28–30]. The second major mass loss, observed at 450–550 °C, corresponds to the dehydroxylation of portlandite ($Ca(OH)_2$). The third loss of mass appears at 750–900 °C and corresponds to the decarbonation of calcium carbonate [23]. In this study, the DTG curves of blended cement cured in water at 25 and 60 °C (Fig. 4a, b) show detection of C–S–H at ≈110–120 °C and $Ca(OH)_2$ at ≈460–480 °C, respectively. In addition, gehlenite hydrate (C_2ASH_8) was shown in specimen cured in water at 25 °C, but it disappeared in specimen cured in water at 60 °C. Moreover, the DTG curves of specimen cured in water at 25 °C show two strong endothermic peaks of $CaCO_3$ at about 700–720 and 890–905 °C. The first peak was decomposed of normal calcite in Portland cement. The second peak may be decomposed of another calcite due to decomposition of calcite is affected by surface area, particle size, partial pressure of CO_2, and impurities such as magnesium [31] or another formation such as carboaluminate ($Ca_4Al_2(OH)_{12}\cdot CO_3\cdot 5H_2O$) [32]. Furthermore, the DTG curves of specimen cured in water at 60 °C show three strong peaks of $CaCO_3$ at about 630–660 °C, 730–765 °C, and 890–905 °C, respectively, but these were observed in blended cement specimens only. From these results, it is found that the intensity of C–S–H curves of specimen containing SF (both cured in water at 25 and 60 °C) was higher than that of specimen containing only FA and it increased with increased SF content. This result was confirmed to the increasing of pozzolanic reaction with increased SF content.

For specimen cured by autoclaved method for 6 h (Fig. 4c), DTG curves show two peaks of C–S–H (tobermorite phase) at about 80–90 °C and 135–150 °C, $Ca(OH)_2$ peak at about 450–475 °C, and two peaks of $CaCO_3$ at about 680–715 °C and 870–900 °C, respectively. In the case of C–S–H peaks, the first peak is the result of dehydration of 1.4 nm tobermorite and the second peak corresponds to the dehydration of 1.1 nm tobermorite. The lower temperature dehydration of 1.4 nm tobermorite is attributed to a single-chain structure of silicate anion while 1.1 nm tobermorite has a double-chain structure of silicate anion [27].

Table 4 shows the percentages of mass loss to overall mass loss of binary and ternary blended cement pastes at 28 days hydration under water curing at 25, 60 °C and autoclaved curing for 6 h. To consider only first group of mass loss, the percentages of mass loss to overall mass loss of binary blended cement pastes under water curing at 25 and 60 °C were lower than PC control. However, the mass loss to overall mass loss of ternary blended cement pastes was higher than PC control and increased with increasing SF replacement. This indicates that the reaction (both of hydration and pozzolanic reaction) of blended cement paste was improved when containing SF replacement. Moreover, it was found that the percentages of mass loss to overall mass loss of all specimens cured with water 60 °C were higher than specimens cured with water 25 °C. This was due to the rate of reaction was increased with increasing temperature during moist curing. In addition, it can be observed that the percentages of mass loss to overall mass loss of $Ca(OH)_2$ group of binary and ternary blended cement decrease, compared to PC control. This was due to the $Ca(OH)_2$ was consumed by pozzolanic reaction of FA and SF which results to increasing C–S–H gel. However, the reduction of $Ca(OH)_2$ group not only decreased by pozzolanic reaction, but also effect by carbonation reaction to $CaCO_3$ formation [33]. For specimens cured with autoclaved, first group of mass loss was mostly the mass loss of C–S–H due to ettringite are not formed at higher temperature. Both the sulfate and alumina apparently enter into the C–S–H and tobermorite structure. The role of alumina is increasing the rate of crystallization of tobermorite [19]. It was found that the percentages of mass loss to overall mass loss of binary and ternary blended cement pastes were higher than PC control. This may be due to the different structure of α-C_2SH, obtained from PC control and tobermorite, which is the main product of binary and ternary blended cement pastes.

Table 4 Mass loss of blended cement pastes under water curing at 25, 60 °C and autoclaved curing for 6 h

Mix	Mass loss to overall mass loss/%								
	Free water + C–S–H + Ettringite + C_2ASH_8/AFm			$Ca(OH)_2$			$CaCO_3$		
	Water cured at 25 °C	Water cured at 60 °C	Autoclaved 6 h	Water cured at 25 °C	Water cured at 60 °C	Autoclaved 6 h	Water cured at 25 °C	Water cured at 60 °C	Autoclaved 6 h
PC	33.48	41.35	31.23	20.76	12.60	21.24	11.88	36.29	22.35
50FA	30.48	40.86	32.84	14.03	9.81	8.17	14.67	24.11	26.24
45FA5SF	40.85	44.48	39.90	11.36	9.86	5.55	11.71	20.83	18.60
40FA10SF	44.31	48.09	47.23	8.92	7.41	7.87	14.13	17.96	15.93

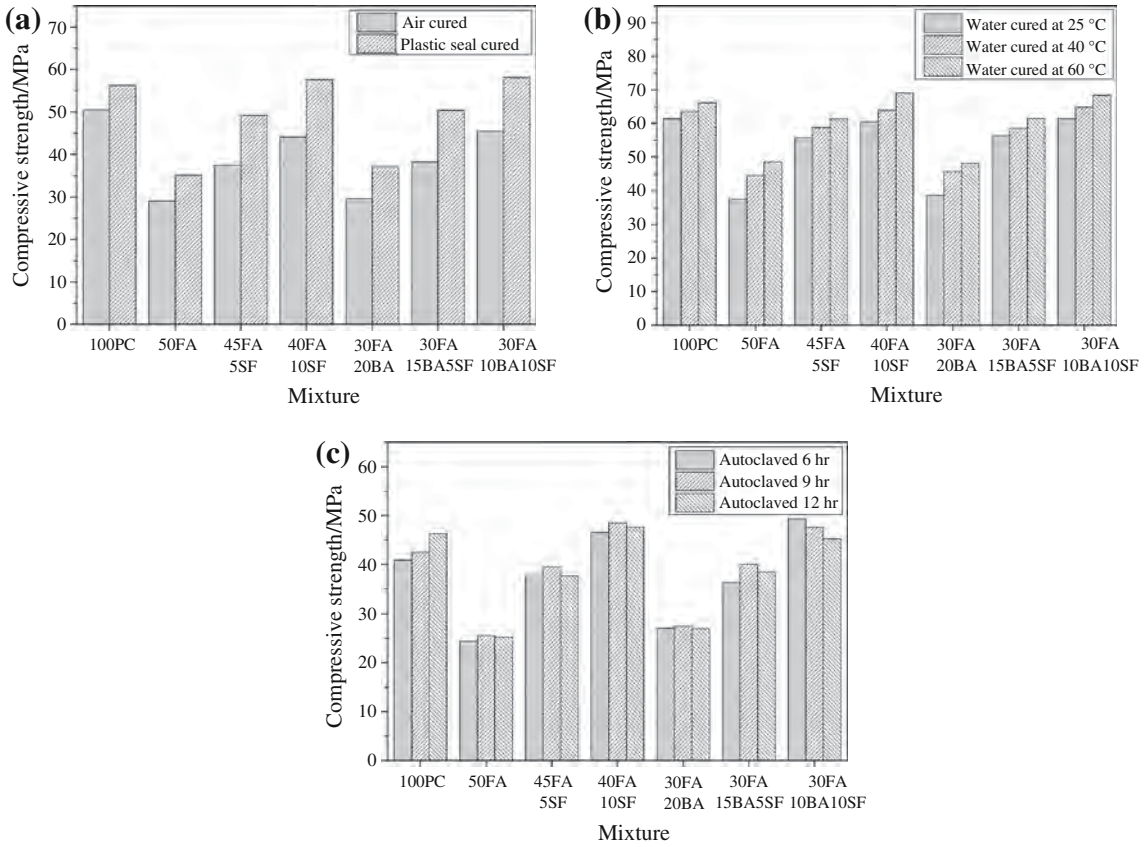


Fig. 5 Compressive strength of blended cement mortars **a** air and sealed curing, **b** water curing at 25, 40, and 60 °C, and **c** autoclaved curing

Compressive strength

The relationship between the compressive strength of 28 days blended (binary, ternary, and quaternary blended) cement under various curing method at ambient temperature and mix designs is presented in Fig. 5. Figure 5a shows the compressive strength of specimens cured in air and those sealed with plastic sheeting. It can be observed that the compressive strength of blended cement cured in air and sealed with plastic sheeting increased with increasing SF replacement. The compressive strength of all mixes cured with plastic sealed was higher than those cured in air. This is due to sealed curing method prevents loss of moisture of specimen and hence allows continued hydration. Therefore, specimen that was cured by sealed method preventing against moisture loss can improve strength more effectively than specimen cured in air. The compressive strength of all blended cements (binary, ternary, and quaternary systems) mixes cured in air was found to be lower than that of PC control. For specimen cured with plastic sealed, the compressive strength of 50FA, 45FA5SF, 30FA20BA, and 30FA15BA5SF mixes were also lower than that of PC control, while 40FA10SF and 30FA10BA10SF mix show the compressive strength similar to that of PC control. From these results, it was found that the compressive strength of the mixes containing only FA and BA cured in air decreased up to 42.45 % (at 50FA mix) and it decreased up to 37.43 % when sealed. While the compressive strength of the mixes containing SF decreased up to 12.69 % (at 40FA10SF mix) when cured in air. In addition, the compressive strength of 40FA10SF mix cured by sealed plastic method was similar to PC control. Therefore, the mix containing SF can improve the compressive strength of ternary and quaternary blended cement, particularly for high cement replacement levels. This is due to the high pozzolanic reaction and high amorphous SiO_2 content of SF. In addition, SF particles fill the micro and/or submicro pore size in paste that is known as a space filling effect [34].

Figure 5b shows the compressive strength of blended cement specimens cured in water at 25, 40, and 60 °C. It is found that the compressive strength of all mixes increased with increasing curing temperature. In addition, the compressive strength of 50FA mix cured at 60 °C decreased up to 26.56 % compared to the mix cured by sealed plastic sheet, but it was still lower than PC control. However, the mixes containing 10 % SF replacement had higher compressive strength than PC control. This is due to the increasing temperature increased the rate of reaction (both of hydration and pozzolanic reaction) of blended cement,

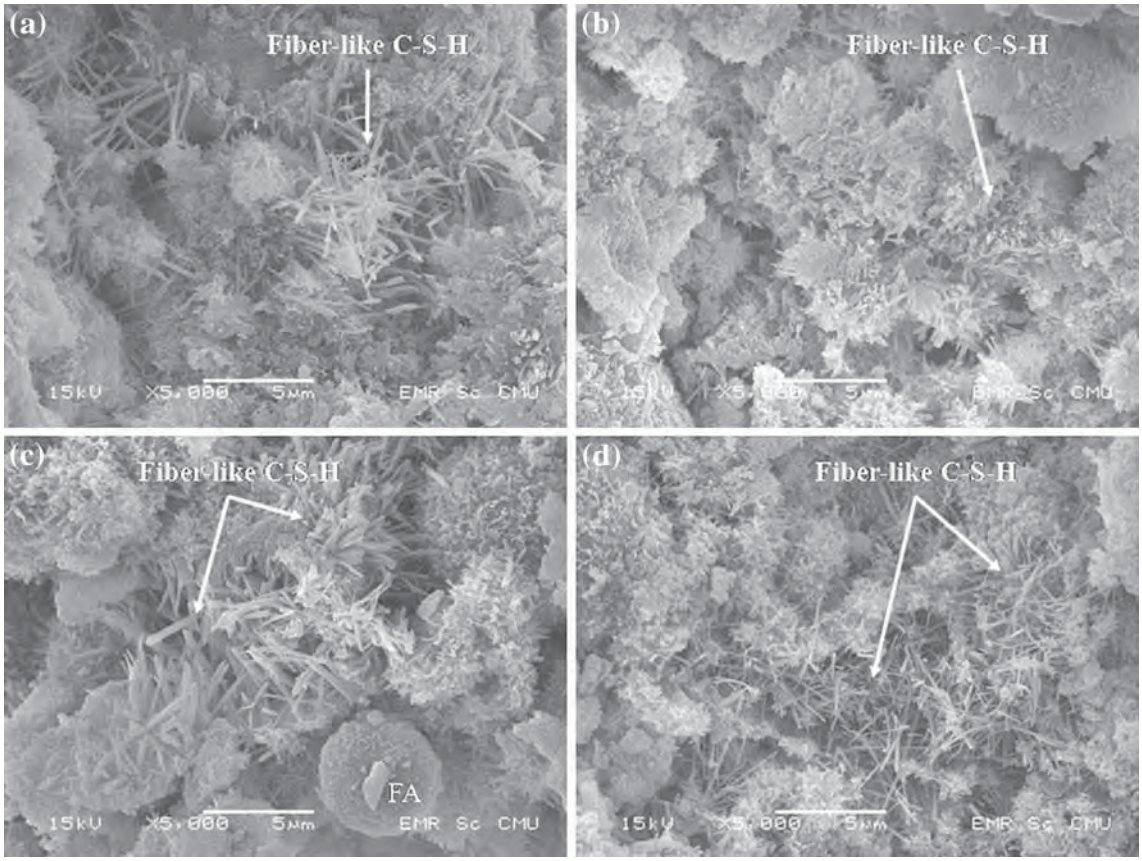


Fig. 6 SEM images of blended cement under water curing at 60 °C **a** PC control, **b** 50FA mix, **c** 45FA5SF mix, and **d** 40FA10SF mix

especially at lower degrees of reaction such as FA and BA. In these results, the compressive strength of all specimens cured in water at 25, 40, and 60 °C were higher than specimens cured in air and sealed with plastic sheeting.

The compressive strength of blended cement specimens under autoclaved curing is shown in Fig. 5c. It can be seen that the compressive strength of blended cement increased with increasing SF replacement at the same autoclaved period, especially at 10 % SF replacement where the compressive strength is higher than PC control. In addition, the compressive strength of PC control tends to increase with increasing autoclaving time while the compressive strength of blended cement increased with increasing autoclaving time up to 9 h and then begin to decrease when autoclaving time increase to 12 h. Under autoclaved method, the CaO/SiO_2 ratio has a significant effect on the compressive strength of blended cement due to the chemical of hydration is substantially altered under high temperature and pressure conditions. In the absence of an external SiO_2 source, α-dicalcium silicate hydrate (α-C_2SH) is formed instead of an amorphous calcium silicate hydrate (C–S–H). In the presence of SiO_2 source, crystalline 1.1 nm tobermorite ($C_5S_6H_5$) is formed [21]. Tobermorite phase has a larger volume of structure than α-C_2SH phase which causes a decrease in porosity and increase in the compressive strength.

Meller et al. [35] reported $CaO–SiO_2–H_2O$ phases from 50 to 1,000 °C. This phase diagram shows relationship between temperature and CaO/SiO_2 mol ratio. It is reported that tobermorite phase is formed at the CaO/SiO_2 ratio between about 0.5–1.5 and at temperature above 110 °C. In this study, it was found that blended cement specimen had a CaO/SiO_2 ratio between 0.95 and 1.12. The CaO/SiO_2 ratio decreased with increasing amount of SF replacement and thereby increased the compressive strength of blended cement. Therefore, FA, BA, and SF can be used as an alternative SiO_2 source in blended cement which results to tobermorite formation. The maximum compressive strength of 48.51 MPa was obtained from 40FA10SF mix using an autoclaved period of 9 h. The reduction of compressive strength of blended cement at 12-h autoclaved period may be due to tobermorite phase becoming unstable at long autoclaving time. Maeshima et al. [27] reported that stable tobermorite is normally treated at 170–210 °C in order to shorten the autoclaving time of approximately 5–8 h.

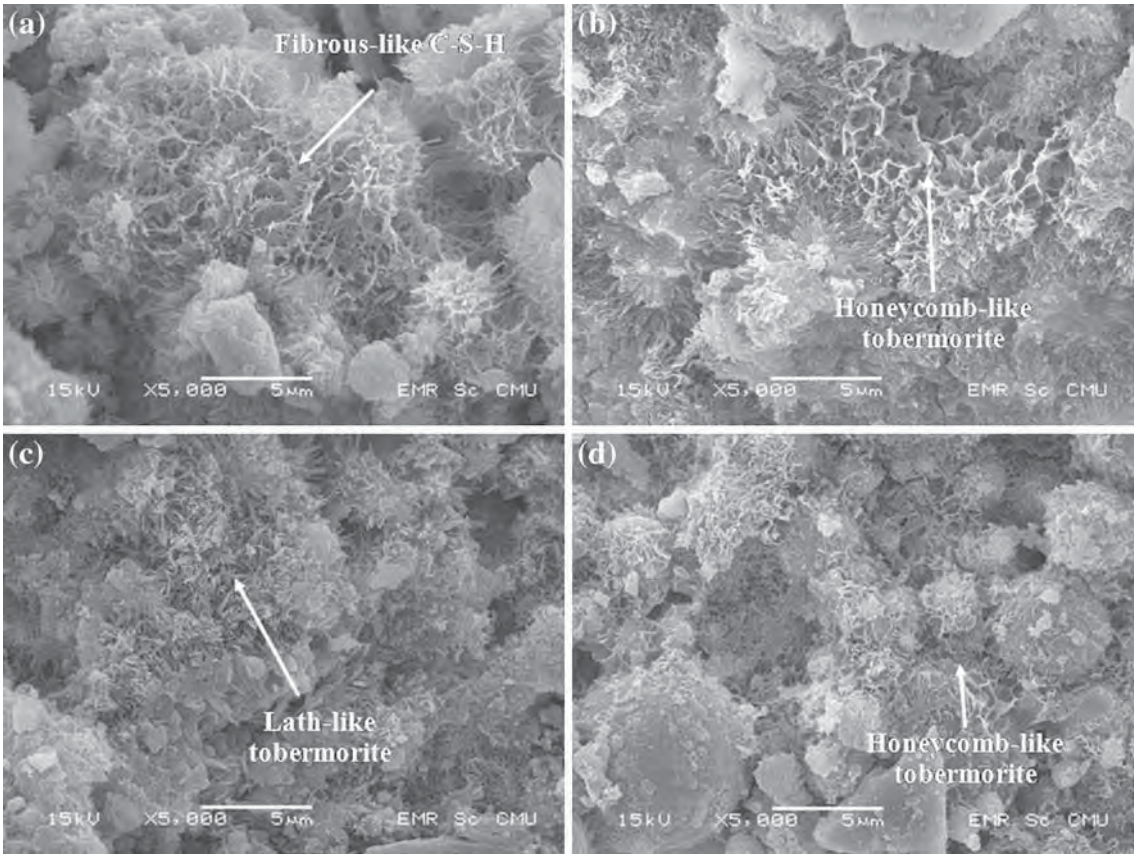


Fig. 7 SEM images of blended cement under autoclaved curing for 6 h. **a** PC control, **b** 50FA mix, **c** 45FA5SF mix, and **d** 40FA10SF mix

Microstructure

The microstructure of 28 day hydrated blended cement under various curing methods using scanning electron microscope (SEM) is shown in Figs. 6 and 7. The fracture specimens of paste were used to determine the microstructure and morphology of blended cement. Figure 6 represents SEM image of specimen under water curing at 60 °C. It can be seen that the fiber-like C–S–H was shown as the main C–S–H product of plain and blended cement. In addition, 50FA mix indicated the length of fiber-like C–S–H to be shorter than that of PC control. The length of fiber-like C–S–H tends to increase with increasing SF content. It can be observed that CaO/SiO_2 ratio decreased with increasing amount of SF which increased the length of fiber-like C–S–H. Therefore, the CaO/SiO_2 ratio has a significant effect on the shape of C–S–H cured in water at 60 °C.

Figure 7 shows SEM images of specimen under autoclaved curing at 130 °C under 20 psi pressure for 6 h. The fibrous-like C–S–H (α-C_2SH) phase can be seen presented in PC control. In addition, the honeycomb-like tobermorite phases were seen in specimens with pozzolanic materials. Moreover, the lath-like tobermorite can be found in the mixes containing SF replacement. Tobermorite phase has a significantly effect on the properties such as compressive strength of blended cement under high temperature and pressure conditions [19]. From SEM images (Fig. 7a–d), it can be seen that the tobermorite phases (both of honeycomb-like and lath-like formation) give denser microstructure than fibrous-like C–S–H phase. The α-C_2SH phase has smaller volume of the solid phase and as a consequence results in an increase in the porosity when compared to the tobermorite phase [19]. Therefore, a denser microstructure due to the presence of tobermorite structure would lead to higher compressive strength.

Conclusions

- To determine percentage of reactive phases, it is found that SF powder has more amorphous phase than FA and BA powder (74.06, 63, and 52.64 %, respectively). The compressive strength of blended cement containing FA and BA was lower than blended cement containing SF at the same curing method. The compressive strength of all mixes cured in air was lower than PC control while the compressive strength of blended cement containing SF 10 % by mass cured with plastic sealed and cured in

water at 25 and 40 °C was equal to PC control. However, the compressive strength of blended cement containing SF 10 % by mass cured in water at 60 °C was higher than PC control. For autoclaved curing, the compressive strength of PC control tends to increase with increasing time of autoclaved while the compressive strength of blended cement increased with increasing time of autoclaved up to 9 h and tends to decrease with increasing time of autoclaved up to 12 h.

- XRD results show that the intensity of $Ca(OH)_2$ peak of blended cement was lower than that of PC control and it decreased with increased SF replacement and temperature curing. This indicates that the pozzolanic reaction was improved with the use of SF. XRD results showed the patterns of 0.9, 1.1, and 1.4 nm tobermorite in the blended cement specimens using autoclaved curing. TG results indicated the decomposition of C–S–H, C_2ASH_8, $Ca(OH)_2$, and $CaCO_3$ of specimen cured in water at 25 °C, while specimen cured in water at 60 °C show the decomposition of C–S–H, $Ca(OH)_2$, and $CaCO_3$. For autoclaved curing, the dehydration of 1.4 nm tobermorite and 1.1 nm tobermorite were showed at about 80–90 °C and 135–150 °C, respectively.
- SEM images of plain and blended cement under water curing at 60 °C indicated the fiber-like C–S–H. For autoclaved curing, SEM image showed fibrous-like C–S–H (α-C_2SH) phase as the main product of plain cement while blended cements exhibit honeycomb-like tobermorite and lath-like tobermorite phases which give denser microstructure than α-C_2SH phase.

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Reducing Loss Tangent by Controlling Microstructure and Electrical Responses in $CaCu_3Ti_4O_{12}$ Ceramics Prepared by a Simple Combustion Method

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The dielectric and electrical properties of $CaCu_3Ti_4O_{12}$ ceramics prepared by a simple combustion method were investigated. Fine-grained $CaCu_3Ti_4O_{12}$ ceramics exhibited good dielectric properties and temperature stability. Very low loss tangents of 0.020–0.016 and high dielectric constant of 5776–6406 (at 1 kHz and 20°C) with temperature coefficient less than ±15% in the temperature range of −70 to 90°C were observed. Dielectric relaxation processes were observed in large-grained $CaCu_3Ti_4O_{12}$ ceramics. The dielectric relaxation in the temperature range of 60–150°C may be associated with sample–electrode contact. The relaxation in temperatures below −40°C is related to the electrical response at grain boundaries.

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Introduction

Recently, the discovery of new materials showing a very high dielectric constant (ε′) has stimulated significant research activity.[1] This is because materials with large dielectric constants are used to fabricate ceramic capacitors. The values of ε′ and loss tangent (tanδ) are the primary parameters determining the performance of capacitors. Among new giant materials, $CaCu_3Ti_4O_{12}$ (CCTO) has gained considerable interest both scientifically and technologically.[2–13] CCTO ceramics can exhibit very high ε′ of about 10^3–10^5 at room temperature, depending on the ceramic microstructures[14–16] and processing conditions.[8] Unfortunately, their tanδ values are still too large and tend to increase as ε′ is increased.[14] Investigation to optimize the values of ε′ and tanδ by controlling the microstructure of CCTO ceramics is therefore important.

Over the past few years, many investigations have been carried out to clarify and understand the physical mechanism(s) related to the apparent giant dielectric response in CCTO ceramics. Unfortunately, the origin of giant dielectric properties is still unclear. Both intrinsic and extrinsic effects have been proposed that describe the unusually high ε′ values of CCTO ceramics and single crystals.[3–6,8,13,15] For the intrinsic effect, several models were proposed to describe the giant dielectric response. These include the mixed-valent structure model,[13,17,18] polaron relaxation model,[19] incipient ferroelectricity model,[20] nanoscale disorder model,[21–23] and dipolar effect related to disordered Ca/Cu sites.[24]

Based on the extrinsic effect, the origin of the giant dielectric response in the CCTO ceramics is widely accepted to be caused by interfacial polarization at grain boundaries (GBs).[3,4] The microstructure of CCTO ceramics consists of semiconducting grains and insulating GBs, that is, an electrical structure model or internal barrier layer capacitor (IBLC) model. Thus, GBs of CCTO ceramics play two significant roles in the overall dielectric properties. First, GBs trap the charge carriers producing electrical polarization. Second, GBs behave as insulating layers blocking the long-range motion of free charges that can cause an increase in tanδ, especially in a low-frequency range. Besides polarization at GBs, polarization can also be introduced at other places such as domain boundaries (DBs) and sample–electrode interfaces.[6,25]

According to the sample–electrode effect, the value of ε′ can be enhanced due to the formation of Schottky barrier at the interface between CCTO surfaces and metal electrodes. In general, formation of the Schottky barrier is caused by the difference between the work functions of the metal electrode and semiconducting surface.[26] Ideally, it depends only on the different levels of work functions. However, for CCTO ceramics, it was found that the sample treatment and aging of electrode contact can also affect the low-frequency ε′ value contributed by the electrode effect.[27] The time constant of the electrical response of a Schottky barrier is usually much longer than that occurring in bulk ceramics.[26] Therefore, such dielectric response appears in a relatively low-frequency range compared to that measured in bulk ceramics. Occasionally, the portion of the dielectric constant contributed by the sample–electrode effect cannot be observed in the measured frequency range. Fortunately, this response can be observed in the radio frequency range by increasing measurement temperature. This is due to the electrical response of Schottky barrier being a thermally activated mechanism. Thus, a strong increase in the value of ε′ at a high temperature might be caused by the sample–electrode effect.

According to the IBLC model, tanδ can be reduced by increasing the total GB resistivity (R_{gb}). Enhancement of R_{gb} can be carried out in several ways such as (1) doping CCTO with suitable metal ions to modify defect equilibrium at GBs,[28] (2) changing Ca and Cu molar ratios to produce CCTO/$CaTiO_3$ composites,[29–31] (3) increasing the molar concentration of Ti in CCTO to produce CCTO/TiO_2 composites,[32] (4) incorporating oxygen at GBs,[33] (5) and reducing the grain size to increase the density of GB layers.[14] To obtain CCTO ceramics with a small grain size and high GB density, CCTO ceramics should be prepared from CCTO nanopowders or smaller submicrometer powders and sintered at a lower temperature and/or short time.

In this work, we prepared CCTO ceramics using a simple combustion method and sintered at low temperature and short reaction times (1040°C for 1 and 3 h). Fine-grained CCTO ceramics with good dielectric properties were obtained. The dielectric relaxations and electrical responses in large-grained CCTO ceramics were studied using an impedance spectroscopy. The possible mechanisms related to the relaxation processes and electrical responses are discussed.

Experimental Procedure

In this work, a simple combustion method was used to synthesize CCTO powder. $Ca(NO_3)_2$ $4H_2O$ (99%, Sigma-Aldrich Chemie, Steinheim, Germany), $Cu(NO_3)_2$ $4H_2O$ (99.5%, Carlo Erba, Milano, Italy), $C_{16}H_{28}O_6Ti$ (75 wt.% in isopropanol, Sigma-Aldrich), citric acid, ethanol, and aqueous ammonia (27%) were employed as starting raw materials. Stoichiometric amounts of $Ca(NO_3)_2$ $4H_2O$ and $Cu(NO_3)_2$ $4H_2O$ were dissolved in the solution of citric acid (5 wt%) in ethanol with constant stirring at room temperature. Then, $C_{16}H_{28}O_6Ti$ solution was mixed with the metal ion solution above under constant stirring at 150°C until a transparent gel was formed. Then, 1 mL of aqueous ammonia was added to the Ca^{2+}, Cu^{2+}, and Ti^{4+} mixture solution with constant stirring at 150°C. This mixed solution was dried at 350°C for 30 min. The resulting dried porous precursor was ground into powder and divided into two portions. One was calcined in air at 750°C for 2 h, and other was calcined at 750°C for 6 h. These two CCTO powders are referred to as P1 and P2 powders, respectively. P1 and P2 powders were ground and pressed into pellets having dimensions of 9.5-mm diameter and ~1–2 mm in thickness by uniaxial compression at 200 MPa. Finally, the green-body disks prepared from P1 powder were sintered in air at 1040°C for 1 and 3 h and referred to as CCTO-1 and CCTO-2 samples, respectively. The green-body disks prepared from P2 powder were sintered in air at 1040°C for 1 and 3 h and referred to as CCTO-3 and CCTO-4 samples, respectively.

The phase composition and microstructure of sintered CCTO powders and ceramics were characterized using X-ray diffraction (XRD) (PW3040, Philips, Eindhoven, The Netherlands) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) (S-3400, Hitachi, Tokyo, Japan), respectively. Transmission electron microscopy (TEM) (Tecnai G^2, FEI, Eindhoven, The Netherlands) was used to characterize the CCTO powders. The dielectric response of the samples was measured using an Agilent E4980A (Agilent Technologies, Palo Alto, CA) Precision LCR Meter over the frequency and temperature ranges of 10^2–10^6 Hz and −70 to 150°C, respectively. An oscillation voltage of 1.0 V was used in each case. Each measured temperature was kept constant with an accuracy of ±1°C. Prior to making measurements, the ceramic samples were polished. Au was sputtered on each pellet surface at a current of 25 mA for 8 min using a Polaron SC500 (Sussex, U.K.) sputter coating unit.

Results and Discussion

The XRD patterns of dried precursor, CCTO powders, and the sintered CCTO ceramics are shown in Fig. 1. CuO phase was observed in the XRD patterns of the dried precursor. The XRD patterns of CCTO powders and the sintered ceramics confirm the formation of the $CaCu_3Ti_4O_{12}$ phase (JCPDS card no. 75-2188). The diffraction peaks corresponding to CCTO phase were detected. All XRD patterns are perfectly indexed based on the body-centered cubic structure with space group *Im*3. The XRD results indicate that CCTO phase can be successfully prepared by a very simple method using a relatively low calcination temperature and short reaction time, that is, 750°C for 2 h. A small amount of CuO and TiO_2 impurity phases still appeared in the XRD patterns of CCTO powders. Only pure phase of CCTO, that is, with no impurities, was detected in the XRD patterns of the sintered CCTO ceramics. The values of lattice parameters were calculated using Cohen's least mean square method and found to be 7.390, 7.390, 7.391, 7.392, 7.391, and 7.390 Å for the P1 powder, P2 powder, CCTO-1, CCTO-2, CCTO-3, and CCTO-4 samples,

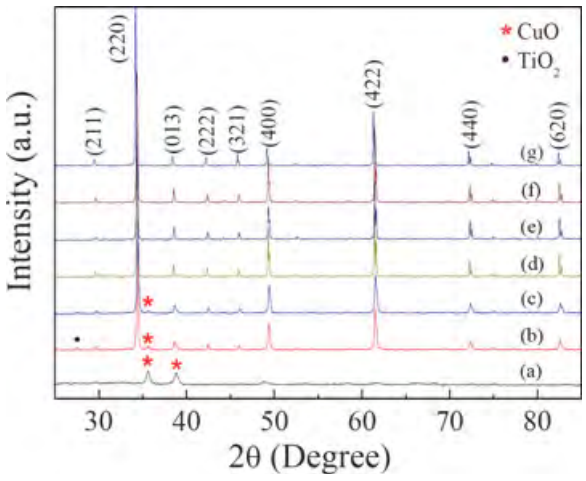


Fig. 1. X-ray diffraction patterns of (a) precursor, (b) CCTO powder calcined at 750°C for 2 h, (c) CCTO powder calcined at 750°C for 6 h, (d) CCTO-1, (e) CCTO-2, (f) CCTO-3, and (g) CCTO-4 samples.

respectively. These values are comparable to the values reported in literature[2] and JCPDS card no. 75-2188 for 7.391 Å. Figures 2a,b show TEM images of CCTO powders calcined at 750°C for 2 and 6 h, respectively. The particle size of CCTO tended to increase as the calcination time was increased. The particle sizes of the P1 and P2 powders were estimated to be 130–260 nm and 150–300 nm, respectively.

Figures 3a–d show SEM images of the surface morphologies of the CCTO samples. The CCTO-1 sample sintered at 1040°C for 1 h shows a fine-grained microstructure with grain sizes of about 2–3 μm (Fig. 3a). As seen in Fig. 3c, the CCTO-3 sample sintered at same condition as the CCTO-1 sample exhibits fine-grained microstructure as was observed in the CCTO-1 sample. However, small grains in some regions start to connect together. Increasing sintering time from 1 to 3 h results in abnormal grain growth. For the CCTO-2 and CCTO-4 samples (the samples that were prepared from P1 and P2 powders, respectively) sintered at 1040°C for 3 h, some grains grow rapidly to sizes of ~10–15 μm. This microstructural evolution in CCTO ceramics has been reported in the literature.[14] The microstructures of the CCTO-1 and CCTO-3 samples were observed to have small grain sizes with narrow distribution of these values. This microstructural feature is required for most applications. The dielectric properties of these two ceramic samples are therefore expected to be improved. Figure 3e shows the EDS spectrum of the CCTO-4 sample, confirming the presence of each chemical, that is, Ca, Cu, Ti, and O.

As shown in Fig. 4, sintering time has an effect on the dielectric properties of CCTO ceramics. ε′ at 20°C of the fine-grained CCTO-1 and CCTO-3 samples is independent of frequency over the measured range, 10^2–10^6 Hz. In contrast with the fine-grained ceramic samples, the CCTO-2 and CCTO-4 samples exhibit a strong frequency dependence upon ε′ especially in a low-frequency range. As demonstrated in the inset of Fig. 4, the low-frequency values of tanδ of the fine-grained CCTO-1 and CCTO-3 ceramics are much lower than the values of tanδ for the CCTO-2 and CCTO-4 samples. tanδ values of these two fine-grained ceramics are lower than 0.1 in the frequency range from 10^2 to 10^5 Hz. The values of ε′ and tanδ at 1 kHz and 20°C for all CCTO samples are summarized in Table I. The dielectric properties of these two samples are comparable to those of 0.1 wt% ZrO_2-doped CCTO ceramic (ε′ ~ 5030 and tanδ ~ 0.016 at 1 kHz).[28] It was also reported that 0.5% ZrO_2-doped CCTO ceramic exhibited tanδ values below 0.05 over a wide frequency range. For the CCTO–1 and CCTO-3 samples, tanδ was found to be lower than 0.05 over frequency ranges of 200 Hz–158 kHz and 100 Hz–50 kHz, respectively.

The exact origin of the giant dielectric response in CCTO ceramics is still unclear. However, it is usually found that the electrical and dielectric properties of CCTO ceramics are strongly related to their prepara-

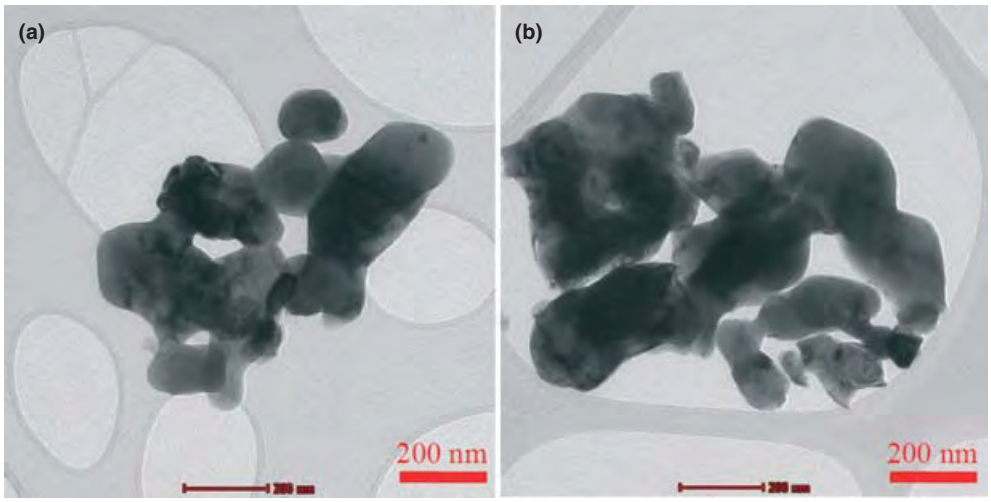


Fig. 2. Transmission electron microscopy images of CCTO powders calcined at 750°C for (a) 2 h and (b) 6 h.

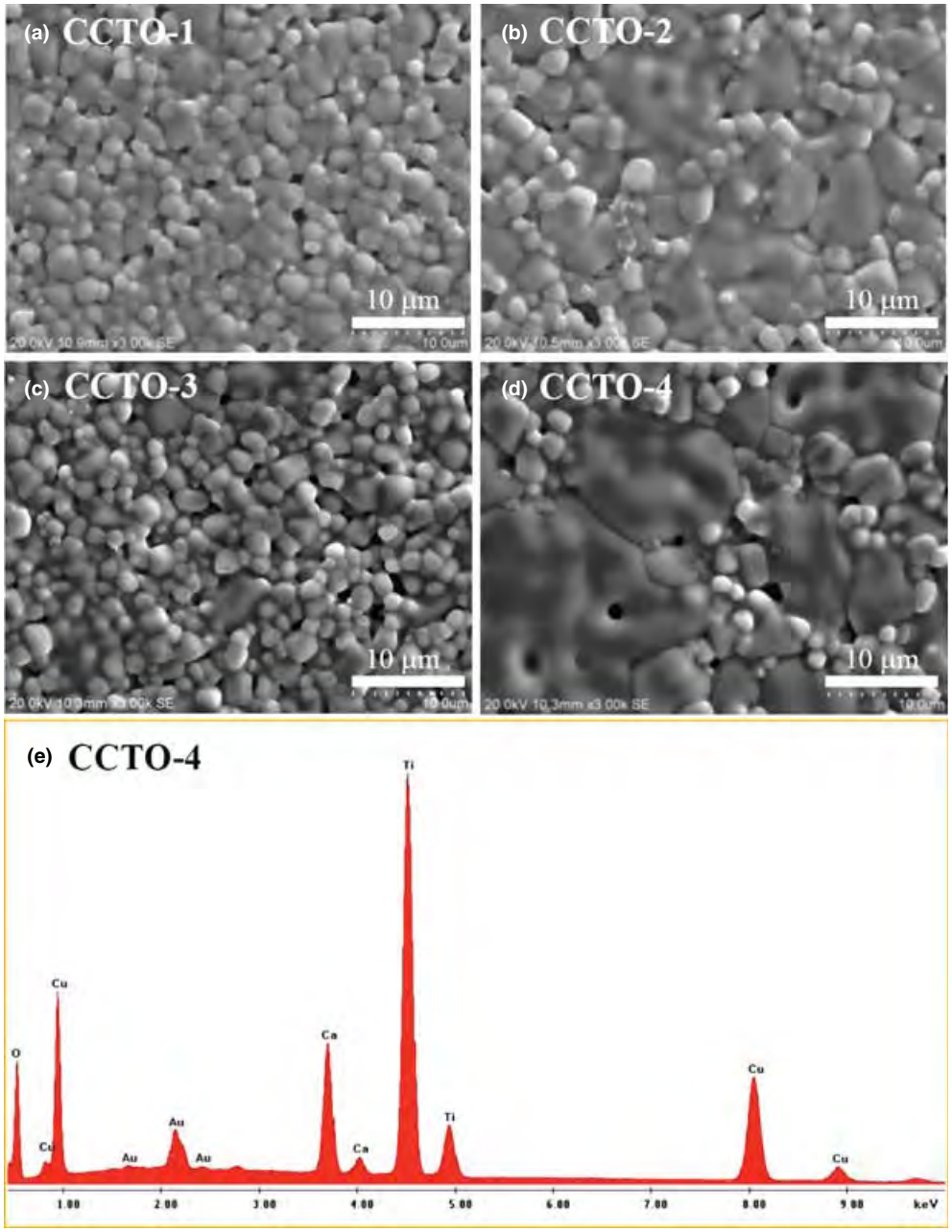


Fig. 3. (a–d) SEM images of surface morphologies of CCTO-1, CCTO-2, CCTO-3, and CCTO-4 samples, respectively. (e) energy dispersive spectroscopy spectrum of CCTO-4 sample.

tion conditions and resulting microstructure. Notably, it has been shown that CCTO ceramics are electrically heterogeneous, consisting of semiconducting grains and insulating GBs.[4] However, changes in microstructure (e.g., the increase in the grain size) may cause the changes in intrinsic factors in grains such as concentration of defects. Therefore, an increase in ε' can be considered in two different ways: (1) an increase in the mean grain size and/or GBs capacitance and (2) changes in intrinsic factors. In this work, we hypothe-

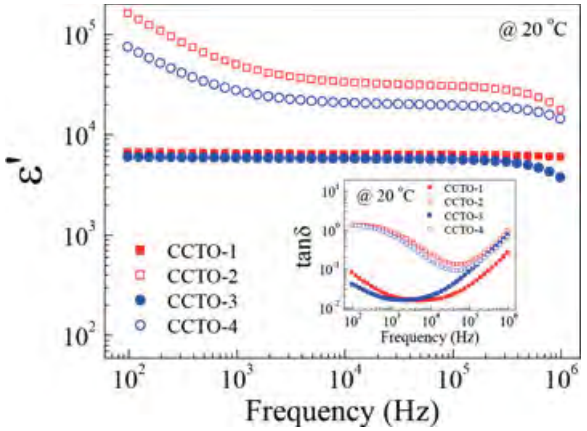


Fig. 4. Frequency dependence of ε′ at 20°C for all CCTO samples; inset shows the frequency dependence of tanδ at 20°C.

sized that microstructural heterogeneity is the primary cause of the giant dielectric properties of CCTO ceramics. This work does not discredit other intrinsic models.[17–24] We just demonstrate that giant dielectric properties of CCTO ceramics can be effectively improved by controlling microstructure. All concepts and models used to describe the giant dielectric behavior of CCTO single crystal and polycrystalline ceramics require further experimental validation.

Based on the electrically heterogeneous microstructure found in insulating GBs and semiconducting grains,[2,3,6] the density of insulating GB layers was increased by controlling the microstructure of CCTO ceramics to obtain small grain sizes with narrow size distribution. The increase in insulating layers caused a decrease in dc conduction in the fine-grained CCTO ceramics. Therefore, the low-frequency tanδ of the CCTO-1 and CCTO-3 ceramics is therefore reduced.

To develop a high-permittivity ceramic that can be used for ceramic capacitor applications, variations in ε′ must be investigated over the standard temperature range.[34] For example, variation in ε′ for high-permittivity ceramics suitable to fabricate X5R and X7R capacitors should be less than ±15% over the temperature ranges of −55 to 85°C and −55 to 125°C, respectively. The variation in ε′ [Δε′(%)] as a function of temperature in °C is defined as $(\varepsilon'_T - \varepsilon'_{20})/\varepsilon'_{20} \times 100$, where ε'_T and ε'_{20} are ε′ at a specific experimental temperature and 20°C, respectively. As shown in Fig. 5, ε′ of the CCTO-1 and CCTO-3 samples seems to be nearly independent on temperature over the range from −70 to 150°C. However, ε′ of the CCTO-2 and CCTO-4 samples is found to be strongly dependent on measurement temperature. Investigation of ε′ temperature variations using conditions of 20°C (at 10^3 Hz) as a basis reveals that the variations of ε′ for the fine-grained CCTO-1 and CCTO-3 samples were less than ±15% over the temperature range of −70 to 90°C and −70 to 100°C, respectively. This result indicates that the CCTO-1 and CCTO-3 ceramics have the potential for capacitor applications, that is, X5R capacitors.

As shown in the inset of Fig. 4, the increase in tanδ for all samples in a high-frequency range (10^5–10^6 Hz) is attributed to the main dielectric relaxation process. This behavior of CCTO ceramics is well reported in the literature.[3,5,6,10,11,13–15] It is likely that the high tanδ values observed for the CCTO-2 and CCTO-4 samples in a low-frequency range may be attributed to the dielectric relaxation process. The CCTO-2 and CCTO-4 samples exhibited two sets of dielectric relaxation processes. To study these two relaxation processes, the frequency dependence of dielectric properties (i.e., ε′, tanδ, and ε″ [ε″ = ε′ × tanδ]) at various temperature was investigated. As shown in Fig. 6 and inset (1), two sets of relaxation peaks for the CCTO-4 sample are observed. These two sets are indicated by ε″ peaks for low-temperature relaxation and tanδ peaks for high-temperature relaxation. The observation of tanδ peaks corresponds to the step-like decrease in ε′ at the same

Table I. ε′ and tanδ Values (at 20°C and 1 kHz), Activation Energies for Low- and High-Temperature Relaxation Processes (E_{a1} and E_{a2}), Grain Boundary Conduction Activation Energy (E_{gb}), and Activation of Electrode Response (E_e) for $CaCu_3TiO_{12}$ Ceramics

Sample	ε′	tanδ	E_{a1} (eV)	E_{a2} (eV)	E_{gb} (eV)	E_e (eV)
CCTO-1	6406	0.020	-	-	0.672	-
CCTO-2	49,261	0.908	0.093	0.577	0.455	0.541
CCTO-3	5776	0.016	-	-	0.676	-
CCTO-4	27,062	0.720	0.108	0.588	0.495	0.582

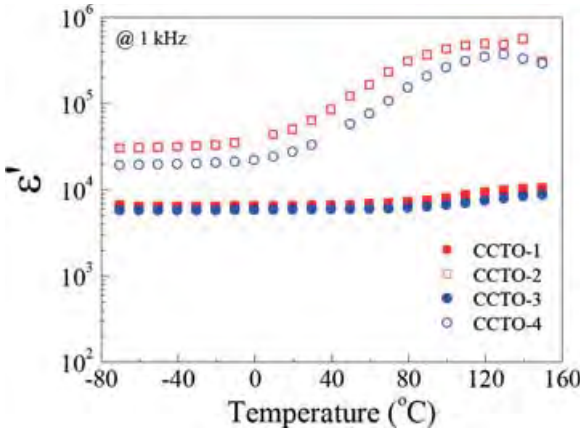


Fig. 5. Temperature dependence of ε′ at 20°C for all CCTO samples.

temperature range, as shown in the inset (2) of Fig. 6. Over the measured ranges of temperature and frequency (−70 to 150°C and 10^2–10^6 Hz), both ε″ and tanδ peaks were observed in the CCTO-2 and CCTO-4 samples only, but were not observed in the fine-grained CCTO-1 and CCTO-3 samples. The ε″ and tanδ peaks shift to higher frequency as the temperature increased, indicating a thermally activated dielectric relaxation processes. The activation energies for the low-temperature relaxation process (E_{a1}) were found to be 0.093 and 0.112 eV for CCTO-2 and CCTO-4, respectively.

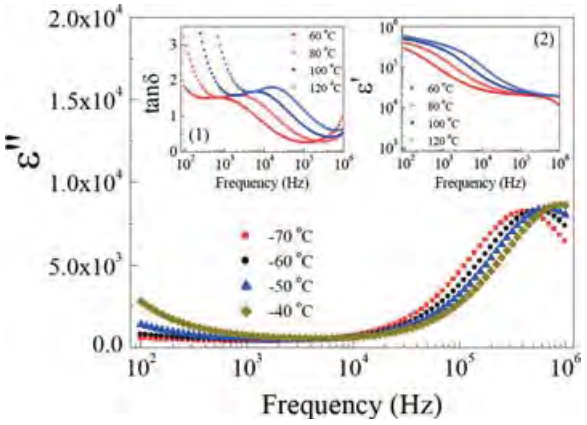


Fig. 6. Frequency dependence of ε″ at low temperatures for CCTO-4 sample showing low-temperature dielectric relaxation. Insets (1) and (2) show, respectively, the frequency dependence of tanδ and ε′ over the temperature range of 60–120°C for CCTO-4 sample.

These values are comparable to the values reported in the literature.[3,11,14] The activation energies for the high-temperature relaxation process (E_{a2}) were found to be 0.577 and 0.588 eV for CCTO-2 and CCTO-4, respectively. Higher E_{a2} values may be related to either the electrical response of GBs or sample–electrode effects.

To study the effects of electrical responses of GBs and sample–electrode interfaces, impedance complex plane (Z*) plots for all samples were used to investigate possible mechanisms. Figures 7a–d show Z* plots at 100°C for all samples. Only one semicircle arc is observed in the fine-grained CCTO-1 and CCTO-3 samples. Two arcs in Z* plots are observed in the CCTO-2 and CCTO-4 samples. Grains, GBs, and sample–electrode effects in combination are possibly responsible for the two electrical responses observed in Figs. 7c and d. To clarify the mechanisms responsible for these two semicircle arcs, combined Z″ and M″ spectroscopic plots at 100°C were used to examine the electrical responses. As shown in Figs. 8a,b, Z″ and M″ of the CCTO-1 and CCTO-3 samples are located in nearly the same frequency range. The low-frequency peaks of Z″ for the CCTO-2 and CCTO-4 samples are observed at 1 kHz and 630 Hz, respectively (Figures 8c, d). The observation of a low-frequency peak in the Z″ spectrum is related to the electrical response of a large semicircle arc. In the high-frequency range, the shoulders of Z″ spectra for the CCTO-2 and CCTO-4 samples are observed at a frequency of about 10^5 Hz. The shoulders are located in nearly the same frequency range as their M″ peaks. This means that the high-frequency Z″ and M″ peaks originated from the same mechanism. At frequencies higher than the frequency of M″ peak, it is observed the values of M″ continue to increase. This increase in the M″ spectrum indicates the presence of another set of M″ peaks.[35] However, very low temperatures (<−70°C) are required to obtain data in the frequency measurement range.[36] The increase in the M″ spectrum suggests an electrical response of grains. Therefore, the high-frequency Z″ and M″ peaks (at $\sim 10^5$ Hz) likely originated from the electrical response of GBs. The low-frequency Z″ peak is therefore attributed to the effect of sample–electrode interfaces.[35,36]

To further study the electrical response of GBs, the frequency dependence of M″ at different temperatures was investigated. As shown in Figs. 9a,b, the M″ peak shifts to higher frequencies as the temperature

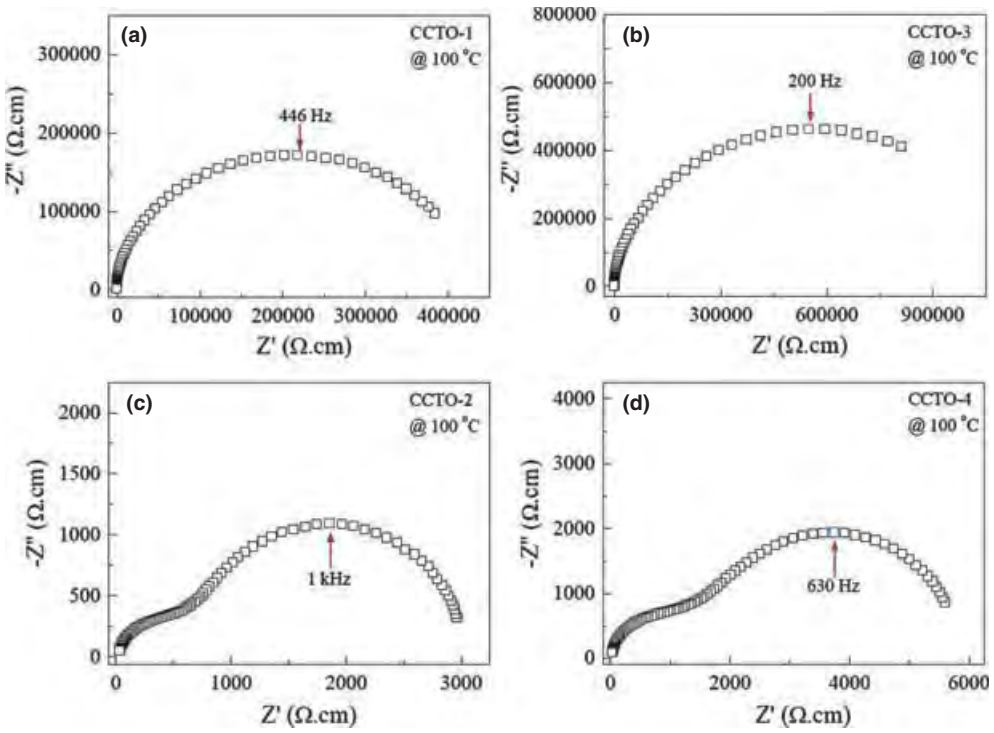


Fig. 7. Impedance complex plane plot (Z) at 100° C for (a) CCTO-1, (b) CCTO-3, (c) CCTO-2, and (d) CCTO-4 samples.*

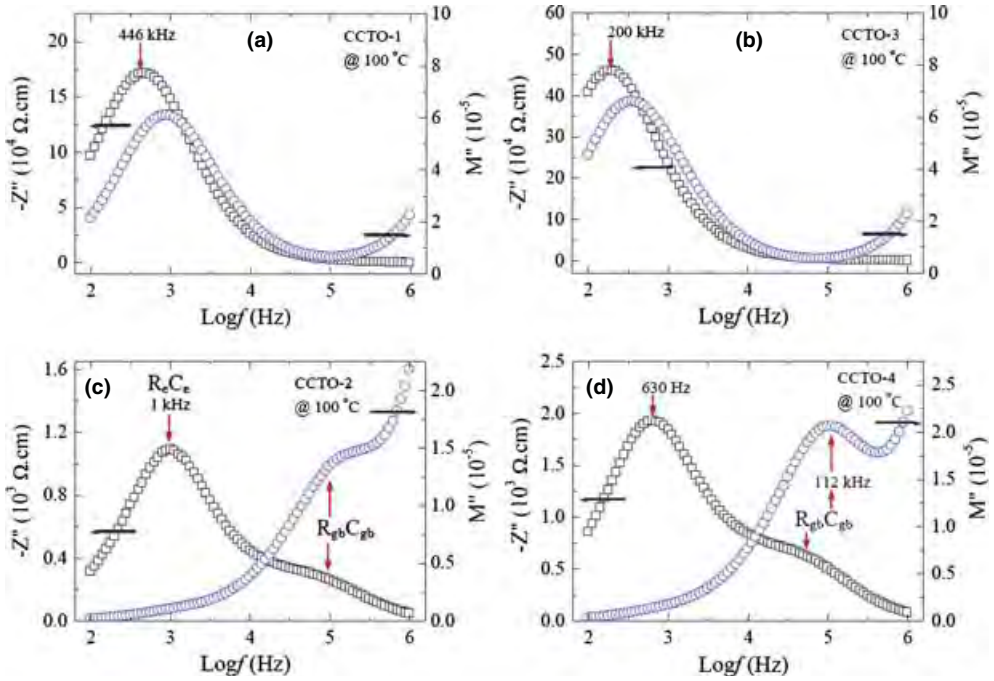


Fig. 8. (a–d) Combined Z'' and M'' spectroscopic plots at 100° C for (a) CCTO-1, (b) CCTO-3, (c) CCTO-2, and (d) CCTO-4 samples.

increases. Note that M″ peak of the CCTO-2 sample cannot be observed at temperature higher than 90°C, as shown in the inset of Fig. 9b. The GB conductivity ($\sigma_{gb} = 1/R_{gb}$) can be calculated from the peak maxima based on the relationships[35,36]:

$$M'' = \frac{C_0}{2C_{gb}}, \tag{1}$$

$$2\pi f_{max} R_{gb} C_{gb} = 1, \tag{2}$$

where R_{gb} and C_{gb} are the resistance and capacitance of GBs, respectively. The electrode contact conductivity ($\sigma_e = 1/R_e$, where R_e is the resistance due to electrode contact) can be calculated from the plots of Z″ as a function of frequency in a high temperature range. At the peak of Z″ related to electrical response of electrode contact, R_e can be estimated from the relationship $Z'' = R_e/2$. σ_e values were calculated at various temperatures. It was found that the temperature dependence of σ_{gb} and σ_e follows the Arrhenius law for conduction processes as shown Fig. 10. This is given by

$$\sigma = \sigma_0 \exp\left(\frac{-E}{k_B T}\right) \tag{3}$$

where σ_0 is the prefactor term, E is the activation energy for conduction process, k_B is Boltzmann constant, and T is absolute temperature. According to the data fitted to Eq. (3), the GB conduction activation energy (E_{gb}) for all samples and the activation energy for electrode response (E_e) of the CCTO-2 and CCTO-4 samples can be calculated from the slopes of the plots. The calculated values are summarized in Table I. It was found that the high-temperature dielectric relaxation activation energy (E_{a2}) and E_e are nearly the same in value. It is likely that that dielectric relaxation behavior in the high-frequency range observed in the CCTO-2 and CCTO-4 samples is mainly related to the effect of sample–electrode contact.

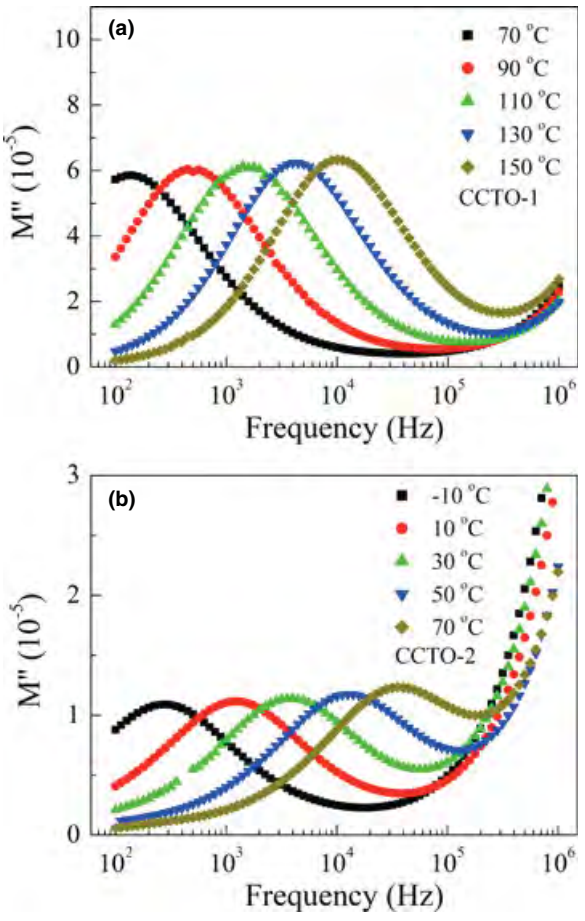


Fig. 9. Frequency dependence of M″ at different temperatures for (a) CCTO-1 and (b) CCTO-2 samples.

Conclusions

The dielectric properties and electrical responses in CCTO ceramics prepared by a simple combustion method were investigated. Fine-grained CCTO

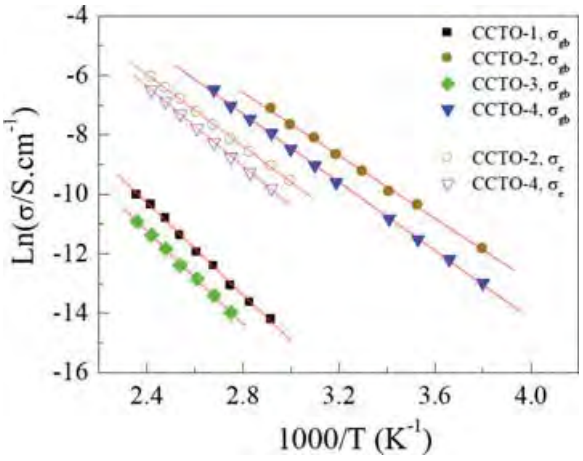


Fig. 10. Arrhenius plot of grain boundary conductivity (σ_{gb}) (extracted from M″ plots) and electrode contact conductivity (extracted from Z″ plots).

ceramics with good dielectric properties ($\tan\delta \sim 0.020$ –0.0.16 and $\varepsilon' \sim 5776$–6406) and temperature stability in the range of −70 to 90°C were obtained by sintered at 1040°C for 1 h. Large-grained CCTO ceramics sintered at 1040°C for 3 h exhibited two sets of dielectric relaxations. Using an impedance spectroscopy analysis, the high-temperature dielectric relaxation was found to be likely caused by the effect of sample–electrode contact.

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Use of lightweight aggregates in pervious concrete

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HIGHLIGHTS

- Three lightweight aggregates were used to make pervious concrete (LWPC).
- Mechanical properties, water permeability, and thermal conductivity were tested.
- LWPCs 558–775 kg/m^3 density and 2.47–5.99 MPa compressive strength were obtained.
- LWPCs density and thermal conductivity had 3–4 times lower than normal aggregate.

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ABSTRACT

In this study, the use of lightweight aggregate (LWA) for making lightweight pervious concrete (LWPC) was presented. Diatomite (DA) and pumice (PA) were used as natural LWAs in pervious concretes. Three cement paste contents of 15%, 20%, and 25% by volume were used. The results were compared to those of LWPC containing recycled LWA from autoclaved aerated concrete (RA). The results indicated that the use of DA, PA, and RA as coarse aggregates in pervious concrete could reduce the density and thermal conductivity about 3–4 times compared with pervious concrete containing natural aggregate. The densities were 558–775 kg/m^3 which were lower than 800 kg/m^3 and suited for use as insulating concrete. The 28-day compressive strengths of LWPCs ranged from 2.47 to 5.99 MPa. The increase in cement paste content improved the mechanical properties of LWPCs. LWPC containing DA showed higher mechanical properties and a lower thermal conductivity than those of RA and PA. However PA exhibited higher water permeability.

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1. Introduction

Lightweight aggregates (LWAs) can be used as aggregates to produce lightweight concretes (LWCs) in a wide range of densities and strengths with different applications. The low density LWCs with compressive strengths ranging from 0.69 to 6.89 MPa are usually employed as insulating concrete. Moderate strength LWCs with compressive strengths ranging from 6.89 to 17.24 MPa are as "fill" concrete. Structural LWCs with compressive in excess of 17.24 MPa with reduced dead load are used for reinforced concrete [1].

The primary benefit of using LWA is the reducing of dead load. LWAs are generally porous materials resulting in superior thermal, acoustic and fire insulations [2,3]. Diatomite is natural lightweight rock resulting from the siliceous fossilized remains of diatoms. It consists of rigid perforated shells called frustules and possesses low density and high porosity. Diatomite can be used as pozzolanic additive to improve plasticity and strengths of concrete [4,5] and can be used in producing lightweight concrete and insulation bricks [3,4]. Pumice is a natural lightweight aggregate with a sponge-like structure created by the release of gases during the solidification of lava. There are two types of pumice: basaltic pumice (scoria) and acidic pumice. The density of acidic pumice is rather less than basaltic pumice. Pumice aggregate can be used in the production of lightweight concrete with sufficient strength and density for use as structural lightweight concrete [6]. Generally, the effective insulating concrete is found in LWCs with high porosity or very low density. The LWCs containing natural LWAs viz., diatomite and pumice [3,7,8] are less effective than insulator materials due to the higher its density as specified in ASTM C332 [9].

Pervious concrete is the concrete with no fine aggregate. The connected void allows water and air to pass through. It can be used in environmental applications such as permeable concrete for pavement, water purifying concrete, noise absorbing concrete, air permeable concrete, and other civil engineering and architectural applications [10–13]. Moreover, pervious concrete contains a large amount of voids and thus its density and thermal conductivity are less than that of conventional concrete [14]. With these special features, the pervious concrete containing natural LWAs further reduces the weight and thermal conductivity of LWCs and therefore

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they may be used as better acoustic and thermal insulating materials. In addition, there are few published studies on the properties of lightweight pervious concrete (LWPC) [15]. Therefore, this study focused on the use of LWA in previous concrete.

In this experiment, the effects of LWA types and cement paste contents on the properties of lightweight pervious concrete (LWPC) were studied. The diatomite and pumice were used as natural coarse LWAs. The cement paste contents of 15%, 20% and 25% by volume were used for each type of LWA. The total void ratio, water permeability coefficient, density, compressive strength, splitting tensile strength, surface abrasion resistance, and thermal conductivity coefficient of LWPCs were evaluated. In addition, the results were compared to those of LWPC containing recycled coarse LWA from autoclaved aerated concrete.

2. Material and sample preparation

2.1. Cement paste

Cement paste was prepared from ordinary Portland cement (OPC) with specific gravity of 3.15 and Blaine fineness of 3120 cm^2/g, type F superplasticizer (SP) at the dosage of 1.25% by weight of cement, and tab water. The constant water to cement ratio (W/C) of 0.24 was used for all mixes with the designed flow value of cement paste of 170–180 mm measured in accordance with JIS R 5201 [16].

2.2. Lightweight aggregates (LWAs)

Three types of LWAs viz., diatomite aggregate (DA), pumice aggregate (PA), and recycled aggregate from autoclaved aerated concrete (RA) were used as coarse aggregates. DA was taken from Lampang province in the north of Thailand. It was calcined at 800 °C for 4 h to reduce clay mineral [17,18]. Commercially variable acidic pumice was used as PA. RA was broken autoclaved aerated concrete blocks obtained from construction site. All types of aggregates were crushed and sieved into the same particle sizes of 4.8–9.5 mm. The coarse aggregates were prepared in saturated surface dry (SSD) condition before the mixing to maintain the same flow value of cement paste of 170–180 mm and to prevent cracking problems due to the water absorption of aggregate [19–21].

2.3. Mix proportions

In order to investigate the effects of different types of LWAs and cement paste contents on the physical and mechanical properties of LWPCs, the mixtures were made with three types of LWAs (DA, PA, and RA) and three cement paste contents of 15%, 20%, and 25% by volume. Nine mix proportions are summarized in Table 1. The names of concretes were given by aggregate type and paste content. For example, RA-15 denotes the LWPC containing RA and 15% of cement paste content by volume.

2.4. Mixing and casting

Cement paste was mixed in a pan-type of mixer for 3 min and then coarse aggregates was added to the mixture and mixed for 2 min. The mixture was placed into a mold and vibrated on vibrating table for 10 s. Two sizes of the samples were cast. The cylindrical samples of 100 mm in diameter and 200 mm in height were used to measure the compressive strength, splitting tensile strength, water permeability, density, total void ratio, and thermal conductivity. The 150 × 300 × 35 mm rectangular samples were used to measure the surface abrasion resistance. The cast samples were covered with damp cloth and plastic sheet to prevent moisture loss and were demolded after 1 day and stored in a moist room until testing age.

Table 1
Mix proportions of LWPCs.

Mix	LWA in SSD (kg/m^3)			OPC (kg/m^3)	Water (kg/m^3)	SP (kg/m^3)
	DA	PA	RA			
DA-15	740	–	–	269	64.6	3.35
DA-20	740	–	–	359	86.1	4.47
DA-25	740	–	–	448	107.6	5.59
PA-15	–	565	–	269	64.6	3.35
PA-20	–	565	–	359	86.1	4.47
PA-25	–	565	–	448	107.6	5.59
RA-15	–	–	630	269	64.6	3.35
RA-20	–	–	630	359	86.1	4.47
RA-25	–	–	630	448	107.6	5.59

3. Tests

3.1. Physical property tests of LWAs

Unit weight and bulk specific gravity with absorption were tested in according with ASTM C29 [22] and ASTM C127 [23], respectively. To determine the resistance to degradation of LWA, the procedure as specified in ASTM C131 [24] was adapted for this study using eight 46-mm diameter steel balls of approximately 400 g each. The volume of LWA for the test was the same as that of natural aggregate. This amounted to 1500 g of oven dry LWA for the Los Angeles test.

3.2. Mechanical property tests of LWPCs

Compressive strengths were tested at the ages of 7 and 28 days in according with ASTM C39 [25]. Before the testing, the samples were capped at both ends with sulfur capping compound to level the loading surface. The splitting tensile strength was tested at 28 days in according with ASTM C496 [26]. The reported results were the averages of 3 samples.

Surface abrasion resistance was tested at 28 days by the rotating-cutting method in accordance with ASTM C944 [27]. The samples were left to dry for 1 day before the test (air-dry condition). The sample was abraded with 98 N loads on the surface for 30 s after contact between the cutter and the surface. The abrasion resistances of each pervious concrete were done six times, three on each side of the concrete samples.

3.3. Total void ratio, density, and water permeability tests of LWPCs

Total void ratio and density of samples was tested in accordance with ASTM C1754 [28]. With the recommendation of ACI 522 [29], the water permeability coefficient of LWPC was measured using the constant head method. To prevent flow between sample and surface of measuring cylinder, the side of cylindrical sample was wrapped by rubber tube and tightened by circular clamps. The time required for a quantity of water to flow through was measured after a steady state flow. The coefficient of water permeability was calculated following Darcy's Law as shown in the following equation:

$$k = QL/HAt \quad (1)$$

where k is the water permeability coefficient (cm/s), Q is the quantity of water collected (cm^3) over time t (s), L is the length of specimen (cm), H is the water head (cm), and A is the cross sectional area of the specimen (cm^2).

3.4. Thermal conductivity test of LWPCs

The thermal conductivity coefficients were tested using a direct measuring instrument with surface probe (ISOMET2114, Applied Precision Ltd.). The measurement ranges of the device are 0.04–6.0 W/m K.

4. Results and discussion

4.1. Properties of LWAs

Visual observation of all LWAs as shown in Fig. 1 clearly showed that surface texture of RA was rougher and more porous than those of DA and PA. For particle shape, PA was rounded, while DA was

slightly rounded and RA was angular. The crushed surfaces of LWAs were examined with Scanning Electron Microscope (SEM) and shown in Fig. 2. It could be clearly observed that RA consisted of large round pores of approximately 200 μm in size while PA consisted of very irregular pores ranging in size of smaller than 10 μm to slightly smaller than 200 μm. The surface texture of DA was different as it appeared denser with uniform pores of size mostly smaller than 10 μm.

The physical properties and chemical composition of all coarse aggregates are shown in Tables 2 and 3. The dry loose bulk densities of DA, PA, and RA were 346, 353, and 361 kg/m^3, respectively which were lower than 880 kg/m^3 of maximum density of LWA for structural concrete as specified in ASTM C330 [30]. The DA, PA, and RA had high water absorptions of 114.1%, 60.3%, and 74.5%, respectively, due to their highly porous surfaces. The values of specific gravity of DA, PA, and RA were 1.32, 1.14, and 1.16, respectively. The Los Angeles abrasion of LWA was presented in the percent weight loss. The weight losses of DA, PA and RA were 52.6%, 66.2%, and 89.9%, respectively. The results showed that DA had higher abrasion resistance than PA and RA and were consistent with the pore and surface texture results.

4.2. Compressive strengths, splitting tensile strengths, and surface abrasion resistances of LWCPs

Table 4 summarizes the compressive strengths, splitting tensile strengths, and weight losses by surface abrasion of LWPCs. When the cement paste content increased from 15% to 25%, the mechanical properties were enhanced. For example, for LWPC containing RA, the 28-day compressive strength increased from 2.62 to 4.45 MPa, the splitting tensile strength increased from 0.58 to 0.93 MPa, and the weight loss decreased from 17.0 to 9.7 g. With regards to the effect of LWA types, DA-25 showed the highest 28-day compressive strength of 5.99 MPa and the lowest weight loss of 8.2 g. The compressive strengths and surface abrasions of LWPC containing DA were higher than those of PA and RA due to its denser texture as also shown by the high resistance to Los Angeles abrasion. In addition, DA in this study was calcined to reduce clay mineral in order to enhance its pozzolanic property [17,18] and this improved the strength of DA concrete. However, the differences between splitting tensile strengths of these three LWAs were not significant.

The 7-day compressive strengths of all LWPCs were approximately 83% of the 28-day compressive strength which was slightly higher than the conventional concrete (70–80%). This may be due to porous and rough surface of LWAs allowed the infiltration of cement paste into aggregate resulting in the absence of wall effect at interfacial zone and the improvement of LWAs [31]. In addition, the strength of the low W/C cement paste developed quite rapidly [32]. The compressive strengths at 28 days of LWPCs were 2.47–5.99 MPa. Although the LWPCs had no fine aggregate and large pore, the compressive strengths were close to those of insulating concrete containing diatomite (3.5–5.8 MPa) [3] and aerated concrete (2.0–8.5 MPa) [33], and were higher than insulating concrete containing micro-sphere from pulverised fuel ash (0.6–2.9 MPa) [34]. The ratios of the splitting tensile strengths to the compressive strengths ranged from 15.2–22.9% with the average of 18.8%. They were higher than those of pervious concrete containing natural aggregate which ranged from 9–14% [35].

4.3. Densities, total void ratios, and water permeability coefficients of LWPCs

The results of densities, total void ratios, and water permeability coefficients of LWPCs are shown in Table 5. The increase in cement paste raised the density while the total void ratio and water permeability coefficient decreased. The densities of LWPCs of 558–775 kg/m^3 were lower than those of pervious concrete containing natural aggregate from crushed limestone (about 3 times) [14,36]. Besides, they were lower than 800 kg/m^3 and thus suited for insulating concrete in according with ASTM C495 [37]. The total void ratios of 15.6–31.8% were within the range recommended by ACI 522 [29] for the appropriate permeability of pervious concrete. When cement paste content of LWPCs increased from 15% to 20%, the water permeability coefficients reduced rapidly such as the reduction of 4.77–1.30 cm/s of PA concrete. This indicated that the connected voids of LWPCs were drastically decreased. The LWPC containing PA tended to have higher water permeability than those containing RA and DA. This may be attributed to the quite round shape of PA.

As the total void content decreased, the compressive strength increased. The increase of cement paste content increased the thickness of paste covering of aggregate and decreased total void ratio, consequently the compressive strength increased. Fig. 3 showed the state of paste covering and voids of LWPC cut surfaces. The total void area was obtained from the image analysis. Each image had a size of 6×6 cm^2 with resolution of 2000×2000 pixels. The obtained void ratios (V_{im}) were similar to the measured values. At 15% cement paste content, the thin layer of paste merely covered aggregate surface resulting in a large void and relatively small contact area. At 20% and 25% cement paste contents, not only the covering of paste was thicker but the excess paste filled the void resulting in a small void and relatively high contact area.

The relationship between the compressive strength and the total void ratio are plotted in Fig. 4. The graph of DA concrete lies on the top and shifts to the right side, while the graphs of RA and PA concretes lie below and are close together. It showed that at the same total void ratio, the compressive strength of LWPC containing DA was higher than those of PA and RA although it used lower cement paste content. The empirical equations relating compressive strengths (σ) and total void ratios (V) are obtained as:

$$\sigma = 13.25e^{-0.0500V},\ R^2 = 0.991 \text{ for LWPC with DA} \quad (2)$$

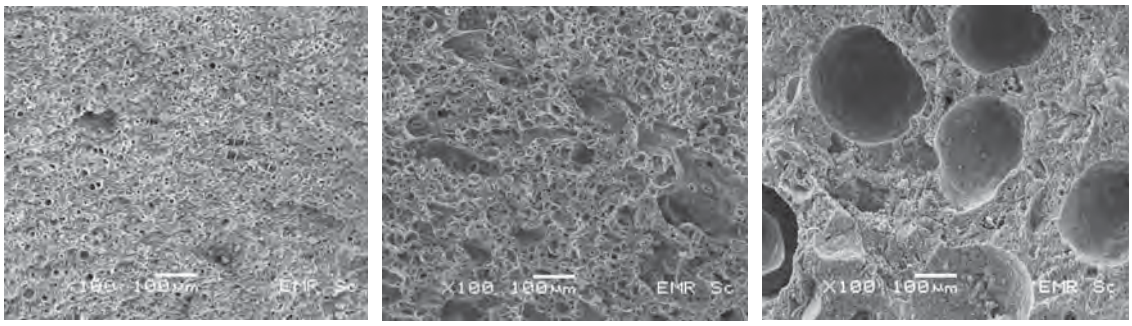
$$\sigma = 10.09e^{-0.0441V},\ R^2 = 0.995 \text{ for LWPC with PA} \quad (3)$$

$$\sigma = 11.95e^{-0.0515V},\ R^2 = 0.989 \text{ for LWPC with RA} \quad (4)$$



(a) DA (b) PA (c) RA

Fig. 1. Particle shapes of LWAs.



(a) DA (b) PA (c) RA

Fig. 2. SEM surfaces of LWAs (100×).

Table 2
Physical properties of LWAs.

Property	DA	PA	RA
Dry loose bulk density (kg/m^3)	346	353	361
Specific gravity	1.32	1.14	1.16
Water absorption (%)	114.1	60.3	74.5
Los Angeles abrasion weight loss (%)	52.6	66.2	89.9

Table 3
Chemical composition of LWAs.

Chemical composition (%)	DA	PA	RA
SiO_2	83.07	61.09	38.48
Al_2O_3	7.78	12.30	2.45
Fe_2O_3	4.60	5.29	1.83
CaO	0.52	3.68	36.33
MgO	0.45	1.11	0.71
Na_2O	0.14	6.11	0.26
K_2O	1.92	5.35	1.48
SO_3	–	0.09	5.71
TiO_2	0.51	0.74	0.11
LOI	0.80	3.30	12.40

Table 4
Mechanical properties of LWPCs.

Mix	7-Day compressive strength (MPa)	28-Day compressive strength (MPa)	28-Day splitting tensile strength (MPa)	Surface abrasion weight loss (g)
DA-15	2.65	3.20	0.57	13.2
DA-20	3.79	4.68	0.71	10.2
DA-25	5.10	5.99	0.93	8.2
PA-15	1.94	2.47	0.47	17.8
PA-20	2.14	3.50	0.75	12.3
PA-25	3.88	4.30	0.99	10.2
RA-15	2.26	2.62	0.58	17.0
RA-20	2.56	3.43	0.67	14.7
RA-25	4.58	4.45	0.93	9.7

In addition, these exponential equations with high correlation coefficient could predict the compressive strengths at zero total void ratios of 11.95, 13.25, and 10.09 MPa for LWPCs with RA, DA, and PA, respectively. The relatively strong relation between the compressive strength and void ratio of LWPC was similar to a porous brittle material and normal pervious concrete as suggested by Ryshkewitch [38] and Chindaprasirt et al. [39,40]. In addition, the relationship between the compressive strength and water permeability coefficient of LWPC with different types of LWAs are plotted in Fig. 5 and the equations could be expressed as:

Table 5
Physical properties of LWPCs.

Mix	Density (kg/m^3)	Total void ratio (%)	Water permeability coefficient (cm/s)
DA-15	558	28.1	2.43
DA-20	644	21.4	0.97
DA-25	740	15.5	0.42
PA-15	602	31.8	4.77
PA-20	690	24.5	1.30
PA-25	765	19.1	0.90
RA-15	602	29.7	2.93
RA-20	701	23.6	0.98
RA-25	775	19.6	0.30

$$\sigma = 6.56e^{-0.301k},\ R^2 = 0.983 \text{ for LWPC with DA} \quad (5)$$

$$\sigma = 4.48e^{-0.127k},\ R^2 = 0.922 \text{ for LWPC with PA} \quad (6)$$

$$\sigma = 4.45e^{-0.187k},\ R^2 = 0.932 \text{ for LWPC with RA} \quad (7)$$

where σ is compressive strength of LWPC (MPa) and k is water permeability coefficient (cm/s).

The linear relationship between the density and void ratio of LWPC with different types of LWAs are plotted in Fig. 6. The DA concrete showed lower density than the PA and RA concretes at the same void content. The correlation coefficient of the results was high with R^2 of 0.995–0.999. The densities and total void ratios could be expressed as:

$$D = 961 - 14.45V,\ R^2 = 0.995 \text{ for LWPC with DA} \quad (8)$$

$$D = 1047 - 14.69V,\ R^2 = 0.999 \text{ for LWPC with PA} \quad (9)$$

$$D = 1105 - 16.99V,\ R^2 = 0.999 \text{ for LWPC with RA} \quad (10)$$

where D is dry density of LWPC (kg/m^3) and V is total void ratio (%).

In this study, the graphs of water permeability coefficient and total void ratio are plotted in Fig. 7. It can be observed that the water permeability coefficients of LWPCs with higher cement paste content were clearly lower than those with low cement paste content because the connected pores reduced with the increase in cement paste content. The graph of PA lies on the top and shifts to the right. It indicated that the permeability and total void ratio of LWPC containing PA was higher than those of LWPC containing DA. Moreover, at the same total void ratio, the permeability of LWPC containing PA was higher than that of LWPC. This could be attributed to the more rounded shape of PA that resulted in higher pore connectivity. For the graph of RA, it lies on the bottom and presents the lowest water permeability. For the graph of RA, it lies

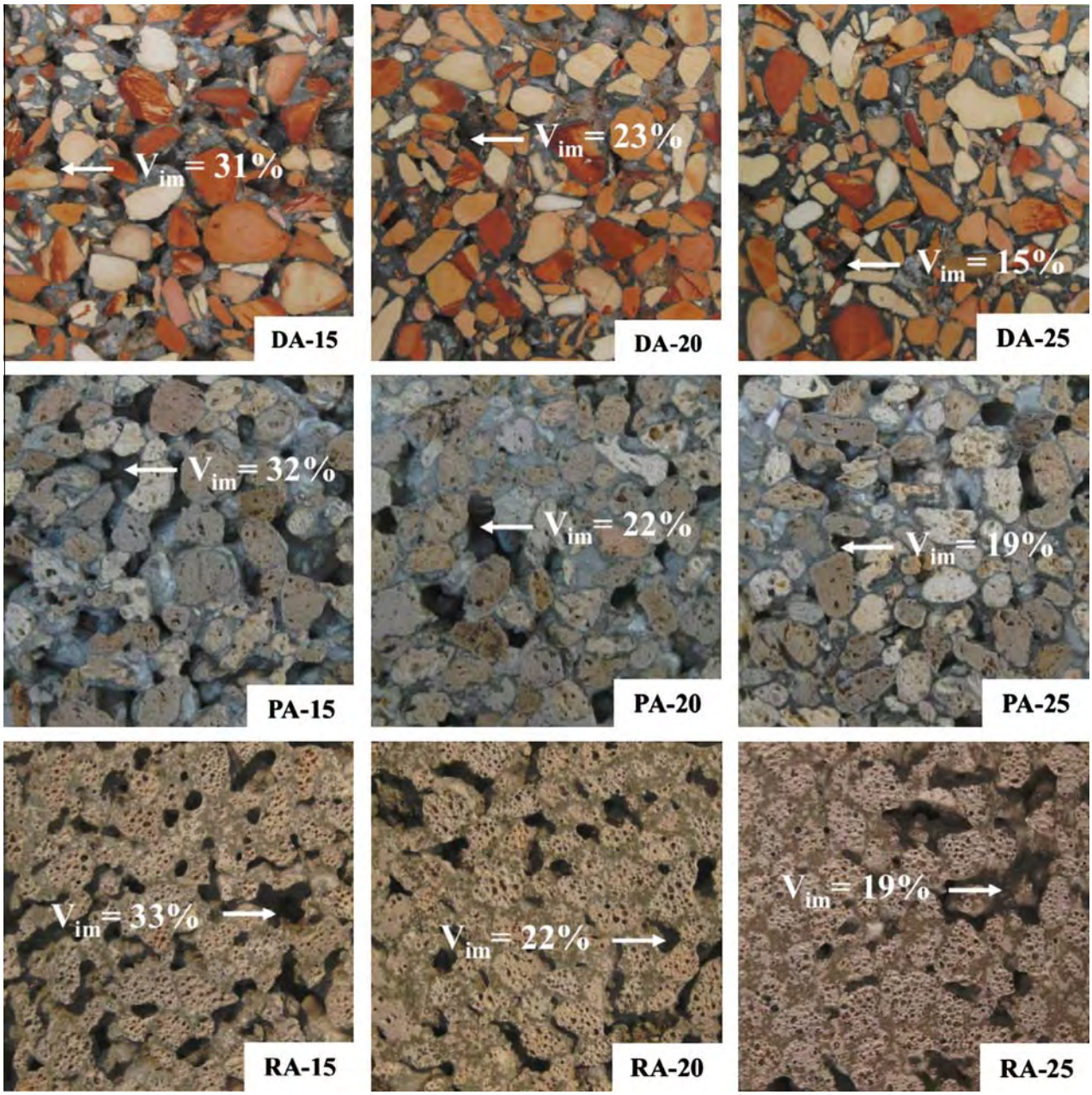


Fig. 3. State of the paste covering and total void content of LWPCs.

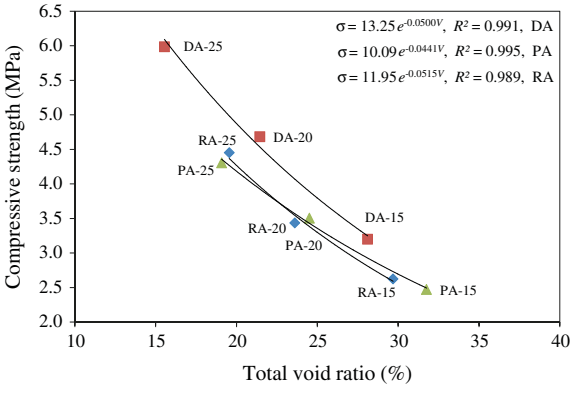


Fig. 4. Compressive strength and total void ratio of LWPCs.

at the bottom and presents the slightly lower water permeability than DA concrete. As already discussed, this may be due to the fact that the RA consisted of large round pores of approximately 200 μm, which are unconnected pores. The strong relationship between water permeability coefficient and total void ratio was an exponential equation as also reported by other researches [41,42]. The three equations could be expressed as:

$$k = 0.047e^{0.140V}, R^2 = 0.999 \text{ for LWPC with DA} \quad (11)$$

$$k = 0.061e^{0.134V}, R^2 = 0.948 \text{ for LWPC with PA} \quad (12)$$

$$k = 0.004e^{0.220V}, R^2 = 0.982 \text{ for LWPC with RA} \quad (13)$$

where k is water permeability coefficient (cm/s) and V is total void ratio (%).

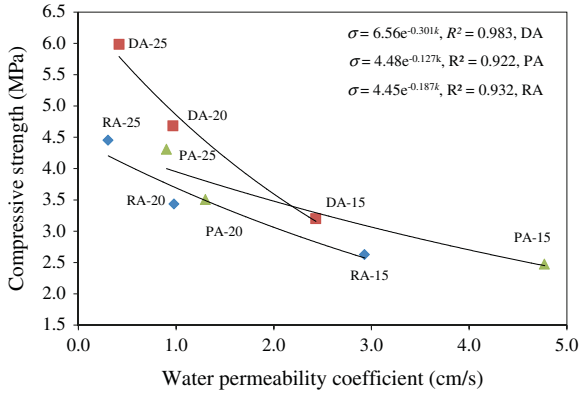


Fig. 5. Compressive strength and water permeability coefficient of LWPCs.

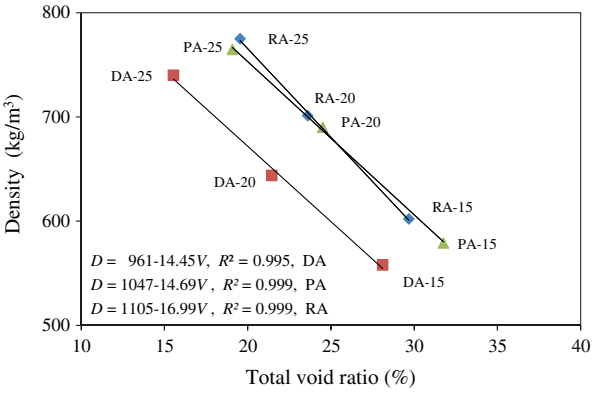


Fig. 6. Density and total void ratio of LWPCs.

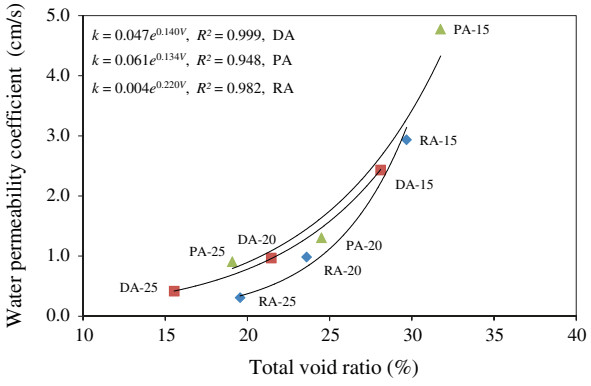


Fig. 7. Water permeability coefficient and total void ratio of LWPCs.

4.4. Thermal conductivity coefficients of LWPCs

The thermal conductivity coefficients are shown in Fig. 8. The results thermal conductivity coefficients depended on the cement paste contents and types of aggregates. When the cement paste content of LWPCs increased from 15% to 25%, the thermal conductivity coefficient increased from 0.16 to 0.23 W/m K for DA concrete, from 0.16 to 0.24 W/m K for PA concrete, and from 0.17 to 0.25 W/m K for RA concrete. The increase in cement paste content caused the filling of paste in voids and increased the density, consequently the thermal conductivity coefficient increased [43]. The thermal conductivity coefficients of LWPC containing

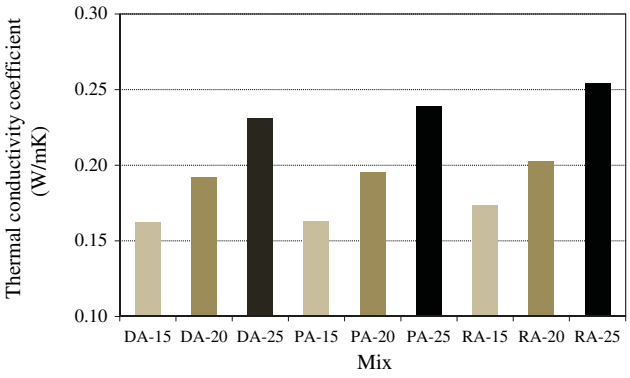


Fig. 8. Thermal conductivity coefficients of LWPCs.

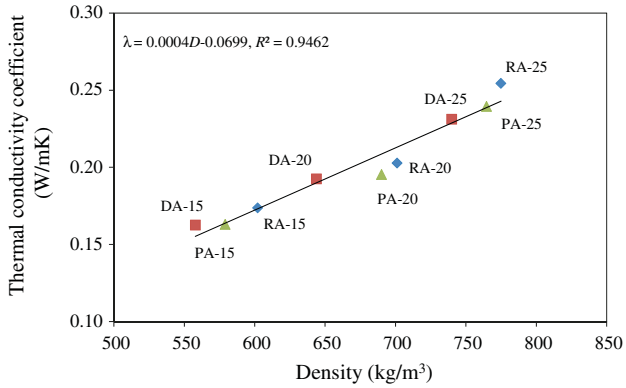


Fig. 9. Thermal conductivity coefficient and density of LWPCs.

DA were slightly lower than those of PA and RA due to its lower density.

The thermal conductivity coefficients of LWPCs (0.16–0.25 W/m K) were slightly higher than autoclaved aerated concrete (0.11–0.21 W/m K) with similar strength of 2.8–8.5 MPa and density of 600–700 kg/m^3 [33]. The LWPCs showed lower thermal conductivities and densities than those of natural LWC (thermal conductivities of 0.23–0.314 W/m K and densities of 900–1190 kg/m^3) [3]. In addition, the thermal conductivities of LWPCs was approximately 3–4 times lower than that of pervious concrete containing natural [13].

The linear relationships between the thermal conductivity coefficients and the densities of LWPCs containing different types of LWAs are plotted in Fig 9. The correlation coefficient of the results was high with R^2 ranging between 0.9462. The equation of results could be expressed as:

$$\lambda = 0.0004D - 0.0699, R^2 = 0.9462 \text{ for LWPCs} \quad (14)$$

where λ is thermal conductivity coefficient (W/m K) and D is dry density of LWPC (kg/m^3).

5. Conclusions

The use of RA, DA, and PA as coarse aggregates in pervious concrete reduced the density and thermal conductivity compared with that of pervious concrete containing natural aggregate (approximate 3–4 times). The densities of all LWPCs ranged from 558 to 775 kg/m^3 with the 28 days compressive strengths varied between 2.47 and 5.99 MPa and could be used for application in insulating material. The thermal conductivity coefficients of LWPCs were 0.16 and 0.25 W/m K which were slightly higher than that of

autoclaved aerated concrete and similar to low density LWCs. The increase in cement paste content decreased total void ratio and water permeability, while mechanical properties and density were increased. The increasing of cement paste content from 15% to 20% could rapidly reduce water permeability. LWPC containing DA exhibited a higher quality of mechanical properties and a lower thermal conductivity than those of RA and PA. However, LWPC containing PA showed the highest water permeability.

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Lightweight geopolymer concrete containing aggregate from recycle lightweight block

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ABSTRACT

In this research, the properties of lightweight geopolymer concrete containing aggregate from recycle lightweight block were studied. The recycle block was crushed and classified as fine, medium and coarse aggregates. The compressive strength and density with various liquid alkaline/ash ratios, sodium silicate/NaOH ratios, NaOH concentrations, aggregate/ash ratios and curing temperatures were tested. In addition, porosity, water absorption, and modulus of elasticity were determined. Results showed that the lightweight geopolymer blocks with satisfactory strength and density could be made. The 28-day compressive strength of 1.0–16.0 MPa, density of 860–1400 kg/m^3, water absorption of 10–31% and porosity of 12–34%, and modulus of elasticity of 2.9–9.9 GPa were obtained. It can be used as lightweight geopolymer concrete for wall and partition.

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1. Introduction

The construction of building and structures in Thailand and many countries relies heavily on the Portland cement products. The structural members are usually made of reinforced concrete. The walls and panels are also Portland cement based products. The problems of the size and weight of reinforced concrete members and wall panels are of great concern [1]. In order to reduce the weight, lightweight structural concrete and normal lightweight concrete in the form of lightweight concrete block or wall using cast-in-place lightweight concrete have been developed. The purpose is to reduce the dead load of structure which also results in smaller and lighter structures and reduced cost of construction.

Lightweight concrete made with natural or artificial lightweight aggregates are available in many parts of the world. It can be used in producing concrete in a wide range of unit weights and suitable strengths for various applications including internal and external walls, inner leaves of roof decks and floors [2,3]. The production of lightweight aggregate concrete has been expanding, and now includes all types of no-fines concrete of low density of 300–1200 kg/m^3 for block production and of medium density of 1000–2000 kg/m^3 for structural concrete. The production of all types of concrete is normally based on the availability of lightweight aggregate, and cost dictates the use of lightweight aggregate concrete in place of normal-weight concrete [2].

The manufacturing of Portland cement results in the release of a large amount of carbondioxide into the Earth's atmosphere. Up to 13,500 tons per year or accounted to 7% of the green house gas produced annually [4]. Therefore, the other form of cementitious materials termed geopolymer was developed. It is made from starting materials containing silicon and aluminum which are activated in a high alkali solution. The starting material is usually based on class F fly ash and sometime called alkali-activated fly ash cement [5–9]. High calcium fly ash (class F) is also suitable for use as source materials [10,11].

The use of lightweight concrete block is increasing and its waste also increases from the damage of blocks from manufacturing, transportation and handling. The increased used especially for the housing industries also indicate the amount of lightweight block to be recycled.

This research aims to study the properties of lightweight geopolymer concrete made of lightweight aggregate from recycle block. The knowledge would be beneficial to future applications of the materials and construction industry.

2. Experimental program

2.1. Materials

Materials used in this research consisted of lignite fly ash from Mae Moh power station in the north of Thailand, sodium silicate with 15.32% Na_2O, 32.87% SiO_2, and 51.8% water, and sodium

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Fig. 1. Coarse, medium and fine recycle aggregates.

Table 1
Physical properties of materials.

Materials	Fly ash	FA	MA	CA
Specific gravity	2.52	2.61	1.96	1.42
Median particle size (μm)	18.6	–	–	–
Particle size (mm)	–	0.001–1.18	1.18–4.75	4.75–12.5
Fineness modulus	–	1.75	3.90	5.74
Density (kg/m^3)	–	720	390	360
Water absorption (%)	–	56	68	76

hydroxide (NaOH) of three concentrations of 5, 10, and 15 M and recycle lightweight block (RLB). RLBs were crushed and classified as fine aggregate (FA), medium aggregate (MA) and coarse aggregate (CA) with particle sizes ranging between 0.001 and 1.18, 1.18–4.75, 4.75–12.5 mm, respectively as shown in Fig 1. Chemical compositions of fly ash were determined using X-ray fluorescence (XRF) are shown in Table 2 and its X-ray diffraction (XRD) is shown in Fig. 2. The fly ash consisted of a high content of 45.23% SiO_2, 19.94% Al_2O_3, 13.15% Fe_2O_3, and 15.5% Ca0 with the loss on ignition (LOI) 0.87%. It was, therefore, a class F in accordance which ASTM:C618. The XRD analysis showed mainly amorphous phase with the peaks of crystals of magnetite, magnesioferrite, dachiardite, and calcium aluminum oxide. The physical properties of materials are shown in Table 1. The fly ash was 48% retained on sieve No. 325 (45 μm) with mean particle sized of 18.6 μm and Blaine finenesses of 2409 cm^2/g. It consists of mainly spherical particles with smooth surface as shown in Fig. 3.

2.2. Mix proportion

2.2.1. Aggregate gradation

To study the effect of aggregate gradation, the FA and MA portions were varied and the CA portion was kept constant at 30%. The effect of the change in the small aggregate portion is larger than that of the large portion [12]. A total of three aggregate gradations with FA:MA:CA ratios of 0:70:30 (0F), 30:40:30 (30F), and 70:0:30 (70F) were used.

2.2.2. Mix compositions

Five series of mixes were used to test the effects of liquid alkaline/ash ratios (series A), sodium silicate/NaOH ratios (series B), concentration of NaOH (series C), temperature of curing (series D), and aggregate/ash ratios (series E). The details of mixes are shown in Table 3.

2.3. Details of mixing

NaOH solution and fly ash were firstly mixed for 5 min in a pan mixer. Sodium silicate solution was then added and mixing was done for another 5 min until the mixture was uniform. The aggregate was added next and mixing was done for 1.5 min. The fresh lightweight geopolymer concretes were placed into 50 mm cube molds in accordance with ASTM:C109, into 100 mm cube molds, and 150 × 300 mm cylindrical molds in accordance with ASTM:C39. The specimens were covered damp cloth and plastic sheet to prevent moisture loss and placed in a 25 °C controlled room for 1 h [10]. The specimens were then transferred to oven curing for 48 h. Finally, the specimens were demolded and wrapped again with plastic sheet and stored in a 25 °C controlled room.

2.4. Details of test

2.4.1. Density and compressive strength

The density was determined at the ages of 28 days using the compressive strength specimens as described in ASTM:C138. The density was measured. After the density determination, the cube specimens were tested to determine the compressive strength in accordance with ASTM:C109. The reported density and compressive strengths were the average of three samples.

2.4.2. Water absorption and porosity

The cube specimens of series E were tested for porosity and water absorption at the age of 28 days in accordance with ASTM:C642. The porosity was calculated using Eq. (1) and the water absorption was calculated using Eq. (2).

$$\text{Porosity}(\%) = (C - A)/(C - D) \quad (1)$$

$$\text{Absorption}(\%) = [(B - A)/A] \times 100 \quad (2)$$

where A is the mass of oven – dry sample in air (g), B is mass of surface – dry sample in air after immersion (g), C is mass of surface – dry sample in air after immersion and boiling (g), and D is apparent mass of sample in water after immersion and boiling (g)

2.4.3. Modulus of elasticity

The cylinder specimens of series E were tested for the chord modulus at the age of 28 days in accordance with ASTM:C469. The reported results were the average of two samples.

3. Results and discussion

3.1. Compressive strength and density

3.1.1. Liquid alkaline/ash ratio

The results of compressive strength of lightweight geopolymer concrete series A with varies liquid alkaline/ash ratios are shown in Fig. 4a. The optimum compressive strength was at L/A ratio of 2.4. At low L/A ratios of 2.0 and 2.2, the mix was difficult to mix and compact due to the low liquid content [13]. The increase in the L/A ratio at this range increased the compressive strength of the geopolymer. However, when the L/A ratio increased from 2.4 to 2.8, the compressive strength decreased due to the excess liquid and bleeding in a similar manner to Portland cement concrete [14–

Table 2
Chemical composition of materials (by weight).

Chemical compositions (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	Na_2O	P_2O_5	MgO	LOI
Fly ash	45.23	19.95	13.15	15.50	2.15	0.39	0.52	0.81	2.02	0.88

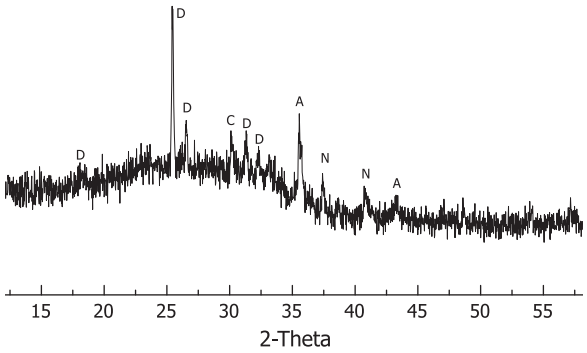


Fig. 2. XRD patterns of fly ash. A-magnetite: Fe_3O_4; C-magnesioferrite: Fe_2MgO_4; D-dachiardite: $Na_{1.1}K_7Ca_{1.7}Al_{5.2}Si_{18.8}O_{48}$ $(H_2O)_{12.7}$; N-calcium aluminum oxide: $CaAl_2O_4$.

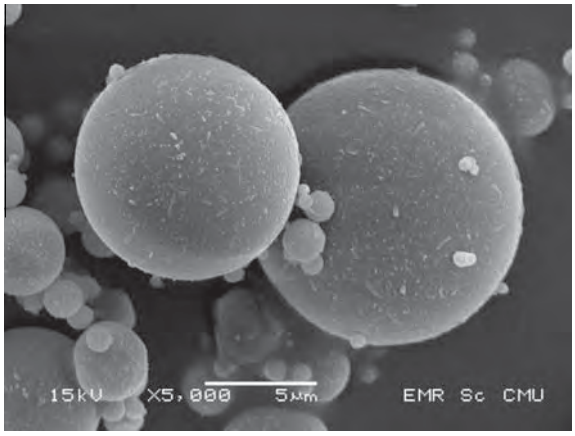
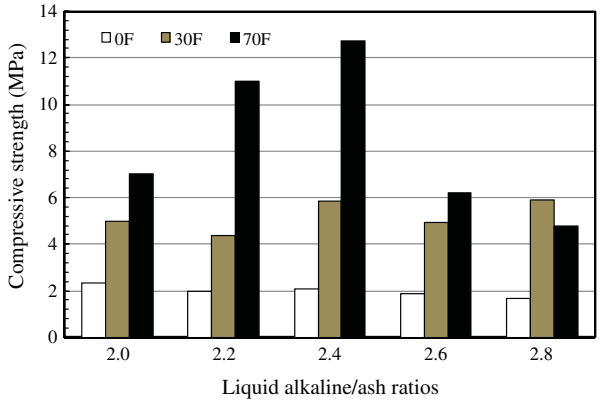
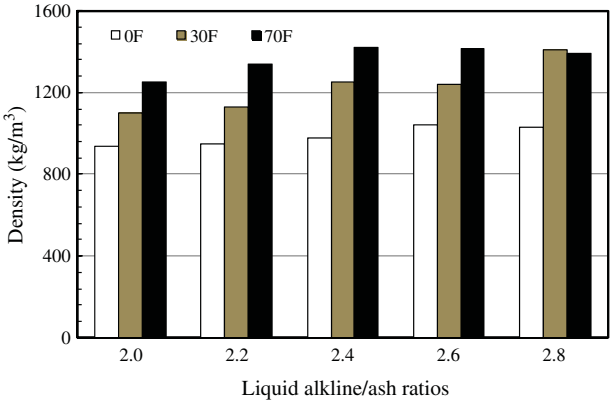


Fig. 3. SEM of fly ash.



(a) Compressive strength



(b) Density

Fig. 4. Compressive strength and density at 28 days of lightweight geopolymer concrete series A at various L/A ratios.

Table 3
Weight ratios of geopolymer lightweight concrete mixes.

Series	L/A ratio	NS/NaOH ratio	NaOH (M)	Temp. of curing (°C)	Aggregate/ash ratio
A	2.0, 2.2, 2.4, 2.6, 2.8	1.0	10	60	2.2
B	2.2	0.33, 0.67, 1.00, 1.50, 3.00	10	60	2.2
C	2.2	1.0	5, 10, 15	60	2.2
D	2.2	1.0	10	25, 40, 60	2.2
E	2.2	1.0	10	60	2.0, 2.2, 2.4, 2.6

16]. For example, the 28-day compressive strengths of 70F series A mixes with L/A ratios of 2.0, 2.2, 2.4, 2.6, and 2.8 were 7.0, 11.0, 12.7, 6.2, and 4.8 MPa, respectively.

With regards to aggregate sizes, the compressive strengths of mixes with the high amount of FA were higher than those with the low amount of FA. For example, the 28-day compressive strengths of L/A ratio of 2.2 mixes with 0F, 30F, and 70F aggregates were 2.0, 4.4, and 11.0 MPa, respectively. The use of FA aggregate with high surface area resulted in the better bonding of matrix and aggregate than that of CA and led to an increase in strength [17]. For the density, the results of lightweight geopolymer concrete with various L/A ratios are shown in Fig. 4b. The increased in L/A ratios resulted in lightweight geopolymer concrete with a slightly increase in density. For example, the density of lightweight geopolymer concretes with L/A ratios of 2.0, 2.2, 2.4, 2.6, and 2.8, and with 30F aggregate were 1099, 1131, 1252, 1237, and 1389 kg/m^3, respectively. The increase was due to the reduced ash which was low in density.

Similarly, the density also increased with the increasing amount of FA. The densities of 0F, 30F, and 70F mixes with L/A ratio of 2.2 were 948, 1132, and 1336 kg/m^3, respectively. The density of FA was high at 720 kg/m^3 compared with the lower values of MA and CA of 390 and 360 kg/m^3, respectively (Table 1) and thus the use of a higher amount of FA resulted in geopolymer with higher density.

3.1.2. Sodium silicate/NaOH ratio

The effects of compressive strength of lightweight geopolymer concrete with varies NS/NaOH ratios are shown in Fig. 5a. The compressive strength increased with the increasing of NS/NaOH ratios. Similar increases in strength were reported with NS/NaOH ratio up to 1.50, however, the increased in NS/NaOH ratio beyond this value resulted in a reduction in strength due to difficulties in compaction of the mixes as the mix was too stiff with the low liquid/ash ratio of 0.6 [13]. For this study, the strength increased even with the NS/NaOH ratio of 3.0. The increase in strength at this NS/NaOH ratio was possible as a result of high liquid/ash ratio of 2.2 which made the mix workable and compactable. For example, the 28-day compressive strength of samples with NS/NaOH ratios of 0.33, 0.67, 1.00, 1.50, and 3.00 were 7.6, 9.7, 10.5, 12.9, and 15.4 MPa, respectively. The NS/NaOH ratios also affected the pH conditions and the strength development of geopolymer [10]. The densities of lightweight geopolymer concrete with various NS/NaOH ratios were

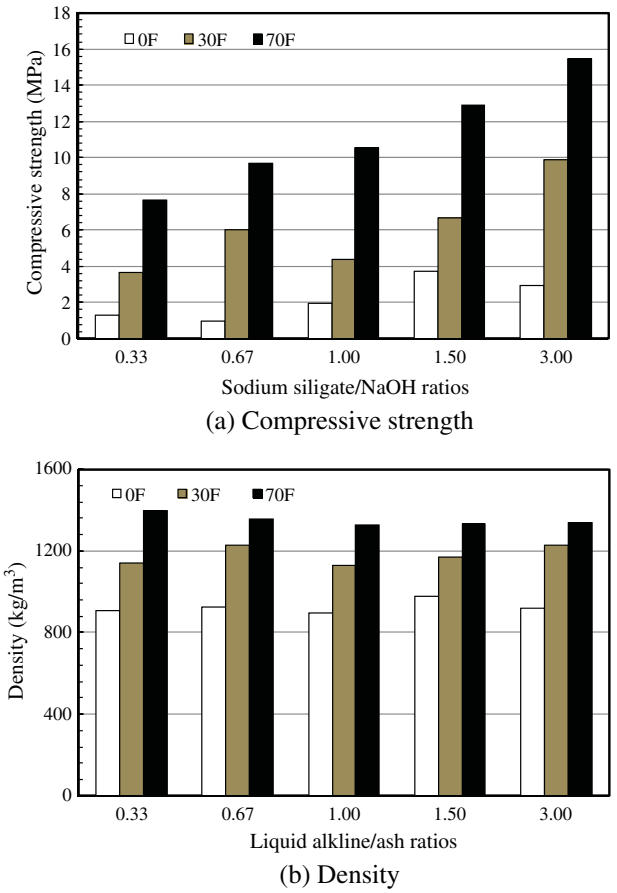


Fig. 5. Compressive strength and density at 28 days of lightweight geopolymer concrete series B at various NS/NaOH ratios.

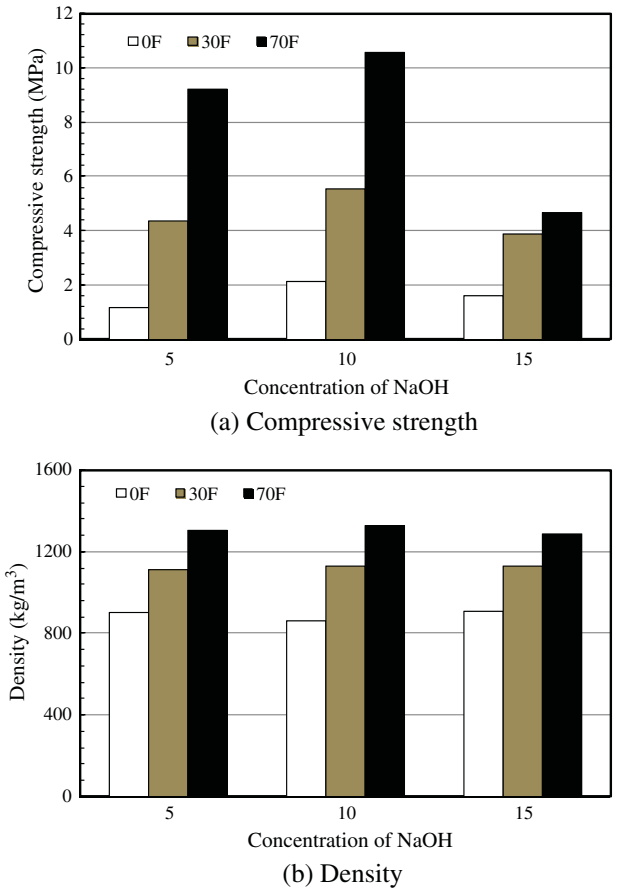


Fig. 6. Compressive strength and density at 28 days of lightweight geopolymer concrete series C at various concentrations of NaOH solution.

not very different as shown in Fig. 5b. This was due to the amount of liquid in the mixes was the same and the change in the liquid density was small.

3.1.3. Concentration of NaOH solution

The results of the compressive strength of lightweight geopolymer concrete with various concentrations of NaOH solution are shown in Fig. 6a. The optimum concentration of NaOH solution was 10 M and the maximum strength of 10.5 MPa was obtained. An increased the concentration of NaOH solution from 5 M to 10 M resulted in the increasing compressive strength. However, an increased the concentration of NaOH solution from 10 to 15 M resulted in a decrease in the compressive strength. At high concentration of NaOH, excessive hydroxide ions caused aluminosilicate gel precipitation at the very early stages. Consequently, compressive strength of geopolymer were lower [18–20]. For example, the 28-day compressive strength of 70F mixes with concentration of NaOH solution of 5, 10, and 15 M were 9.2, 10.5, and 4.7 MPa, respectively.

The densities of lightweight geopolymer concretes with various concentrations of NaOH solution were similar as shown in Fig. 6b. The densities were not affected by the concentrations of NaOH solution as the densities of the liquid in the mixes were similar with various concentrations of NaOH solution.

3.1.4. Temperature of curing

The results of compressive strength of lightweight geopolymer concrete with various temperatures of curing are shown in Fig. 7a. The compressive strength increased with the increasing temperature of curing. For example, the 28-day compressive strength of 70F mixes with temperature of curing of 25, 40, and 60 °C were 6.6, 9.4, and 10.5 MPa, respectively. The increase in temperature of curing to 60 °C enhanced the geopolymerization and increased the strength of geopolymer [10,21–23]. The results of densities of lightweight geopolymer concrete with various temperatures of curing are shown in Fig. 7b. The densities of lightweight concrete, however, decreased with the increase in temperature of curing due to the increased geopolymerization and the loss of moisture from the sample [8]. For example, the 28-day densities of 0F mixes with temperatures of curing of 25, 40, and 60 °C were 984, 975, and 861 kg/m^3, respectively.

3.1.5. Aggregate/ash ratio

The results of compressive strength of lightweight geopolymer concrete with various aggregate/ash ratios are shown in Fig. 8a. The compressive strength significantly decreased with the increasing aggregate/ash ratios. For example, the 28-day compressive strength of 70F mixes with aggregate/ash ratios of 2.0, 2.2, 2.4, and 2.6 were 13.5, 10.5, 7.5, and 4.9 MPa, respectively. The lightweight aggregate is normally weaker than the geopolymer matrix and its increased amount reduced the strength of lightweight concrete [24–26]. The results of densities of lightweight geopolymer concrete with various aggregate/ash ratios are shown in Fig. 8b. The increasing the amount of lightweight aggregate resulted in density reductions due to the lighter weight aggregate. When lightweight aggregate was inserted into the matrices, the porosities of concrete increased and densities decreased [27]. For example, the 28-day densities of 30F mix with aggregate/ash ratios of 2.0, 2.2, 2.4, and 2.6 were 1219, 1131, 1090, and 1037 kg/m^3, respectively.

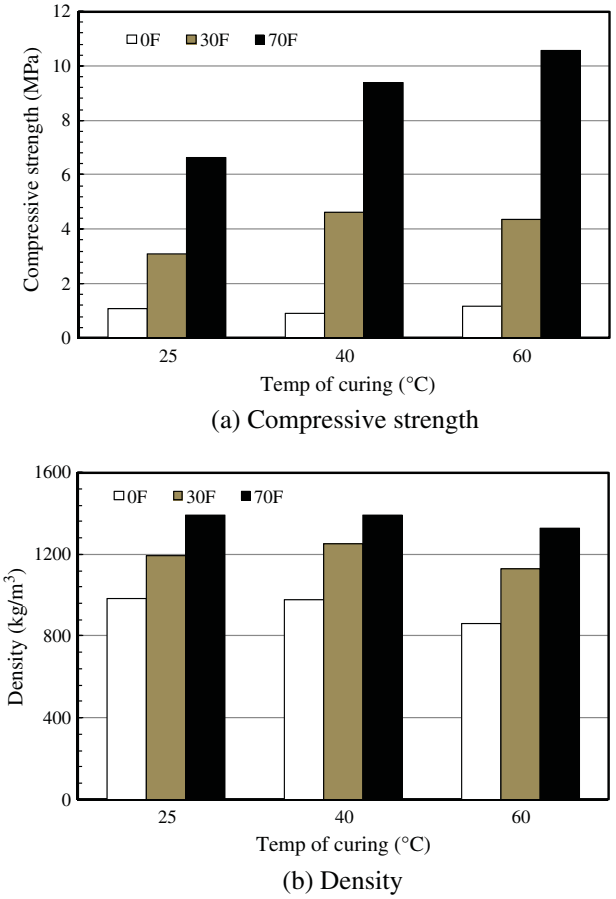


Fig. 7. Compressive strength and density at 28 days of lightweight geopolymer concrete series D at various temperatures of curing.

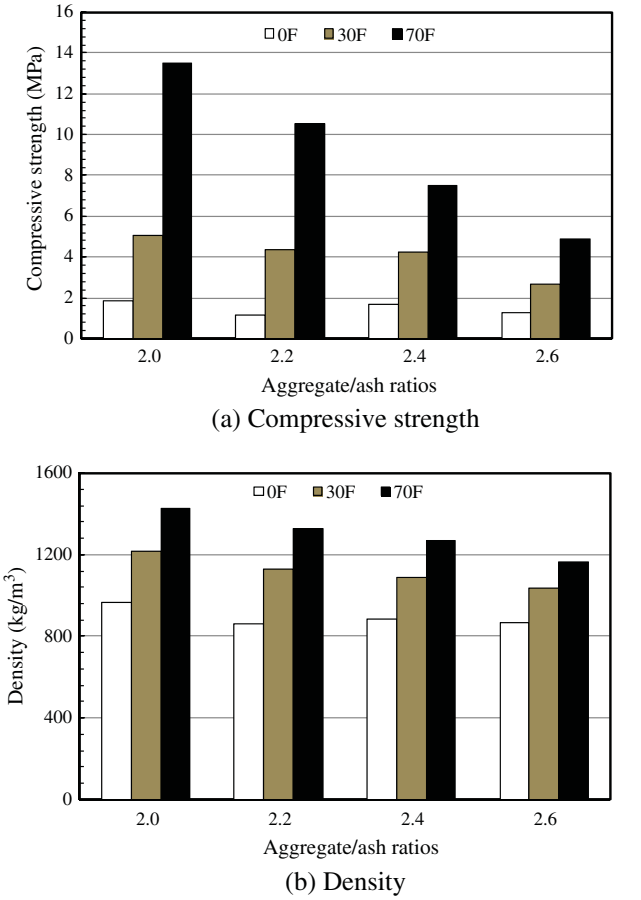


Fig. 8. Compressive strength and density at 28 days of lightweight geopolymer concrete series E at various aggregate/ash ratios.

3.2. Water absorption and porosity

The result of water absorption of lightweight geopolymer concrete with various aggregate/ash ratios are shown in Fig. 9. The water absorption slightly increased with the increase in the amount of aggregate/ash ratios. For example, the water absorption at 28 day of 0F mixes with aggregate/ash ratios of 2.0, 2.2, 2.4, and 2.6 were 30.13%, 30.70%, 31.40%, and 32.15%, respectively. The results of porosity were similar to those of water absorption as shown in Fig. 10. The porosity values increased with the increasing aggregate/ash ratios.

With regard to amount of fine aggregate, the water absorption decreased with the increasing amount of fine aggregate. This was due to the fine aggregate filled the voids in the matrices and thus reduced the porosity. This also resulted in a low water absorption concrete [12].

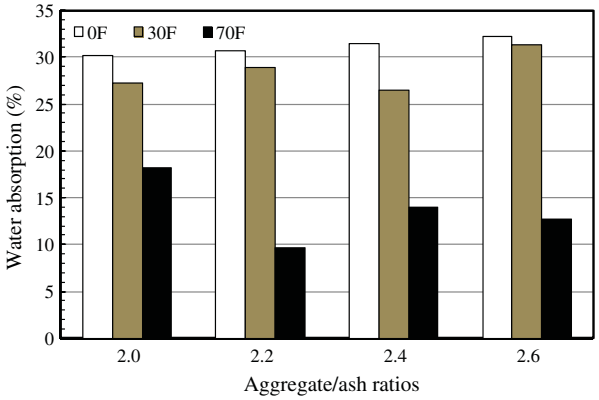


Fig. 9. Water absorption at 28 days of lightweight geopolymer concrete.

3.3. Modulus of elasticity

The results of modulus of elasticity of lightweight geopolymer concrete with various aggregate/ash ratios are shown in Fig. 11. The modulus of elasticity of lightweight concrete showed a similar pattern to those of strength with various aggregate/ash ratios. The optimum density was at aggregate/ash ratio of 2.2 whereas the optimum strength was at a slightly higher aggregate/ash ratio of 2.4. The initial increase in the volume of lightweight aggregate decreased the compressive strength and modulus of elasticity [12,25,28]. For example, the modulii of elasticity of 70F mixes of aggregate/ash ratios of 2.0, 2.2, 2.4, and 2.6 were 7.0, 9.9, 9.2, and 4.5 GPa, respectively. The increase in amount of fine aggregate also resulted in the increase in modulus of elasticity due to the small aggregates filled the pore in matrices which made the concrete more compact and stronger than that with large aggregate.

3.4. Relationship of compressive strength, density, and modulus of elasticity

The relationships between compressive strength and density of lightweight concrete with various aggregate/ash ratios were presented by Eq. (3) and shown Fig. 12. The compressive strength in-

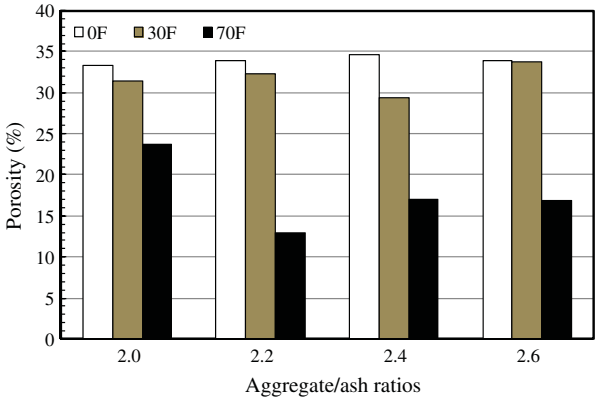


Fig. 10. Porosity at 28 days of lightweight geopolymer concrete.

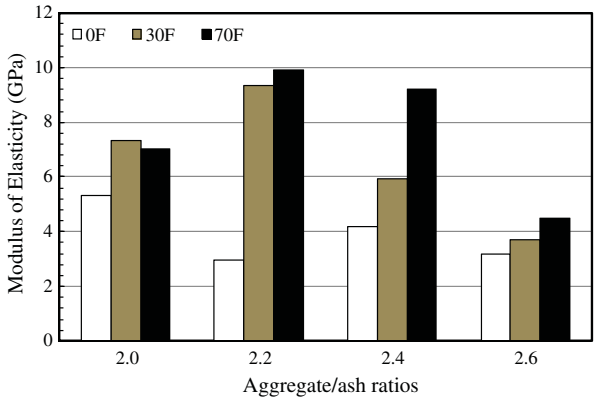


Fig. 11. Modulus of elasticity at 28 days of lightweight concrete.

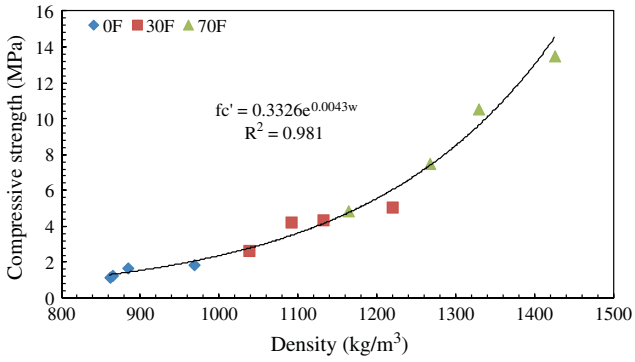


Fig. 12. Relationship of compressive strength and density of lightweight geopolymer concrete.

creased with the increasing density of lightweight geopolymer concrete [11].

$$f_c' = 0.3326e^{0.0043w} \quad (3)$$

where f_c' is compressive strength of lightweight geopolymer concrete (MPa) and w is density of lightweight geopolymer concrete (kg/m^3).

The relationship between modulus of elasticity and compressive strength of lightweight geopolymer concrete is shown in Fig. 13. The modulus of elasticity tended to increase linearly to the square root of compressive strength. The relationship could be predicted in the form shown in Eq. (4). The results indicated the modulus of elasticity between 2.9 and 9.9 GPa which is substantially lower than that of ACI 318 for normal concrete [12,16]. The trends of the relationship of the modulus of elasticity and the square root of compressive strength were similar. The results showed the same trend as that of other research [29].

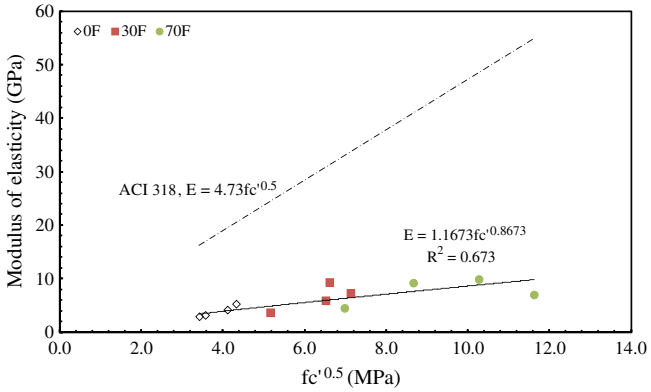


Fig. 13. Relationship of compressive strength and modulus of elasticity of lightweight geopolymer concrete.

$$E = 1.1673f_c'^{0.8673} \quad (4)$$

where E is modulus of elasticity (GPa) and f_c' is compressive strength (MPa).

4. Conclusion

Based on the obtained data, the following conclusion can be draw.

(1) The recycle lightweight block (RLC) could be used as lightweight aggregate for making lightweight geopolymer concrete. The compressive strength increased with the increasing NS/NaOH ratio and temperature of curing but decreased with the increasing aggregate/ash ratio. The optimum L/A ratio was 2.4 and NaOH concentration was 10 M for maximum compressive strength.
(2) The density of lightweight geopolymer concrete increased with the increasing L/A ratio and decreased with the increasing temperature of curing and aggregate/ash ratio. In addition, NS/NaOH ratio and concentration of NaOH did not have a significant effect on the density of lightweight geopolymer concrete.
(3) The aggregate/ash ratios had significant effect on the properties of lightweight geopolymer concrete. The increase in the aggregate portion increased the water adsorption capacity and the porosity of the geopolymer block. The increase in aggregate/ash ratio also increased with compressive strength, density, and modulus of elasticity of the geopolymers.
(4) The results showed that the lightweight geopolymer concrete with 28-day compressive strength of 1.0–16.0 MPa and density of 860–1400 kg/m^3 could be made. It can be used as lightweight geopolymer concrete for masonry wall and partitions.

Acknowledgement

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Ph.d-01, and the Thailand Research Fund (TRF) under the TRF Senior Research Scholar, Grant No. RTA5480004.

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Dielectric and Piezoelectric Properties of 2–2 PZT-Portland Cement Composites

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Piezoelectric composites made from lead zirconate titanate (PZT) and cement are developed as sensors in smart concrete structures due to its compatibility to the host structure concrete. In this work, PZT ceramic-Portland cement composites of 2–2 connectivity were produced using a dice and fill method and their dielectric and piezoelectric properties are reported. The piezoelectric coefficients, d_{33}*, value of the 2–2 PZT-cement composite at PZT volume content of 60% and 70% are 99 pC/N and 113 pC/N respectively which are noticeably higher than that of previously tested 0–3 PZT-cement composites. The dielectric values in 2–2 composites are also higher than that of previously tested 0–3 composites.*

Keywords Composites; PZT ceramic; Portland cement; dielectric properties; piezoelectric properties

1. Introduction

A number of cement-based piezoelectric composites consisting of piezoelectric ceramic has been developed recently [1–9]. Piezoelectric ceramic material such as lead zirconate titanate ($Pb(Zr_{0.52}Ti_{0.48})O_3$ or PZT) ceramic exhibits high dielectric constant and high piezoelectric coupling coefficient and is recognised as a smart material [10–11]. Applications of smart PZT ceramics are found in ultrasonic transducers, sensors, actuators and control systems in the automotive, medical, military and consumer electronic industries [11]. For civil engineering applications, piezoelectric PZT-cement based composites have been developed for use as sensors in smart structures [12–23]. This is due to its better compatibility to concrete, the main structural material used in civil engineering, over other piezoelectric materials such as piezoelectric ceramics, piezoelectric polymer and polymer-based pieozoelectric composites [3]. The use of such composite would provide an advantage in the matching of structural concrete. Thus the ideal cement-based piezoelectric composites should have good piezoelectric properties as well as good compatibility to concrete. Piezoelectric-cement

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composites can therefore be ideally used as sensors having similar acoustic matching with the host structure material, concrete. The acoustic impedance of the composite can be calculated using Eq. 1 as follows;

$$I_c = \rho_c V_c \tag{1}$$

where I_c is the acoustic impedance of the composite, ρ_c is the density of the composite and V_c is the acoustic velocity of the composite. Therefore, research and development of the cement based piezoelectric composites play an important role in the development of structural health monitoring of concrete structure where they can be used as sensor making the structure so called smart or intelligent. Other connectivities other than 0–3 connectivity such as 1–3 and 2–2 of piezoelectric-cement composites has been reported to have better properties than 0–3 connectivity [18]. In this work, PZT ceramic-Portland cement composites of 2–2 connectivity were produced using a dice and fill method and their dielectric and piezoelectric properties were investigated.

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2. Experimental Procedure

Lead zirconate titanate (PZT) powder of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ was produced from the two-stage mixed oxide method by calcining lead titanate and lead zirconate at 800°C. After calcining, PZT particles were sintered at 1,250°C for 3 hours to produce PZT ceramic disks of ≈12 mm diameter and ≈1.5 mm thickness. Poling of the PZT ceramics was then carried out under a poling field of 3 kV/mm for 20 mins in silicone oil at 130°C. After poling, PZT-cement composite of 2–2 connectivity was fabricated by cutting the PZT disk as the dispersed phase to make gaps in one horizontal direction using a diamond saw of ≈0.3 mm thick blade in order to obtain the volume content of 60, 70 and 80% (as shown in Fig. 1). The gaps were then filled with cement paste matrix using water to cement ratio of 0.5. Thereafter, the samples were cured at a temperature of 60°C and at 98% relatively humidity for five days.

The capacitance and the dissipation factor (dielectric loss or *tanδ*) of the composites were measured using an impedance meter (Hewlett Packard 4194A) at room temperature and at various frequencies (0.1 kHz–20 kHz) and the relative dielectric constant (ε_r) was then calculated from the following equation:

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A} \tag{2}$$



Figure 1. Schematic diagram of the 2–2 PZT-cement composite.

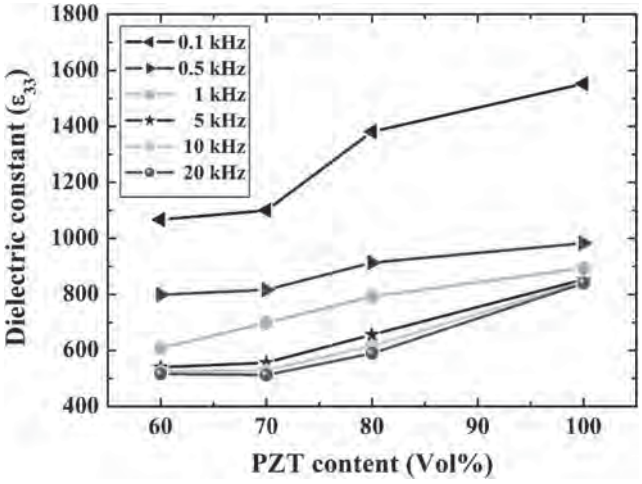


Figure 2. Dielectric constant results of 2–2 PZT-cement composites.

where C is the sample capacitance, t is the thickness, ε_0 is the permittivity of free space constant (8.854×10^{-12} Fm^{-1}), and A is the electrode area. The piezoelectric coefficient (d_{33}) was then measured using a d_{33} meter (piezometer System Model PM25).

3. Results and Discussion

The effect of PZT on the dielectric constant of 2–2 PZT-cement composites at various frequencies (0.1 kHz–20 kHz) can be seen in Fig. 2 where the dielectric constant is plotted against PZT content. The dielectric constant of the 2–2 composites can be seen to increase with PZT content since the dielectric constant of cement paste is much lower (≈79) than the pure PZT ceramic of ≈900–1,000 at 1 kHz [18] for all frequencies and that the dielectric constant at 0.1 kHz, 1 kHz and 20 kHz are 1,067, 608 and 516 for the composite with 60% PZT composite respectively. Where as for the composite with 70% composite at 1 kHz, the dielectric constant is 698. The values at 1 kHz are significantly higher than previously reported 0-3 PZT-cement composites [10, 21] where the dielectric value is in the region of 200–300 for 50–70% PZT by volume. Also, the value of 2–2 composite is comparatively much closer to the value of 100% PZT ceramic due to the better resemblance of the disk to the pure ceramic as a parallel model (Fig. 1).

The effect of PZT on the dielectric loss using the frequency from 0.1 kHz to 20 kHz can be seen in Fig. 3. In general, the dielectric loss of 2–2 PZT-cement composites was found to reduce when compared to the previous work reported on 0–3 composite at the same PZT volume content. The benefit of using a 2–2 connectivity can therefore be clearly observed where a significant reduction was found for example $tan\delta$ value of 60% PZT composite at 1 kHz is 0.44 when compared to that 0–3 composite of 0.75 [21] at the same frequency. However, both these values are higher than the pure PZT ceramic of 0.02 but much lower than that of cement paste of 2.41 [18].

Measured piezoelectric coefficient (d_{33}) results of PZT-PC composites showing the effect of PZT content can be seen in Fig. 4. The piezoelectric coefficient can be seen to increase with PZT content, as expected. The piezoelectric coefficient, d_{33}, value of the 2–2

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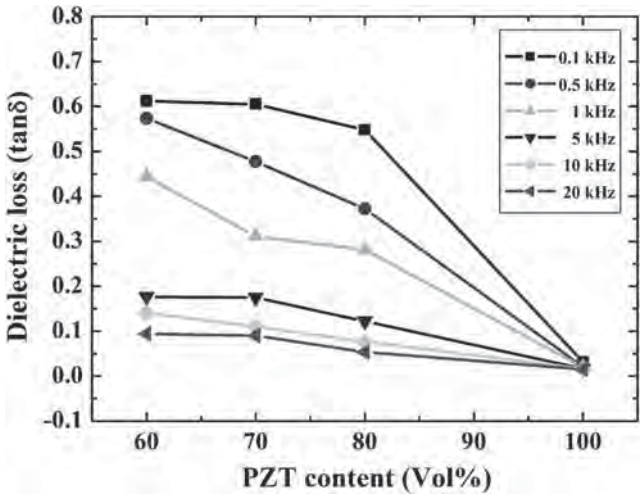


Figure 3. Dielectric loss results of 2–2 PZT-cement composites.

PZT-cement composite at PZT volume content of 60% is 99 pC/N which is significantly higher than that of previously tested 0–3 PZT-cement composites where d_{33} value is 42 [21]. For 2–2 composites with 70% and 80% PZT volume, d_{33} values are 113 pC/N and 146 pC/N respectively. This was found to be very close to the pure PZT ceramic where d_{33} value is ≈170 pC/N. Therefore, 2–2 composites, which represent a parallel model, are closer in resemblance to the pure PZT ceramic than those of 0-3 ceramics resulting in higher dielectric constant and piezoelectric coefficient.

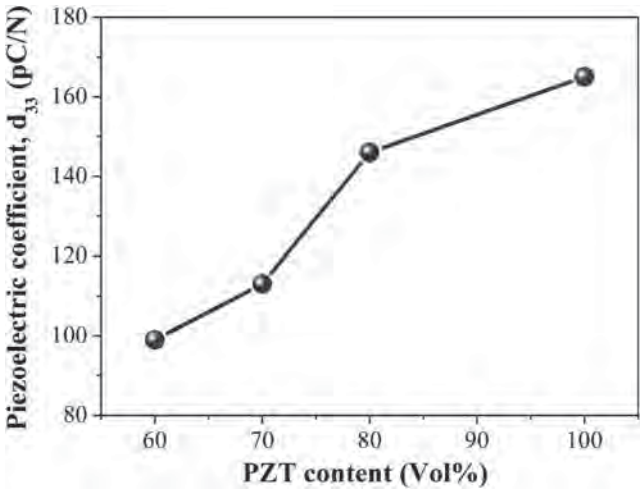


Figure 4. Piezoelectric coefficient results of 2–2 PZT-cement composites.

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4. Conclusions

PZT ceramic-Portland cement composites of 2–2 connectivity were produced using dice and fill method. The dielectric constant of the 2–2 composites can be seen to increase with PZT content and that the dielectric constant at 1 kHz for 70% PZT is 698. The dielectric loss of 2–2 PZT-cement composites was found to be noticeably lower than previous work reported on 0–3 composite at the same PZT volume content. The piezoelectric coefficient, d_{33}, value of the 2–2 PZT-cement composite at PZT volume content of 60% is 99 pC/N, which is significantly higher than that of previously tested 0–3 PZT-cement composites. For 2–2 composites with 70% and 80% PZT volume, d_{33} values are 113 pC/N and 146 pC/N respectively. This was found to be very close to the pure PZT ceramic at the same condition. These results are very high when compared to previously published 0–3 PZT-cement composites at the same volume content. This is due to the 2–2 composites represent a parallel model and therefore, is closer to that of the PZT ceramic with improvement in dielectric and piezoelectric properties in comparison to that of 0–3 composites.

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Influence of curing conditions on properties of high calcium fly ash geopolymer containing Portland cement as additive

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ABSTRACT

This paper investigated the mechanical properties and microstructure of high calcium fly ash geopolymer containing ordinary Portland cement (OPC) as additive with different curing conditions. Fly ash (FA) was replaced with OPC at dosages of 0%, 5%, 10%, and 15% by weight of binders. Setting time and microstructure of geopolymer pastes, and flow, compressive strength, porosity and water absorption of geopolymer mortars were studied. Three curing methods viz., vapour-proof membrane curing, wet curing and temperature curing were used. The results showed that the use of OPC as additive improved the properties of high calcium fly ash geopolymer. The strength increased due to the formation of additional C–S–H and C–A–S–H gel. Curing methods also significantly affected the properties of geopolymers with OPC. Vapour-proof membrane curing and water curing resulted in additional OPC hydration and led to higher compressive strength. The temperature curing resulted in a high early compressive strength development.
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1. Introduction

Clinker production process in the cement industry requires a lot of energy and emits a large amount of carbon dioxide (CO_2) to the atmosphere. The production of cement in 2005 accounted for around 7% of CO_2 world emission [1]. The negative environmental impact must be reduced by a reduction in the use of Portland cement. Fly ash, silica fumes and agro-waste ashes can be used as pozzolanic materials to reduce Portland cement usage and to curb emission of CO_2. Geopolymer is now receiving more attention as an alternative binder for use as building material. It is made from aluminosilicate source materials activated with high alkali solutions [2].

Fly ash is a by-product from coal burning to produce electricity. For Thailand, the major source of fly ash is from Mae Moh power station in the north. Approximately 3 million tons is produced annually and it is used extensively in the construction industry as supplementary cementitious materials to replace part of Portland cement. Many researchers have shown that it can be used for making good geopolymer [3–5].

At ambient temperature of around 25 °C, the fly ash geopolymer gains strength slowly [6]. To obtain reasonable strength fly ash geopolymers, temperature curing at 40–75 °C is normally required [7]. This is difficult for the construction practice in real construction. A number of researchers have, therefore, tried to improve the strength development of fly ash geopolymers. Some additives such as ground granulated blast furnace slag, flue gas desulfurization gypsum and Portland cement are used [6,8,9].

The use of OPC to improve strength of fly ash geopolymer is very attractive as OPC is a common commodity in construction industry. The reaction of OPC and water is an exothermal process at normal temperature and the developed heat should be beneficial to the enhancement of mechanical properties of geopolymer. In this research, the mechanical properties and microstructure of geopolymer with various levels of OPC replacement and curing condition were studied. The knowledge should be useful in the understanding and future utilization of the high calcium fly ash geopolymer containing OPC as additive.

2. Experimental details

2.1. Materials

Fly ash (FA) from Mae Moh power plant in Lampang province in northern Thailand, and ordinary Portland cement (OPC) were the materials used. The Blaine finenesses of FA and OPC were 2460 and 3600 cm^2/g. The alkaline solutions were 10 M sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) with 15.32% Na_2O, 32.87% SiO_2, and 51.81% H_2O. Local river sand with specific gravity of 2.62 and fineness modulus of 2.90 was used for making geopolymer mortar.

The chemical compositions of materials are given in Table 1. The FA consisted of 36.0% SiO_2, 14.9% Al_2O_3 and 19.7% Fe_2O_3, and the CaO content was high at 19.4%. The sum of $SiO_2 + Al_2O_3 + Fe_2O_3$

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Table 1
Chemical composition of FA and OPC.

Materials	Chemical composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI
FA	36.0	14.9	19.7	19.4	2.6	0.7	1.0	4.6	1.1
OPC	20.8	4.7	3.4	65.3	1.5	0.4	0.1	2.7	0.9

content of the FA were 70.6%. The high calcium content suggested that it was class C fly ash as specified by ASTM: C618.

2.2. Sample preparation

2.2.1. Mix proportion

Table 2 shows the mix proportion of the geopolymers. The mixes were named FA, 5PC, 10PC, and 15PC mixes with FA replaced by OPC at the dosages of 0%, 5%, 10%, and 15% by weight of binder, respectively. Constant liquid alkaline/binder ratio (L/B) of 0.40 and Na_2SiO_3/NaOH ratio of 0.67 were used for all mixes. The SiO_2/Al_2O_3 and CaO/SiO_2 ratios were computed and also presented in Table 2. For the geopolymer mortar mixes, sand/binder ratio of 2.75 was employed.

2.2.2. Mixing and curing method

For mixing of pastes, FA and OPC were thoroughly mixed until a uniform mixture was obtained which took approximately 2 min. For mortar mixes, sand was incorporated in the mixes with FA and OPC. Then NaOH was added and mixed for 5 min and Na_2SiO_3 was incorporated and mixed for another 5 min. The mixing was done in an air conditioned room with temperature around 25 °C.

After mixing, the fresh geopolymer pastes and mortars were placed into 50 × 50 × 50 mm cube moulds as described in ASTM: C109. The samples were covered with damp cloth and vinyl sheet and placed in 23 °C controlled room for a period of 24 h. They were then demoulded and put into different curing conditions as follows.

(1) Vapour-proof membrane curing (MC). The demoulded samples were wrapped with a vapour-proof membrane to prevent moisture loss and kept in a control 23 °C room.
(2) Temperature curing (TC). The samples were wrapped with a plastic membrane to prevent moisture loss and then oven-cured at 40 °C for 24 h. After that, the samples were demoulded and kept in a 23 °C room.
(3) Wet curing (WC). The demoulded samples were immersed in water in a 23 °C room until the testing age.

2.3. Setting time and flow

The setting time of geopolymer pastes were tested using Vicat apparatus in accordance with ASTM: C191. The flow of fresh geopolymer mortars were tested in accordance with ASTM: C1437. The reported results were the average of two tests.

Table 2
Mix proportions of geopolymer.

Mixes	FA:OPC	Na_2SiO_3/NaOH	SiO_2/Al_2O_3	CaO/SiO_2
FA	100:0	0.67	2.77	0.47
5PC	95:5	0.67	2.80	0.54
10PC	90:10	0.67	2.83	0.61
15PC	85:15	0.67	2.86	0.69

2.4. Compressive strength, porosity and water absorption

Compressive strengths of geopolymer mortars were tested at the ages of 3, 7, 28, and 90 days in accordance with ASTM: C109. The reported results were the average of three samples.

Porosity and water absorption of geopolymer mortars were tested at the age of 7 days in accordance with ASTM: C642. The measured values were calculated using Eqs. (1) and (2). The reported results were the average of two samples. The methods for measuring porosity and absorption were used successfully in a number of researches [10,11].

$$\text{Porosity}\ (\%) = \left(\frac{W_a - W_d}{W_a - W_w}\right) \times 100 \tag{1}$$

$$\text{Absorption}\ (\%) = \left(\frac{W_a - W_d}{W_d}\right) \times 100 \tag{2}$$

where Porosity is the vacuum saturation porosity of geopolymer mortar (%), Absorption is water absorption of geopolymer mortar (%), W_a is weight in air of saturated sample (g), W_d is weight of dried sample (g), and W_w is the weight in water of saturated sample (g).

2.5. SEM and XRD analysis

Scanning electron microscopy (SEM) and X-ray Diffraction (XRD) were used to study the microstructure of geopolymer pastes. The XRD scans were performed between 5 and 70° 2θ, with an increment of 0.02 deg/step and a scan speed of 0.5 s/step. The amorphous structure in geopolymer was determined by quantitative XRD using Bruker's TOPAS software.

3. Results and discussions

3.1. Setting time and flow

The results of setting time of geopolymer paste and flow of mortar are shown in Figs. 1 and 2. The addition of OPC resulted in the reduction of setting time of pastes and flow of fresh mortars. For the 0%, 5%, 10% and 15% OPC mixes, the initial setting times were 124, 66, 39 and 28 min. while the final setting times were 144, 82, 53 and 47 min. respectively, and the flow values reduced from 136% to 111%. As the OPC contained a reasonably high CaO content (65.3%), the incorporation of OPC, therefore, resulted in the

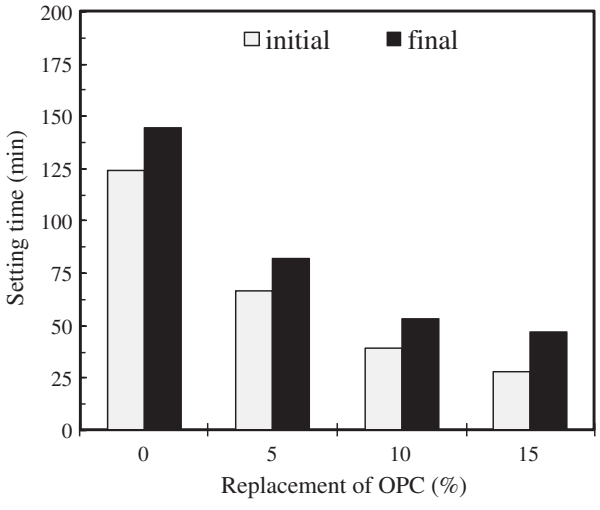


Fig. 1. Setting time of geopolymer paste.

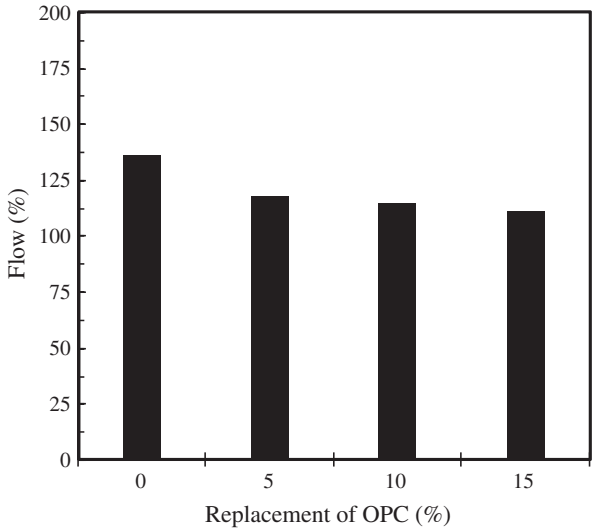


Fig. 2. Flow of geopolymer mortar.

Table 3
Compressive strengths of geopolymer mortars.

Mixes-cured	Compressive strength (MPa)			
	3 days	7 days	28 days	90 days
FA-MC	18.3	32.4	45.0	55.0
5PC-MC	30.4	37.7	52.1	59.0
10PC-MC	37.4	41.7	53.6	62.6
15PC-MC	39.3	41.4	57.8	67.9
FA-TC	40.8	50.7	57.3	59.0
5PC-TC	49.3	53.6	61.9	68.6
10PC-TC	53.5	55.6	65.4	73.5
15PC-TC	55.0	55.4	56.7	57.6
FA-WC	25.8	38.6	45.6	57.6
5PC-WC	37.9	48.8	55.7	68.4
10PC-WC	43.2	52.7	67.4	78.9
15PC-WC	46.4	53.4	67.8	75.3

increase in calcium content in the geopolymer system. The addition of calcium significantly accelerated the setting and hardening of pastes [12]. Additional calcium provided extra nucleation sites for precipitation of dissolved species which increased its solidification rate and cause rapid hardening [13].

3.2. Compressive strength

The results of compressive strengths of geopolymer mortars are shown in Table 3 and Fig. 3. The increase in OPC replacement level increased the compressive strength of geopolymer mortars. For example, the compressive strengths at 28 days of membrane cured FA, 5PC, 10PC and 15PC mortars were 18.3, 32.4, 45.0 and 55.0 MPa, respectively. The calcium elements reacted and formed additional C–S–H and C–A–S–H which coexisted with geopolymer products [14] and contributed to the strength development of mortar. The compressive strengths increased with curing age for all of MC, TC and WC series similar to that of OPC system. The increase in strength was more pronounced with the increase in OPC content and indicated additional reaction of calcium element. Moreover, the strength increases of WC series were larger than those of MC series suggesting the additional hydration of OPC due to wet curing. This led to the pore refinement similar to pozzolanic reaction in blended cements [15]. It was also suggested that the pozzolanic reaction in fly ash-alkaline liquid occurred much faster than the normal pozzolanic reaction in the Portland cement system [16].

The TC series exhibited higher early compressive strength than MC and WC series due to the strength development at an accelerated rate with characterize of quick geopolymerization process [17]. The TC series compressive strength was equivalent to those of MC and WC series at the later ages. It should be noted that the compressive strengths of geopolymer mortars with OPC as additive cured at ambient temperature were approximately the same as those of FA series temperature cured at 40 °C. For the high OPC content 15PC-TC mix, the compressive strength gain at early age was noticeable with the slowdown of strength gain at long term. The negative effects of temperature curing for the long term strength gain were related to modifications of the microstructure of the hydration products phase [18].

3.3. Porosity and water absorption

The results of porosities and water absorptions of mortars are shown in Table 4. The porosities and water absorption decreased with the increasing replacement of OPC compared with the control mortar as expected. For example, the porosities and water of water cured FA, 5PC, 10PC and 15PC mortars were 12.43%, 11.11%, 10.75% and 10.12%, respectively with the corresponding absorptions of 5.78%, 5.07%, 4.81% and 4.59%, respectively. The addition of OPC increased the hydration and amount of C–S–H and C–A–S–H. The products filled the pores and thus reduced both porosities and water absorptions with corresponding increase in compressive strengths. Thokchom et al. [11] reported a similar value of mortar

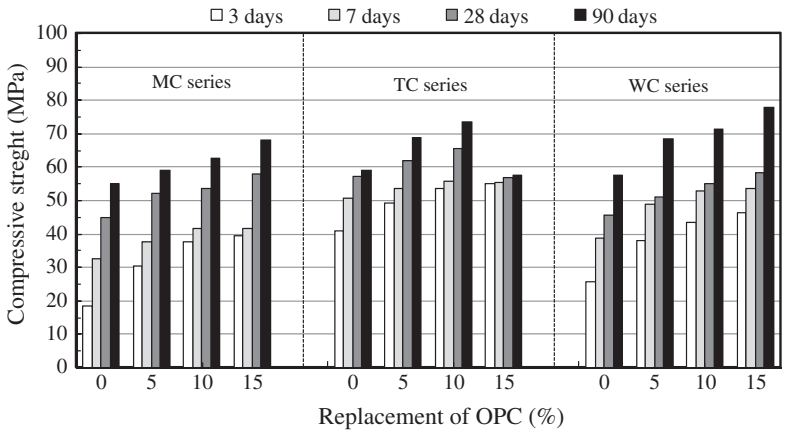


Fig. 3. Compressive strength of geopolymer mortar.

Table 4
Porosity and water absorption of geopolymer mortar at the age of 7 days.

Mixes	Porosity (%)			Water absorption (%)		
	MC	TC	WC	MC	TC	WC
FA	9.76	9.41	12.43	4.46	4.25	5.78
5PC	9.06	8.89	11.11	4.08	3.99	5.07
10PC	8.98	8.70	10.75	4.05	3.92	4.81
15PC	8.85	8.40	10.12	3.98	3.77	4.59

porosity of 12.54% for similar strengths between 32.4 and 53.4 MPa.

The porosities and water absorptions of WC series were, however, larger than those of MC and TC series. For example, the porosities at 7 days of FA-WC, FA-MC and FA-TC mortars were 12.43%, 9.76% and 9.41% and the water absorptions were 5.78%, 4.46% and 4.25% respectively. It was reported that the high calcium fly ash geopolymer mortars showed significant drying shrinkage in the dry atmosphere and swelling in the presence of water [19]. This contributed to the increase in porosities and water absorptions of WC mixes compared with those of MC and TC samples.

3.4. XRD analysis

The results of XRD of FA-TC, PC10-MC, PC10-TC and PC10-WC geopolymer pastes are shown in Fig. 4. The major phase of geopolymer was amorphous as indicated by the broad hump at the region of 25−37° 2θ. The FA-MC paste contained crystalline phases of vishnevite ($Na_8Al_6Si_6O_{24}(SO_4)_2{\cdot}H_2O$), quartz ($SiO_2$), magnesioferrite ($Fe_2MgO_4$) and calcite ($CaCO_3$). For addition of OPC, the 10PC-MC and 10PC-TC paste showed similar phases to those of FA-TC paste with some additional portlandite ($Ca(OH)_2$) and a small amount of chabazite ($Ca_{1.95}Al_{3.9}Si_{8.1}O_{24}$). The increase in porlandite phase was a direct result of OPC addition. For the WC paste, the 10PC-WC paste showed significant different crystalline phases to those of 10PC-MC and 10PC-TC paste. The vishnevite phase reduced, portlandite disappeared and calcite increased with water curing. With the presence of water, portlandite reacted with silica and alumina and formed C–S–H and C–A–S–H similar to the pozzolanic reaction in the blended cement paste [15]. The presence of geopolymer (or N–A–S–H gel) phases in the XRD patterns are usually associated with a broad peak around 28–35° 2θ and the C–S–H and C–A–S–H phases are indicated by the main peak at 30° 2θ [20–22]. The hydration products was shown to co-exist with the geopolymer products [14] and contributed to additional strength development.

3.5. SEM analysis

The SEM images of geopolymer pastes as shown in Fig. 5 showed the similar morphologies of control FA paste and 10PC paste. As mentioned, the additional C–S–H and C–A–S–H from the reaction of OPC and leached calcium from fly ash co-existed with the geopolymer products. Noticeable difference was observed between the differently cured samples. For the FA-MC paste, a large amount of non-reacted fly ash particles in the matrix was observed indicating a relatively low stage of geopolymerization. The FA-TC and FA-WC paste matrices appeared denser than the FA-MC paste and the 10PC-TC and 10PC-WC pastes also appeared denser than the 10PC-MC paste. Normally, the high calcium fly ash geopolymerization was slow at room temperature and needed temperature curing to accelerate the strength development [3]. The increases in the OPC content increased the calcium in the system and its reaction produced extra hydration products and liberated heat which also promoted the geopolymerization. The water curing resulted in the increasing hydration reaction of OPC in the geopolymer system compared with that of the MC series.

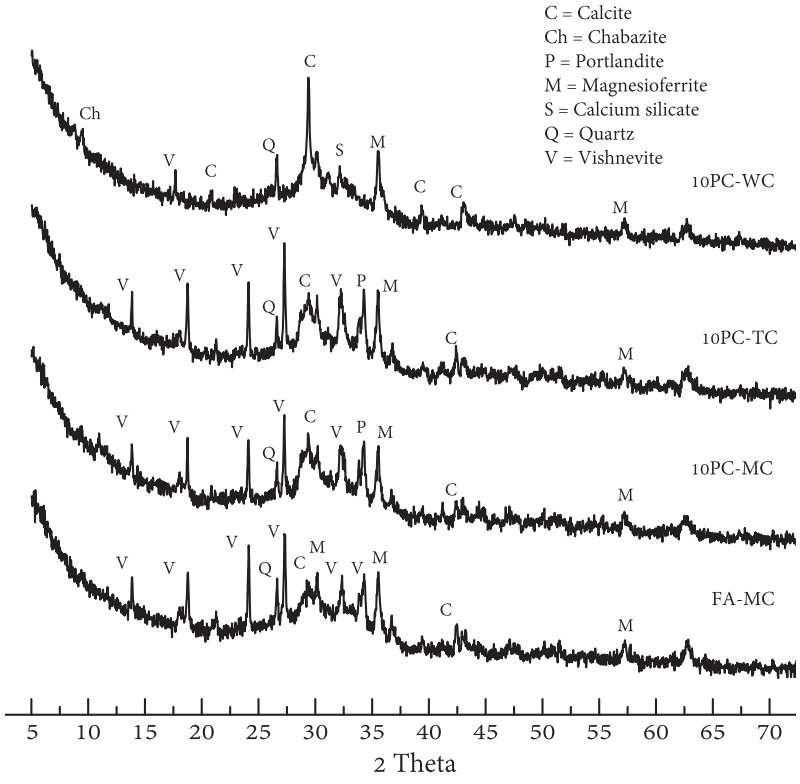


Fig. 4. XRD of geopolymer at the age of 7 days.

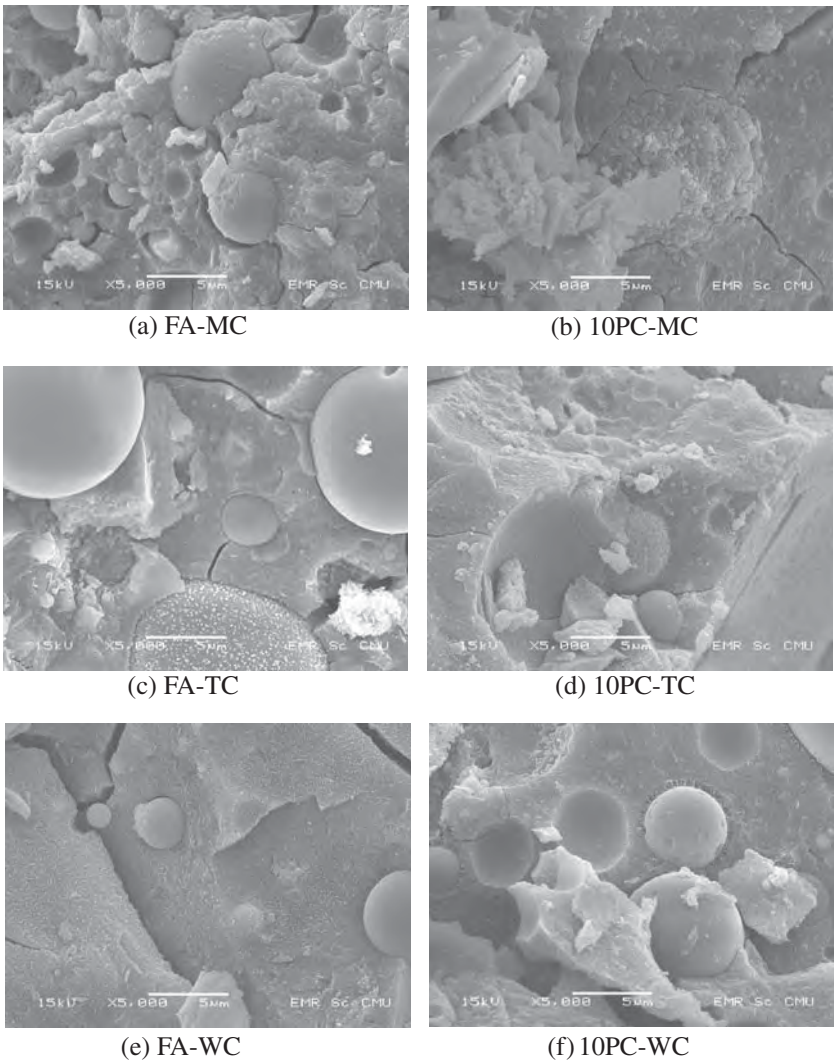


Fig. 5. SEM of geopolymer at the age of 7 days.

4. Conclusions

The use of OPC as additive in high calcium FA geopolymer resulted in enhancement of mechanical properties viz., the reduction of porosities, and water absorption and an associated increase in the compressive strength as a result of additional formation of C–S–H and C–A–S–H gel which modified the microstructure and the pore, resulting in a dense and strong matrix. Curing methods also significantly affected the properties of geopolymers with OPC. The vapour-proof membrane curing and the water curing resulted in the addition OPC hydration and high compressive strength at a later age. The temperature curing resulted in a high early compressive strength.

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Compressive Strength and Microstructure of 0–3 Lead Zirconate Titanate Ceramic-Portland Cement Composites

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Lead zirconate titanate (PZT)-Portland cement (PC) composites have been reported to have good potential for use in smart structures. In this work, PZT-PC composites containing 40%, 50% and 60% of PZT by volume were produced and their mechanical and hydration properties were investigated. Compressive strengths of those typically used in normal concrete were found for all PZT-PC composites, with measured values of 41.5–45.0 MPa. Hydration products of Portland cement detected by thermal analysis were calcium silicate hydrates (the main cement hydration product), calcium hydroxide and ettringite. Furthermore, calcium silicate hydrates and ettringite can also be observed surrounding the PZT grains in the SEM micrograph.

Keywords PZT; cement; composites; compressive strength; microstructure

1. Introduction

Piezoelectric lead zirconate titanate – $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) – ceramic is well known for its high dielectric constant and high piezoelectric coupling coefficient. Uses of PZT are found in numerous applications such as sensors, transducers and actuators [1–3]. For smart civil engineering applications where a structure can sense and detect a movement, cement-based composites consisting of PZT have been developed [4–23] in order to provide matching with the host structure, concrete. Such piezoelectric–cement-based composites are known to exhibit better properties than other piezoelectric composites.

Li *et al*. [4] developed 0–3 PZT–white Portland cement composites using a spreading method where the composites were cast as pastes before setting. The composites were cured at 20°C before measurement. Difficulty in casting paste containing greater than 50% PZT by volume was reported due to reduction in paste workability caused by the increase of PZT particles. Using a pressing method before subjecting to curing at 20°C, Huang *et al*.

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Table 1
Dielectric and piezoelectric results of the composite investigated [9]

MIX	PZT (% by volume)	ε_r	d_{33} (pC/N)
PZT40	40	139	22
PZT50	50	176	26
PZT60	60	290	42

[5] developed 0–3 PZT-sulfoaluminate cement composites where PZT of up to 85% by weight was investigated.

PZT compositions giving the closest match to concrete were reported to be between 40–60% by volume [4]. Chaipanich *et al*. [9] reported the fabrication and piezoelectric properties of 0-3 PZT-PC composites. Measured d_{33} values for composites with 50% and 60% PZT content were found to be 26 and 42 pC/N, respectively (Table 1). However, no reported works have been found on the mechanical properties in terms of compressive strength of such piezoelectric-cement composites. In this work, a normal Portland cement (also known as ordinary Portland cement) is used, since it is the most common cement type used in general concrete construction. PZT ceramic particles were mixed with Portland cement (PC) to form PZT-PC composites. In addition to compressive strength, the microstructure and hydration properties of the composites were also investigated.

2. Experimental

Lead zirconate titanate ceramic (PZT)–Portland cement (PC) composites were produced using PZT ceramics (median of 450 μm) and ordinary Portland cement. The dry solids were then pressed together to produce PZT-PC composites of 0–3 connectivity using different PZT volume contents of 40%, 50% and 60%. Composite samples were cast as cubes of 1 cm $\times$ 1 cm $\times$ 1 cm for compressive strength tests (S-series; Hounsfield Test Equipment, Surrey, UK) which were carried out after the samples were subjected to curing for 3 d. Thermal analysis of the composite at 50% PZT by volume (selected as representative) using the thermogravimetric analysis (TGA) technique was carried out after curing in order to determine the hydration products. The samples were heated from room temperature to 1,000°C with a scanning rate of 10°C/min under nitrogen atmosphere condition using a Mettler Toledo TGA/SDTA 851e.

A scanning electron microscope (SEM; JEOL JSM-840A,) was used to study the interfacial zone of the composites. Phase characterizations of the composites were also carried out by room temperature X-ray diffraction (XRD; Philips PW 1729 diffractometer) using Ni-filtered CuK radiation.

3. Results and Discussion

Densities of the PZT-PC composite samples were determined using the Archimedes principle; the results are plotted in Fig. 1. It can be seen that, as expected, the density increased with the addition of PZT due to PZT being a denser material (measured at 7.8 g/cm^3) when compared to the pure cement disk of 2.6 g/cm^3. The densities of these composites were found to be close to 4.5, 5.1 and 5.6 g/cm^3 for composites containing 40, 50 and

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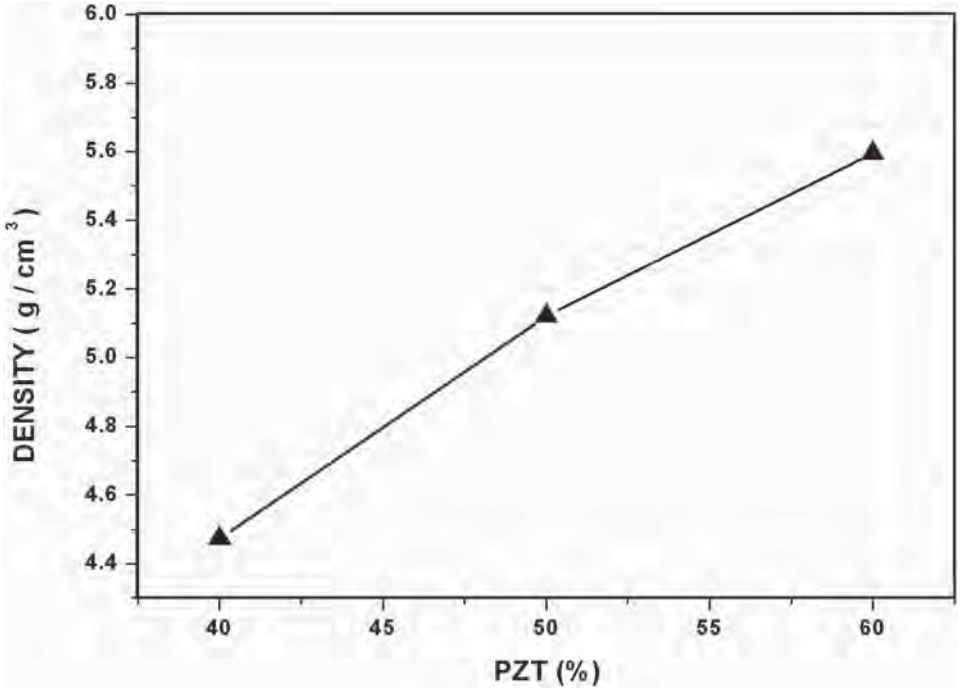


Figure 1. Density results of PZT-PC composites.

60% PZT by volume, respectively. Figure 2 shows the compressive strength test results of PZT-PC composites at 40–60% of PZT by volume. Compressive strength results were found in the region of 41.5–45.0 MPa for these PZT-PC composites, showing an increase of 3.5 MPa when PZT volume increases from 40% to 60%. This increase is similar to the results (≈4 MPa increase) for composite made of cement and aggregate when aggregate volume content increase from 40% to 60% [24]. Moreover, these mechanical strengths are similar to those used in normal concrete, and therefore would be able to resist the same mechanical loading as would the concrete host structure. Compressive strength of the PZT-PC composites can therefore be seen to increase when the PZT volume content increased from 40–60%. When further compared to the compressive strength of Portland cement (with no PZT) where the compressive strength is 56 MPa, these strength values are generally less than that of Portland cement with no PZT. However, when considering PZT as an aggregate in the cement-matrix composite, a comparison can be made to the report by Stock *et al*. [24] where the effect of construction aggregate type on compressive strength was studied. This finding was also mentioned by Neville [25], although the reason for this effect is not clear. Stock *et al*. [24] reported that when an aggregate of different volume is added, the compressive strength is found to decrease by up to 40% by volume; thereafter, there is an increase in strength when the aggregate volume is higher than 40%. Therefore, the compressive strength results of PZT-cement composites and the results reported previously for conventional construction aggregates were found to be in agreement.

XRD traces of Portland cement, PZT-PC composites (40%, 50% and 60% PZT) and PZT ceramic are shown in Fig. 3. In order to allow for a direct comparison, the XRD conditions used for both samples were the same. For Portland cement, crystalline peaks of calcium hydroxide ($Ca(OH)_2$), dicalcium silicates ($2CaO.SiO_2$ shown as Ca_2SiO_4) and

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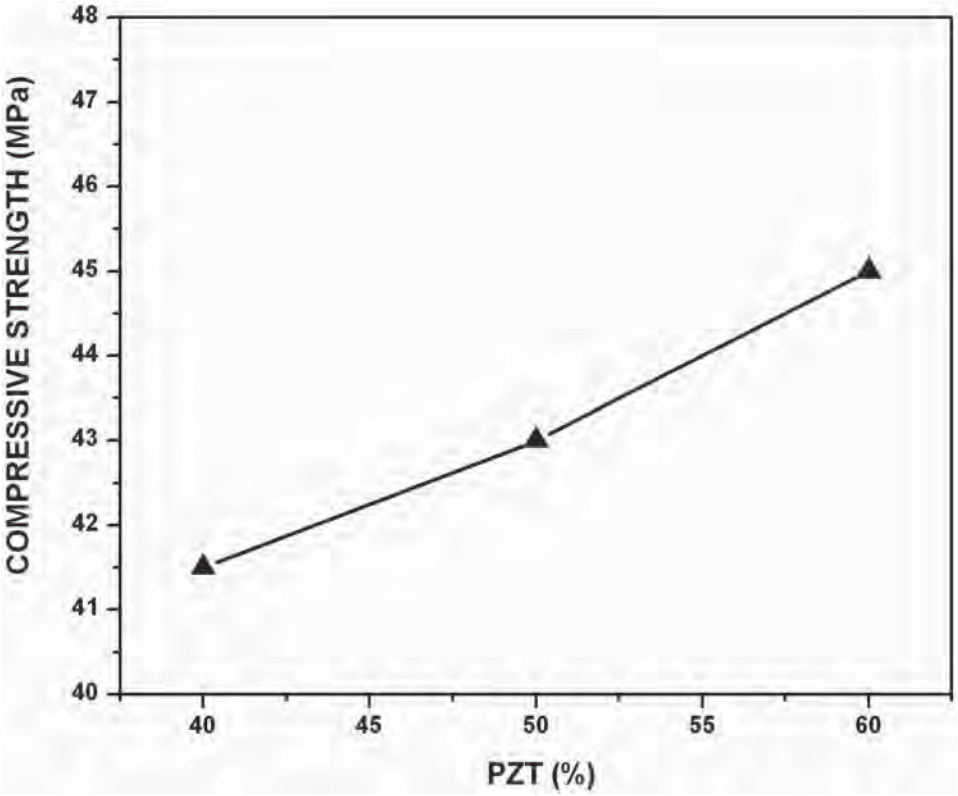


Figure 2. Compressive strength results of PZT-PC composites.

calcium carbonate ($CaCO_3$) can be seen. The most likely explanation for detected dicalcium silicates is that the samples were cured for 3 days using accelerated curing and that dicalcium silicates may remains since this particular compound require longer curing period [24–26]. Calcium hydroxide and calcium silicate hydrates (C−S−H) are the hydration products of tricalcium silicates ($3CaO.SiO_2$ or C_3S) in cement. Calcium hydroxide is therefore detected while the latter C−S−H on the other hand is poorly crystalline and is detected as an amorphous phase. Calcium carbonate is also seen detected as the result of a reaction between CO_2 and $Ca(OH)_2$ due to the sample exposure to air. For PZT-PC composites, the crystalline peaks attributed to PZT can be seen where these XRD peaks of the composites resemble those of a PZT ceramic matching JCPDS file no. 33–0784 [9]. The intensity of these peaks increases as PZT volume content increases. Nonetheless in the XRD trace of the composite, amorphous glassy phase was also detected due to the appearance of the main cement hydration product (calcium silicate hydrate or C−S−H). Furthermore, other crystalline peaks of hydrated phases from cement were not as dominant as those of PZT due to both the preferred orientation of PZT and the relatively greater quantity of PZT compared to the crystal hydrated products formed from cement hydration, such as ettringite or calcium hydroxide.

SEM micrographs of the PZT-PC composite at 50% PZT by volume are shown in Fig. 4(a,b). PZT ceramic particles with grain size of $\approx$2–3 μm can be seen quite clearly in the SEM micrographs. Cement hydration products such as calcium silicate hydrate (C−S−H)

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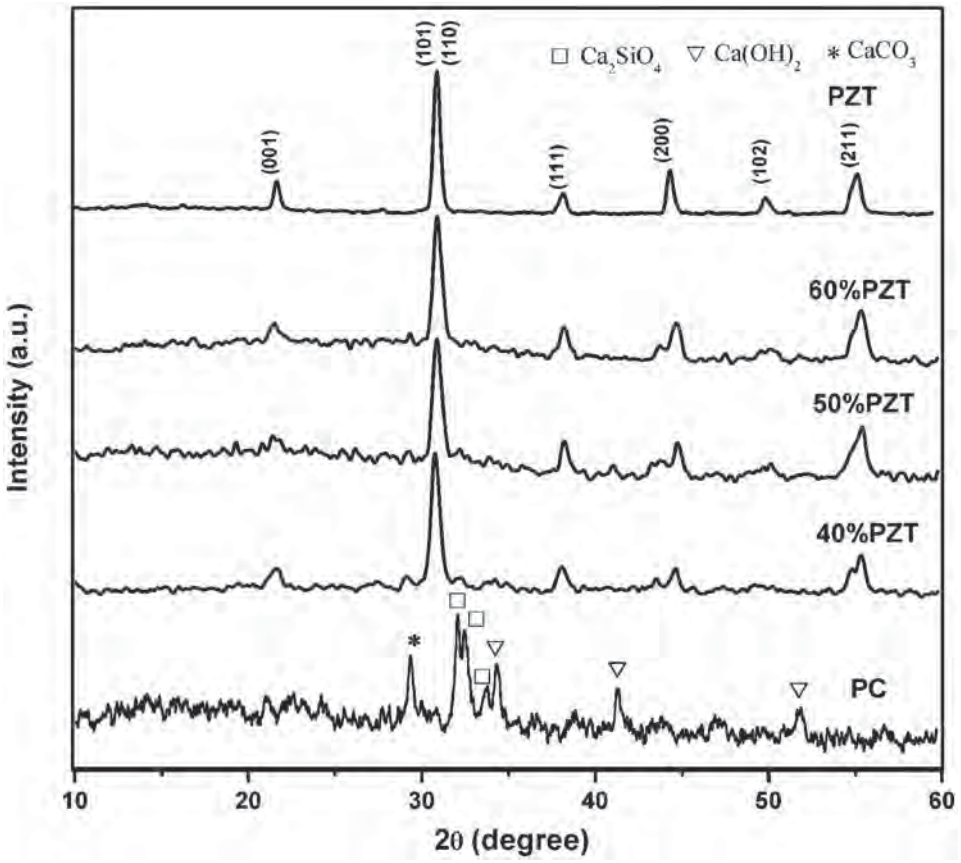


Figure 3. XRD patterns of PC, hydrated PZT-PC composites and PZT ceramic.

and $Ca(OH_2)$ can also be seen surrounding PZT ceramic particles in Fig. 4(a) [17]. These hydration products occurred as the result of hydration of calcium silicates (tricalcium silicate (C_3S) and dicalcium silicate (C_2S)). Another hydration product resulting from the hydration reaction of tricalcium aluminate (C_3A) was ettringite (ETT) – $6CaO.Al_2O_3.3SO_3.32H_2O$ – which can clearly be seen as needle shapes in the SEM micrograph (Fig. 4(b)). Furthermore, good binding between these cement hydration products and PZT ceramic particles is also apparent from the SEM micrographs. C—S—H occurred as hydration product from C_3S and is an important hydration product (as shown in SEM micrographs) that contributes significantly to the strength of the composite since C—S—H existed by more than half the volume of total hydration products resulted from the cement hydration [25–27].

While X-ray diffraction detected only crystalline peaks of PZT with amorphous glassy phase of CSH, other crystalline peaks would be diminished due to greater intensity of PZT in the composite. SEM micrographs, on the other hand, are pinpointed and are generally used to observe selected areas such as the interfacial zone, and may not detect all the phases occurring in the composite. In this case, thermogravimetric analysis (TGA) is used in combination with the above technique to give a more precise and overall analysis of the cement hydration products. Figure 5(a) shows the TGA result of the composite plotted as a weight percentage and as a derivative thermogravimetric (DTG) of the composite at

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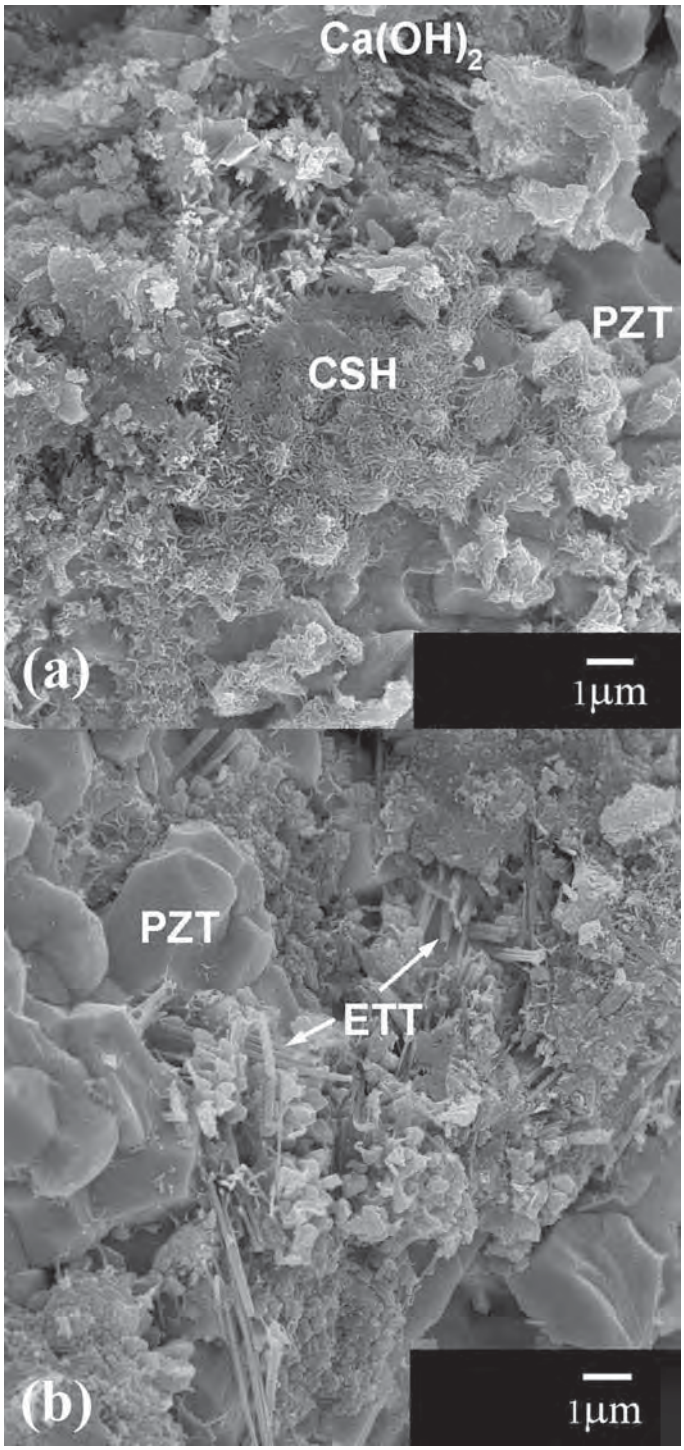


Figure 4. SEM micrographs of the interfacial zone of typical PZT-PC composite showing **(a)** PZT grains with CSH and $Ca(OH_2)$, and **(b)** PZT grains with ettringite (ETT).

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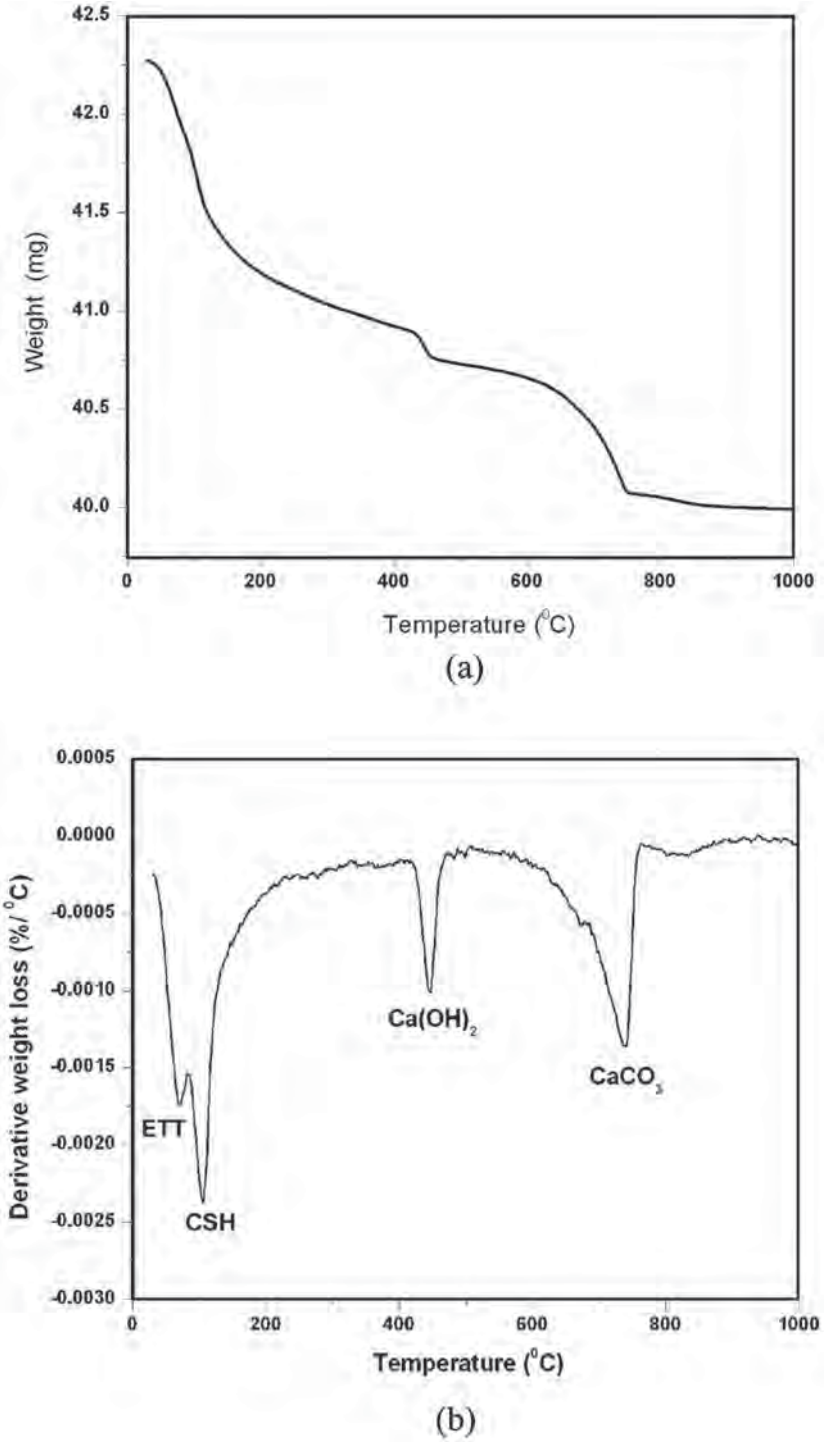


Figure 5. TGA results plotted as **(a)** weight loss, and **(b)** as DTG curve result of PZT-PC composites.

50% PZT by volume representing a typical hydration products occurring in PZT-Portland cement composites. The weight loss can be seen to occur mostly at ≈60°C, ≈120°C, 400–450°C and ≈600–750°C where peaks can be seen clearly using the derivative of the weight loss with temperature (DTG) as shown in Fig. 5b. DTG curve shows the weight loss due to dehydration of ettringite, CSH and $Ca(OH)_2$. All of which are hydration products of Portland cement, thus agreeing with the phases detected in the matrix of the composites as shown in the SEM micrographs.

Calcium carbonate was also detected as a result of the carbonation process, when part of the calcium hydroxide reacts with carbon dioxide to form calcium carbonate. Results concerning the dielectric constant and piezoelectric coefficient (d_{33}) of PZT-PC composites have been reported earlier [9], and are also given in Table 1. From this work, it can therefore be seen that good binding between PZT ceramic and cement hydration products is evident, and that typical cement hydration products were found to occur under an accelerated curing regime at 60°C.

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4. Conclusions

Compressive strength results typical of those used in normal concrete were found at 41.5–45.0 MPa for all PZT-PC composites, and therefore would be able to resist the same mechanical loading as would the concrete host structure. The results showed a good binding between the cement matrix and PZT ceramic particles, where cement hydration products such as calcium silicate hydrates and ettringite were seen to surround PZT ceramic particles in the SEM micrograph. Using thermal analysis, calcium silicate hydrates, ettringite and calcium hydroxide, all of which are cement hydration products, were detected.

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The effect of adding nano-SiO_2 and nano-Al_2O_3 on properties of high calcium fly ash geopolymer cured at ambient temperature

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ABSTRACT

This article presents the effect of adding nano-SiO_2 and nano-Al_2O_3 on the properties of high calcium fly ash geopolymer pastes. Nano-particles were added to fly ash at the dosages of 0%, 1%, 2%, and 3% by weight. The sodium hydroxide concentration of 10 molars, sodium silicate to sodium hydroxide weight ratio of 2.0, the alkaline liquid/binder ratio of 0.60 and curing at ambient temperature of 23 °C were used in all mixtures. The results showed that the use of nano-SiO_2 as additive to fly ash results in the decrease of the setting time, while the addition of nano-Al_2O_3 results in only a slight reduction in setting time. Adding 1–2% nano-particles could improve compressive strength, flexural strength, and elastic modulus of pastes due to the formation of additional calcium silicate hydrate (CSH) or calcium aluminosilicate hydrate (CASH) and sodium aluminosilicate hydrate (NASH) or geopolymer gel in geopolymer matrix. In addition, the additions of both nano-SiO_2 and nano-Al_2O_3 enhances the shear bond strength between concrete substrate and geopolymer.

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1. Introduction

At present, geopolymer is getting more attention as an alternative binder to normal cement binders for applications in concrete industry [1,2]. It is made from rich silica and alumina source materials such as fly ash, calcined kaolin, and blast furnace slag. In Thailand, the major source of fly ash is Mae Moh power station in the north. Approximately 3 million tons is produced annually and it is used mainly as supplementary cementitious materials to replace of Portland cement in construction industry. Many researchers have shown that it can also be used as starting material for making good geopolymer [3,4].

Geopolymeric reaction relies on the activation with alkali solutions and temperature curing at 40–75 °C [3,5]. The obtained geopolymer paste possesses similarly strength and appearance to normal Portland cement paste. However, when fly ash geopolymer material is cured at ambient temperature of around 25 °C, the strength development is rather slow and low strength is obtained [6]. Many researchers have tried to improve the strength development of fly ash geopolymers [7,8]. Khater et al. [9] and Riahi and Nazari [10] reported that the compressive strength of geopolymer depends on the type of starting material and its fineness. The fine particles induce higher leaching of silica and alumina in the alkali environment and leads to a higher strength geopolymer [3].

Recently, nanoparticle is receiving more attention as an alternative binder used for the improvement of nanostructure of building materials [9]. Nano-SiO_2 and nano-Al_2O_3 are most commonly used [11] to enhance compressive and tensile strengths of concrete by additional pozzolanic and filler effects [12]. The nano-SiO_2 particle belongs to highly pozzolanic materials because it consists essentially of SiO_2 in amorphous form with a high specific surface, therefore, exhibits great pozzolanic activity [13]. This research aims to study the properties and application of geopolymer paste made from high calcium fly ash containing nano-SiO_2 and nano-Al_2O_3. The obtained results should be very beneficial to the understanding and to the future applications of the materials.

2. Experimental details and testing analysis

2.1. Materials

The materials used in this study were high calcium fly ash (FA) from Mae Moh power plant in northern Thailand, nano-SiO_2 (S), and nano-Al_2O_3 (A). The liquid portions in the mixture were 10 M sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) with 13.89% Na_2O, 32.15% SiO_2, and 46.04% H_2O.

The chemical composition and physical properties of FA are shown in Tables 1 and 2. The FA had specific gravity, Blaine

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fineness, and average particle sizes of 2.61, 4300 cm^2/g and 8.5 μm, respectively. The average particle sizes of S and A were 12 and 13 nm with specific surface areas (BET) of 200 ± 25 and 100 ± 15 m^2/g. The properties of S and A are shown in Table 3 and the mineral compositions are shown in Fig. 1.

2.2. Mix proportion and mix detail

The nano-particles (S and A) were added to high calcium FA at the dosages of 0%, 1%, 2%, and 3% by weight. Constant liquid to binder (L/B) ratio of 0.60 and Na_2SiO_3/NaOH ratio of 2.0 were used in all mixtures. The mix proportions of geopolymer pastes are shown in Table 4. For the mixing of pastes, NaOH and Na_2SiO_3 solutions were firstly mixed together and used as the liquid solution. The FA and S or A were dry mixed until the mixture was homogenous. Right after, the liquid solution was added and the mixing of pastes was done for 5 min.

2.3. Testing

2.3.1. X-ray diffraction (XRD)

At the age of 28 days, the geopolymer cube specimens were broken and ground to fine powder. The XRD scans were performed at 5 to 60 °2theta with an increment of 0.02 degree/step and a scan speed of 0.5 s/step. The amorphous phases of geopolymer pastes at the age of 28 days were determined by quantitative XRD analysis using Bruker's TOPAS software.

2.3.2. Scanning electron microscopy (SEM)

The geopolymer cube samples at the age of 28 days were broken and the middle portions were used for the SEM analyses. The specimen was placed on a brass stub sample holder with double stick carbon tape. The specimen was dried using infrared light for 5 min and then coated with a layer of gold approximately 20–25A thick using a blazer sputtering coater. The micrographs were recorded at 15 kV and 1000× magnification.

2.3.3. Setting time

The setting time of geopolymer pastes were tested in accordance with ASTM: C191.

2.3.4. Compressive strength and modulus of elasticity

The 50 × 50 × 50 mm cube specimens were used for compressive strength test in accordance with the ASTM: C109. The 25 mm diameter and 50 mm height cylindrical specimens were used for the determination of modulus of elasticity as described in ASTM: C469. The specimens were demolded at the age of 1 day and immediately wrapped with vinyl sheet to protect moisture loss and kept in the 23 °C controlled room. The compressive strength and modulus of elasticity were measured at the ages of 7, 28, and 90 days. The reported results were the average of three samples.

2.3.5. Flexural strength

The flexural strength of geopolymer pastes were obtained from modulus of rupture tests using 40 × 40 × 160 mm prisms in accordance with the ASTM: C293. The specimens were tested in deflection controlled with loading rate of 0.05 mm/min [14]. The flexural strength was measured at the ages of 7, 28, and 90 days. The reported results were the average of three samples.

Table 1
Chemical composition of FA (by weight).

Materials	Chemical composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
FA	29.32	12.96	15.64	25.79	2.94	2.93	2.83	7.29	0.30

2.3.6. Shear bond strength between concrete substrate and geopolymer pastes

The adhesion strength or shear bond strength was evaluated using the slant shear test as described in ASTM: C882 of geopolymer and concrete. The concrete specimens were cured in water for 28 days and then they were wrapped with vinyl sheet to protect moisture loss for 60 days. This long curing period was chosen to provide advanced concrete hydration as in the old concretes in field of construction [15]. The properties of concrete substrate are shown in Table 5. The slant shear 50 × 50 × 125 mm prisms with the interface line at 45° to the vertical as shown in Fig. 2 were used [2,16]. For casting of specimens, the paste was placed into a mold with concrete substrate in two equal layers. Each layer was tamped 25 times and then vibrated for 45 s to obtain good compaction. After the casting of samples, they were covered with vinyl sheet to protect moisture loss and kept in the 23 °C controlled room until the testing ages. The shear bond strength was the ratio of maximum load at failure and the bond area, and the specimens were tested in constant loading rate of 0.30 MPa/s. The shear bond strength was measured at the ages of 7, 28 and 90 days, and the reported results were the average of five samples.

3. Results and discussions

3.1. XRD analysis

The XRD patterns of fly ash and geopolymer pastes containing nano-SiO_2 are shown in Fig. 3. The as-received FA consisted of a glassy matrix as shown by the hump at 25–35 °2theta and crystalline phases of quartz (SiO_2), magnesioferrite ($MgFe_2O_4$) and calcium carbonate ($CaCO_3$). The XRD patterns of the geopolymer pastes containing nano-SiO_2 (Control, S1, S2, and S3) are similar with that of FA, with the presence of a larger amount of quartz and some magnesioferrite and the disappearance of calcium carbonate. The increase in the intensity of quartz is due to the presence of additional SiO_2 in the system. However, the amorphous phases were easily detected as broad hump around 25–38 °2theta due to transformation of the amorphous component in the geopolymer matrix [9], which was also reflected in a small shift of this hump compared with that of FA [17,18]. The presence of CSH phase could be confirmed by the presence of peaks at 29.5 and 32.05 °2theta [19]. The CSH co-existed with the geopolymer products and enhanced the strength of the geopolymer [20].

The XRD patterns of FA and geopolymer pastes containing nano-Al_2O_3 are shown in Fig. 4. The trends of XRD patterns of geopolymer pastes containing nano-Al_2O_3 were also similar to those of control and nano-SiO_2 pastes. The lower peak of quartz compared with that containing nano-SiO_2 was evident. The broad hump of amorphous gel was very significant indicating the advanced degree of reaction to form NASH gel.

3.2. SEM analysis

The SEM photos of geopolymer pastes are shown in Fig. 5. The control paste contained less dense matrix with a larger number of non-reacted and/or partially reacted fly ash particles embedded in a continuous matrix (Fig. 5a). For the 1–2% nano-SiO_2 (Fig. 5b and c) and nano-Al_2O_3 (Fig. 5e and f), less number of fly ash particles were observed, and the matrix appeared denser than that of the control paste. The high magnification (3000×) of 1% nano-SiO_2 (Fig. 5h) and nano-Al_2O_3 (Fig. 5i) showed the denser matrices compared with that of control paste. The uses of nano-SiO_2 and

Table 2
Physical properties of FA.

Materials	Specific gravity	Average particle size (μm)	Blaine fineness (cm^2/g)
FA	2.61	8.5	4300

Table 3
The properties of nano-SiO_2 and nano-Al_2O_3.

Materials	Average particle size (nm)	Specific surface area, BET (m^2/g)	Density (g/cm^3)	Purity (%)	Appearance
S	12	200 ± 25	<0.05	>99.98	White powder
A	13	100 ± 15	<0.12	>99.38	White powder

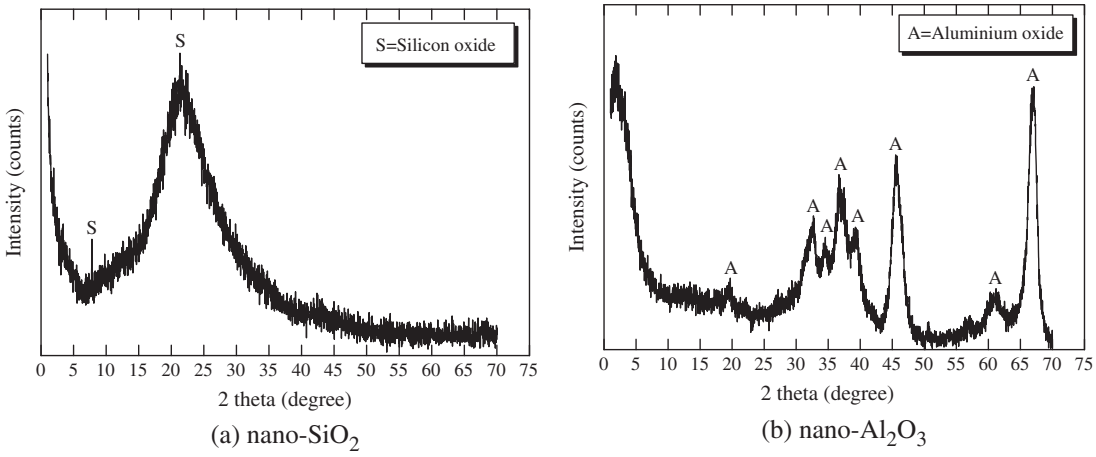


Fig. 1. XRD of nano-SiO_2 and nano-Al_2O_3.

Table 4
Mix proportions of geopolymer pastes.

Mix no.	Mix symbol	FA (g)	*S* (g)	*A* (g)	*L*/*B* ratio	NaOH (g)	Na_2SiO_3 (g)
1	Control	100	–	–	0.60	20	40
2	S1	100	1	–	0.60	20	40
3	S2	100	2	–	0.60	20	40
4	S3	100	3	–	0.60	20	40
5	A1	100	–	1	0.60	20	40
6	A2	100	–	2	0.60	20	40
7	A3	100	–	3	0.60	20	40

Table 5
Mix properties and main properties of concrete substrate.

Components	OPC (kg/m^3)	Aggregates (kg/m^3)		Water (kg/m^3)	Main properties of concrete substrate at 28 days (MPa)	
		Fine	Coarse		f_c	f_t
Proportions	495	1210	338	238	35.9	8.5

f_c = compressive strength at the age of 28 days, and average value of five specimens (100 mm in diameter and 200 mm in length).
f_t = flexural strength at the age of 28 days, and average value of five specimens (40 × 40 × 160 mm^3).

nano-Al_2O_3 in high calcium fly ash geopolymer results in the additional formation of CSH or CASH gels which co-existed with NASH gel [9] and thus led to the overall improvement in compressive strength of geopolymer. On the other hand, addition of 3% nano-SiO_2 (Fig. 5d) and nano-Al_2O_3 (Fig. 5e) resulted in a large amount of nano-SiO_2 and nano-Al_2O_3 observed and the matrix appeared less dense than the other mixtures indicating that the amount of nano-particles addition at this level of 3% was excessive.

3.3. Setting time

The setting time of geopolymer pastes at various addition levels of nano-SiO_2 and nano-Al_2O_3 are shown in Fig. 6. The initial setting time of control, S1, S2, and S3 pastes were 30, 27, 19, and 12 min, and the final setting time were 58, 53, 40, and 26 min, respectively. The initial setting time of A1, A2, and A3 pastes were 29, 29, and 28 min, and the final setting time of pastes were 57, 55, and 54 min, respectively. The setting time of pastes tended to obviously

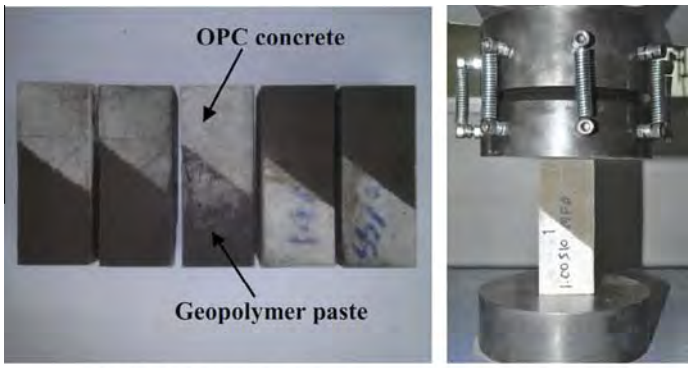


Fig. 2. Slant shear specimens and testing procedure.

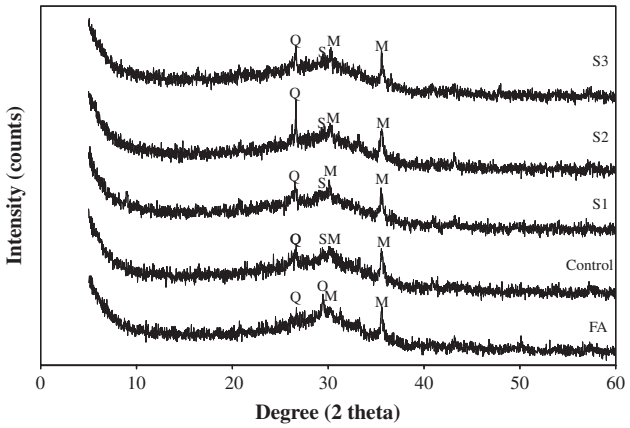


Fig. 3. XRD of geopolymer pastes at 28 days with various nano-SiO_2.

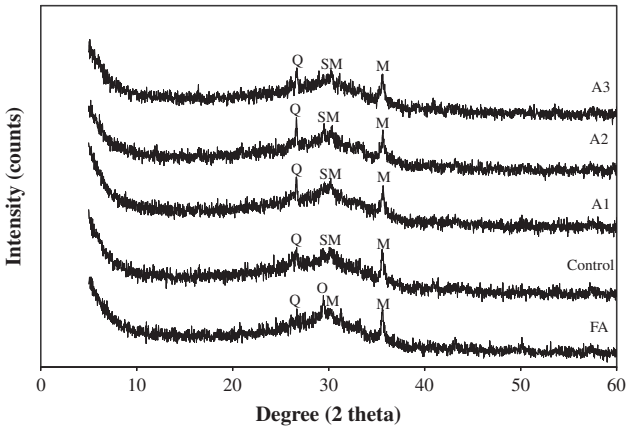


Fig. 4. XRD of geopolymer pastes at 28 days with various nano-Al_2O_3.

decreased with the addition of nano-SiO_2 due to the faster activation with readily available free calcium ions from high calcium FA and formed CSH [17]. The addition of nano-Al_2O_3 seemed to have a smaller effect on setting time compared with adding of nano-SiO_2. Chindaprasirt et al. [17] reported that the increase in nano-Al_2O_3 content more than 7% by weight of binder also resulted in a large reduction of setting time. The fast setting time of FA containing nano-SiO_2 at this level of addition could be used as repair binding materials.

3.4. Compressive strength and flexural strength

The compressive strengths and flexural strength of pastes are shown in Table 6. The compressive strength and flexural strengths of geopolymer pastes containing nano-SiO_2 and nano-Al_2O_3 were obviously higher than that of control paste. At 90 days, the compressive strengths of pastes containing 2% nano-SiO_2 and nano-Al_2O_3increased to 51.8 and 56.4 MPa, respectively compared with 39.4 MPa of the control paste. At 90 days, the flexural strengths of pastes containing 2% nano-SiO_2 and nano-Al_2O_3 were 5.98 and 5.92 MPa compared with 4.31 MPa of the control paste. The results followed the same trended as those of the compressive strength, and confirmed with other researches [11,21] that addition of nano-particles improved the strength of cement paste and concrete. The addition of 3% of nano-particles, however, started to adversely affect the strength of geopolymer. The compressive strengths at 90 days of 3% of nano-SiO_2 and nano-Al_2O_3 reduced to 48.1 and 46.1 MPa, respectively whereas the corresponding flexural strengths dropped to 5.23 and 5.26 MPa, respectively.

The compressive strength and flexural strength of the pastes were significantly improved due to the increase in the reaction products of the geopolymer matrix [22]. In the presence of high alkali environment and the presence of calcium from high calcium FA, the additional SiO_2 and Al_2O_3 could react and form CSH or CASH and NASH gels and led to a higher strength geopolymer [8,17]. The addition of SiO_2 and Al_2O_3 reduced the $Ca(OH)_2$ content of matrix, and the microstructure was refined similar to the pozzolanic reaction in the blended cement paste [23]. The results thus show that the properties of high calcium FA geopolymer could be enhanced with addition of 2% nano-SiO_2 and nano-Al_2O_3 by weight.

The relationship between compressive strength and flexural strength of geopolymer pastes is shown in Fig. 7. The flexural strength tended to increase linearly with the square root of ultimate compressive strength. The equation predicting this relationship can be written as;

$$f_t = 1.430\sqrt{f'_c} - 4.223 \quad (1)$$

where f_t is the flexural strength (MPa), and f'_c is the ultimate compressive strength (MPa).

The flexural strength of geopolymer pastes at age of 7 days expressed as a function of compressive strength was lower than those predicted by ACI 318 [24] as shown in Fig. 7. At an early age of 7 days, the flexural strengths were lower than the values given by ACI 318. However, at the ages of 28 and 90 days, they were higher than the values given by ACI 318. The results conformed with that of Sofi et al. [25] which indicated that the flexural strength of inorganic polymer concrete was generally higher than

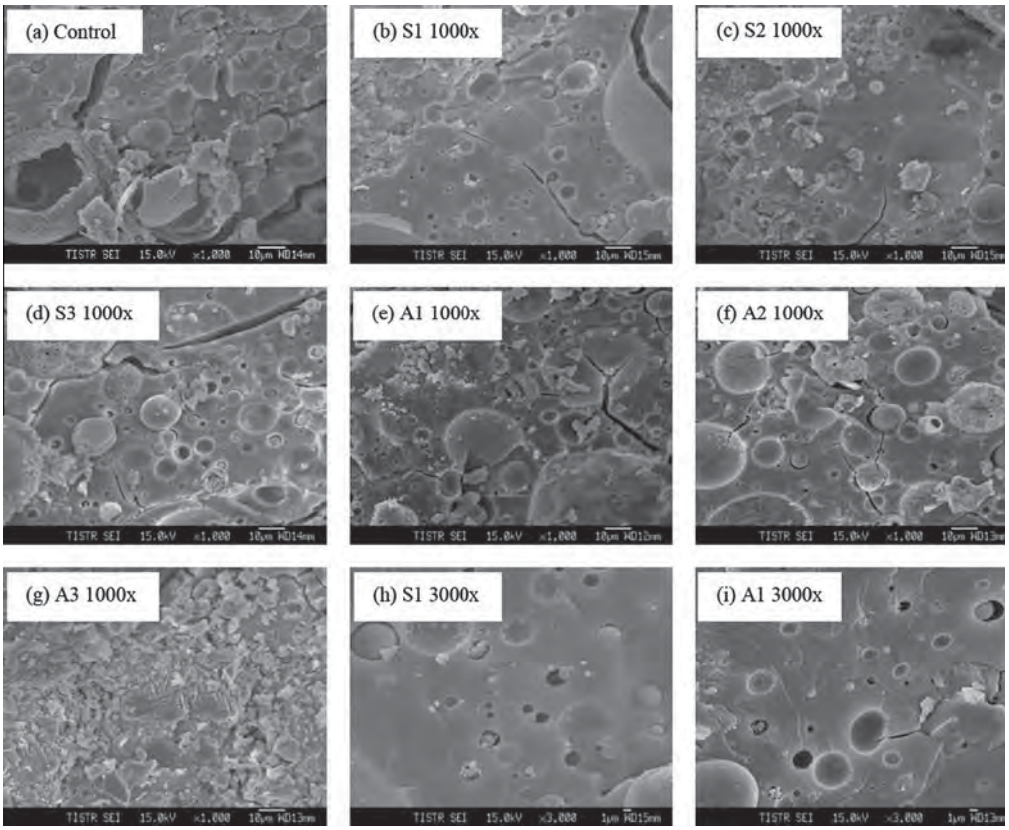


Fig. 5. SEM of geopolymer pastes at 28 days.

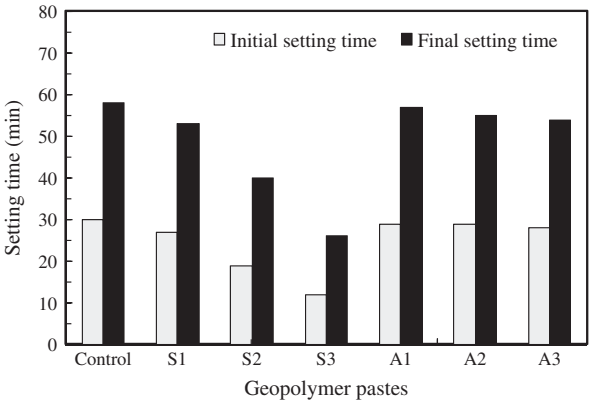


Fig. 6. Setting time of geopolymer pastes.

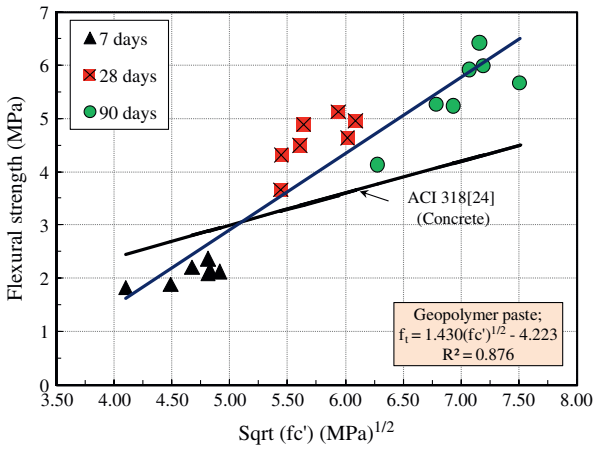


Fig. 7. Relationship between compressive strength and flexural strength of geopolymer pastes.

Table 6
Compressive strength and flexural strength of geopolymer pastes.

Mix	Compressive strength (MPa)			Flexural strength (MPa)		
	7 days	28 days	90 days	7 days	28 days	90 days
Control	16.8	29.6	39.4	1.83	3.66	4.13
S1	20.2	35.3	51.3	1.89	5.12	6.41
S2	24.1	31.8	51.8	2.13	4.89	5.98
S3	23.1	29.7	48.1	2.10	4.31	5.23
A1	21.8	36.2	56.4	2.22	4.63	5.67
A2	23.2	37.1	50.0	2.36	4.95	5.92
A3	23.3	31.4	46.1	2.14	4.49	5.26

that of the standard ordinary Portland cement concrete due to the dense and strong interfacial transition zone within geopolymer matrix. The increases in both compressive and flexural strengths from 28 days to 90 days were substantial and were the characteristics of samples with ambient temperature curing.

3.5. Modulus of elasticity

The elastic modulus of geopolymer pastes are shown in Table 7. The values of elastic modulus tended to increase with the addition of nano-particles. The pastes containing nano-particles were denser and stronger than that of control paste and this led to the increase of elasticity modulus (between 6.00 and 17.65 GPa). The elasticity modulus values of normal strength Portland cement pastes varied between 12.5 and 17.5 GPa [26,27] which were

Table 7
Elastic modulus of geopolymer pastes.

Mix	Modulus of elasticity (GPa)		
	7 days	28 days	90 days
Control	5.37	9.23	10.29
S1	6.30	11.67	16.00
S2	6.76	10.91	17.65
S3	6.15	9.60	14.12
A1	6.00	12.31	16.47
A2	6.92	11.32	14.48
A3	6.86	9.73	11.76

similar to those of pastes with1 to 2% nano-SiO_2 and nano-Al_2O_3. When adding nano-SiO_2 and nano-Al_2O_3, additional CSH, CASH and NASH formed within geopolymeric matrix and the rate of compressive strength and elastic modulus gain was significantly improved [28,29].

The relationship between elasticity modulus and compressive strength of geopolymer pastes is shown in Fig. 8. The elasticity modulus tended to increase linearly with the square root of compressive strength. The equation predicting this relationship can be written as;

$$E = 3.527\sqrt{f_c'} - 9.979 \quad (2)$$

where E is the modulus of elasticity (GPa), and f_c' is the ultimate compressive strength (MPa).

As shown in Fig. 8, the elasticity modulus of pastes containing nano-SiO_2 and nano-Al_2O_3 were slightly lower than that of Portland cement paste and geopolymer paste containing Portland cement [8,30]. The elastic modulus of geopolymer paste depended primarily on the strength of paste [6] which was related to the mix composition such as SiO_2/Al_2O_3 molar ratio [31] and curing temperature for the accelerated geopolymerization. In this study, the curing was at ambient temperature, therefore, the strength development was not really enhanced and this resulted in a more deformable characteristics [32]. Also, the strength and modulus of elasticity of pastes at the age of 90 days increased compared with those at the age of 28 days due to the increased reaction of SiO_2 and Al_2O_3 and Ca [8,17].

3.6. Shear bond strength between concrete substrate and geopolymer pastes

The 45° slant shear load carrying capacity of concrete substrate and geopolymer pastes are shown in Fig. 9. The shear bond strength could be calculated by performing stress transformation based on the peak strength of prism specimens. The shear bond strengths of geopolymer pastes containing nano-SiO_2 and nano-Al_2O_3 were obviously higher than that of control paste. At 28 days, the shear bond strength of pastes containing 1%, 2% and 3% nano-SiO_2 were 23.36, 20.64 and 17.49 MPa, respectively, whereas the pastes containing 1%, 2% and 3% nano-Al_2O_3 were 19.61, 20.61 and 20.32 MPa, respectively compared with 10.73 MPa of the control sample. The noticeable increase in shear bond strength due to the adding nano-SiO_2 and nano-Al_2O_3 could be attributed to the improvement of strength of geopolymers and the increased reaction products at the interface transition zone between concrete substrate and geopolymer pastes due to the reaction between the alkaline activator and surface product of old substrate, therefore, lead to denser interface zone and higher strength [1]. In addition, Pacheco-Torgal et al. [2] explained that a large amount of calcium hydroxide was found at the surfaces of concrete substrate, therefore the improved shear bond strength was due to SiO_2 and Al_2O_3 from raw materials reacted with $Ca(OH)_2$.

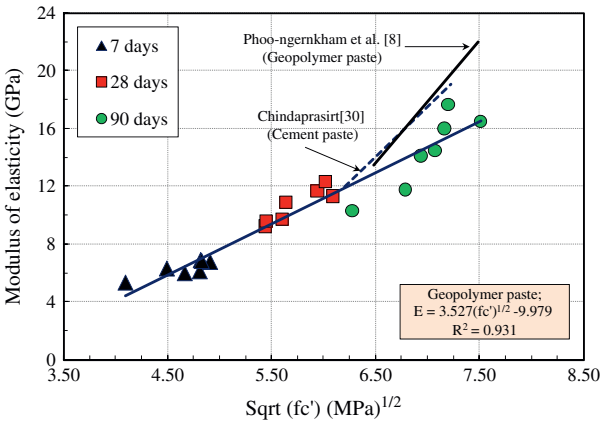


Fig. 8. Relationship between elasticity modulus and compressive strength of geopolymer pastes.

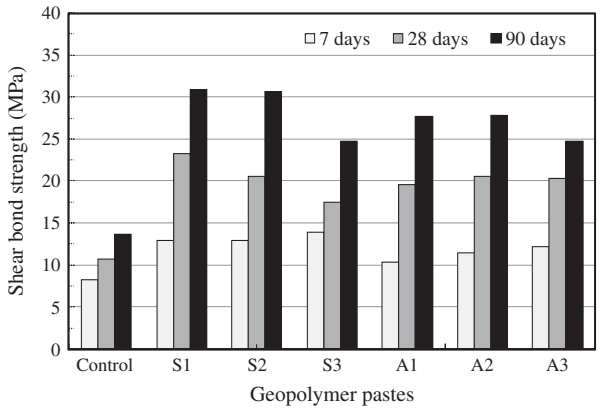


Fig. 9. Shear bond strength between concrete substrate and geopolymer pastes with interface line at 45° to the vertical.

The failure modes of the slant shear bond tests are shown in Fig. 10. The control sample with the normal geopolymer paste failed by cracking in the geopolymer paste (Fig. 10a) and the portion of geopolymer paste was severely damaged indicating the strength and stability of concrete substrate. For the geopolymers containing nano-SiO_2 and nano-Al_2O_3, the failures were all in the monolithic failure mode with concrete substrate and geopolymer containing nano-SiO_2 and nano-Al_2O_3 acted as a unit. The cracked samples showed that crackings in the vertical direction passed through the slant bond area and resulted in the monolithic failure mode. The slant of 45° in this experiment did not produce the shear failure mode, however, Pacheco-Torgal et al. [2] showed that the shear bond failure mode could be obtained with the reduction of slant to 30° to the vertical plane due to the high bond strength of geopolymer and concrete substrate. This test, however, indicated that the addition of 1–3% nano-SiO_2 and nano-Al_2O_3 improved the bonding of geopolymer and the concrete substrate.

4. Conclusions

Based on the results of this study, the follow conclusions could be drawn.

(1) The SEM and XRD results indicated that the microstructures of geopolymer pastes containing 1–2% nano-SiO_2 and nano-Al_2O_3 were enhanced with denser matrix and increased

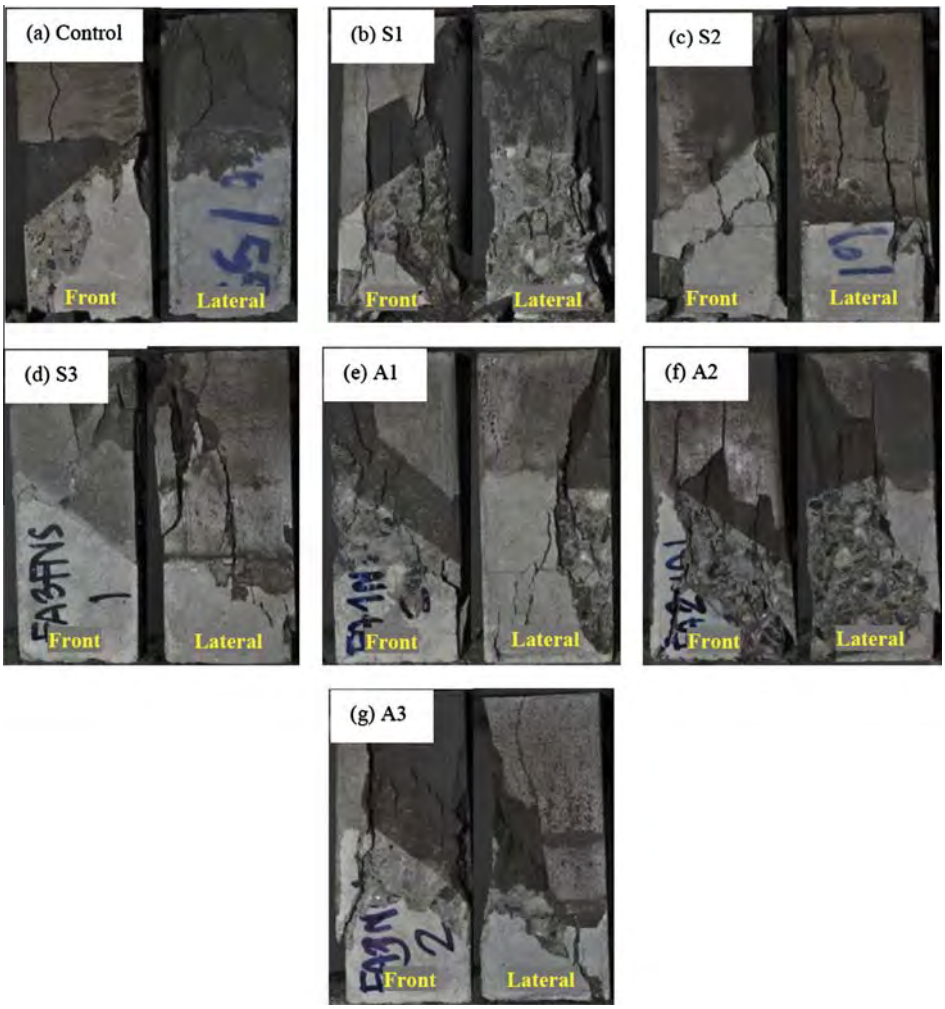


Fig. 10. Specimens failure mode at 28 days.

reaction product. However, the additional of 3% nano-SiO_2 and nano-Al_2O_3 resulted in an excessive amount of nano-particles and less dense structures were formed.

(2) The use of nano-SiO_2 as additive to high calcium fly ash geopolymer paste resulted in the decrease of setting time due to the formation of CSH which accelerated the setting and hardening of geopolymer pastes. While, the addition of same amount of nano-Al_2O_3 resulted in only a slight reduction in setting time. The fast setting time of high calcium FA geopolymer paste containing nano-SiO_2 could be beneficial for use as repair binding materials.

(3) The compressive strength, flexural strength, and elastic modulus of high calcium FA geopolymer paste containing nano-SiO_2 and nano-Al_2O_3 increased due to the formation of additional CSH or CASH and NASH gels in geopolymer matrix. These products are formed and filled the pore to make the dense and strong geopolymer. The relatively high compressive strengths of geopolymer pastes containing 2% nano-SiO_2 and 1% nano-Al_2O_3 cured for 90 days were 51.8 and 56.4 MPa, respectively.

(4) The addition of both nano-SiO_2 and nano-Al_2O_3 also improved the shear bond strength between concrete substrate and geopolymer. The high shear bond strength for 2% nano-SiO_2 and nano-Al_2O_3 cured for 28 days at 45° slant shear angle were 20.64 and 20.61 MPa, respectively comparing with 10.73 MPa of the control. The large increase was due to the improvement of strength of geopolymer pastes and the added reaction between the geopolymer paste and the concrete substrate at the contact zone.

Acknowledgements

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Effects of NaOH concentrations on physical and electrical properties of high calcium fly ash geopolymer paste

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ABSTRACT

The effects of sodium hydroxide (NaOH) concentration on setting time, compressive strength and electrical properties at the frequencies of 100 Hz–10 MHz of high calcium fly ash geopolymer pastes were investigated. Five NaOH concentrations (8, 10, 12, 15 and 18 molar) were studied. The liquid to ash ratio of 0.4, sodium silicate to sodium hydroxide ratio of 0.67 and low temperature curing at 40 °C were selected in making geopolymer pastes. The results showed that NaOH concentration had significant influence on the physical and electrical properties of geopolymer paste. The pastes with high NaOH concentrations showed increased setting time and compressive strength due to a high degree of geopolymerization as a result of the increased leaching of silica and alumina from fly ash. The dielectric constant and conductivity increased with NaOH concentration while $\tan\delta$ decreased due to an increase in geopolymerization. At the frequency of 10^3 Hz, the dielectric constants of all pastes were approximately 10^4 S/cm and decreased with increased frequency. The relaxation peaks of $\tan\delta$ reduced with an increase in NaOH concentration and ranged between 2.5 and 4.5. The AC conductivity behavior followed the universal power law and the values were in the range of 3.7×10^{-3}–1.5×10^{-2} at 10^5–10^6 Hz.
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1. Introduction

Fly ash is an industrial by-product generated during the combustion of coal for energy production. Currently the annual production of coal ash worldwide is estimated around 600 million tons, with fly ash constituting about 500 million tons at 75–80% of the total ash produced [1]. In Thailand, the annual output of lignite fly ash from Mae Moh power station is around 3.0 million tons. Approximately 1.8 million tons are used as pozzolanic material in the cement and concrete industry. However, around 1.2 million tons are still left over and discarded at landfill site [2] which poses a serious environmental problem. This lignite fly ash contains a substantial amount of silica and alumina which can be used as a source material for making geopolymer [2–4]. The geopolymer materials have recently received considerable attention owing to their excellent fire resistance, excellent thermal properties, and environmentally friendly nature [5,6].

Aluminosilicate inorganic polymers, also called geopolymers, were firstly described by Davidovits as materials formed under high alkali condition from aluminosilicate solid and alkali silicate solutions [7]. The geopolymer is a type of cross-linked long chain inorganic polymer material between tetrahedral AlO_4 and SiO_4 units built in three dimensional structures. The linkages of AlO_4 and SiO_4 units require charge balancing from alkali ions such as Li^+, Na^+ and K^+. The mechanism of the existence of alkali ions in the molecular structure of geopolymer materials is not clearly understood at present. Usually the accustomed viewpoint is that the alkali metal ions play a charge balancing role or are actively bonded to the matrix. Therefore, the typical geopolymer composition is usually expressed as $n\boldsymbol{M}_2O{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$ where $\boldsymbol{M}$ is alkali metal element such as Li, Na or K [8]. Several materials containing silica and alumina can be used as starting source materials. These include the conventional starting materials viz., slag, metakaolin and class C fly ash [9,10]; other wastes or waste ashes such as rice husk ash, fluidized bed fly ash, glass cullet powder and waste concrete powder [11–14]; and Portland cement [15,16].

Recently it has been found that the chemosynthetic Al_2O_3–$2SiO_2$ geopolymer prepared by sol–gel method exhibits a high ionic electrical conductivity of about 1.5×10^{-6} S/cm in air at room temperature [8]. Such a high level of the ionic electrical conductivity observed in this geopolymer may be important properties as a promising fast-ionic conducting material for many applications such as solid-state batteries and other solid-state electrochemical

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parts. It has also been found that the water content does not directly affect the electrical conductivity of hardened geopolymer materials [8]. However, the free Na ions, water molecules and hydroxide ions are the major components determining the dielectric loss. The $2.4H_3PO_4$–Al_2O_3–$2SiO_2$ geopolymer can reduce the ion transfer due to the lack of free alkali cations within the structure. In addition, the heat treatment can reduce dielectric loss from 10^{-2} to 10^{-3} due to the decrease in water from the structure [17].

In general, the ions that can conduct in ionic conductors are Li^+, Na^+, H^+, K^+, Ag^{2+}, O^{2-}, and F^- [18]. For geopolymer materials, free alkali metal ions are expected to play a role on the electrical properties. The concentrations of these free alkali metal ions are, therefore, closely related to the ionic electrical conductivity of fly ash geopolymer materials. Moreover, the electrical conductivity and dielectric constant of fly ash geopolymer pastes are dependent on the frequency range and liquid alkali to ash ratio [19].

In this study, the effects of NaOH concentrations on the physical and electrical properties, and the related dielectric response in fly ash geopolymer pastes (FAGP) were studied.

2. Materials and experimental procedures

2.1. Materials

Lignite high calcium fly ash from Mae Moh power plant in Thailand was used for this study. The median particle size was 23.5 μm and the percentage retained on sieve no. 325 was 40%. The chemical compositions were 35.21% SiO_2, 16.57% Al_2O_3, 25.52% CaO, 13.66% Fe_2O_3, 2.73% Na_2O and 6.31% other. The loss on ignition was low at 0.37. Sodium silicate with 32.39% SiO_2, 13.44% Na_2O and 54.17% H_2O by weight and NaOH solutions were used as alkali activators.

2.2. Geopolymer synthesis

The mixing procedure started with mixing fly ash (FA) and NaOH solution for 5 min. Sodium silicate solution was added and mixed for another 5 min. Liquid alkali solution to fly ash ratios (L/A) of 0.4 and sodium silicate to sodium hydroxide ratio of 0.67 were used. The concentrations of NaOH of 8, 10, 12, 15 and 18 molar were used. These values were selected based on the previous researches using the same lignite fly ash as source material [3,4,20]. The samples that contain the 8, 10, 12, 15 and 18 molar NaOH solutions are abbreviated as G8, G10, G12, G15, and G18 samples, respectively.

2.3. Sample preparation and testing

After being mixed, the fresh pastes were tested for setting times in a 25 °C room using standard Vicat needle apparatus in accordance with the ASTM C191 [21]. The reported results are the average of two tests.

The paste was then cast in a 3 cm diameter and 6 cm height plastic moulds for strength test. The cast samples were left standing in the 25 °C controlled room for 1 h. They were covered with clingfilm to avoid loss of water and put to cure in an electric oven at 40 °C for 24 h. After being cured, the specimens were left in the 25 °C controlled room until the age of 7 days. The compressive strength test was performed at the age of 7 days in accordance with the ASTM D1633 [22]. The reported results are the average of three specimens.

The microstructures of the pastes were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The broken portion of the compressive strength specimens were used for these analyses.

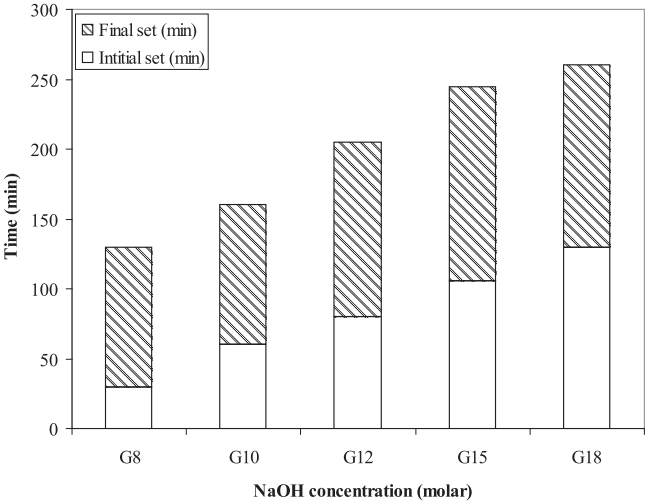


Fig. 1. Setting time of FAGP with various NaOH concentrations.

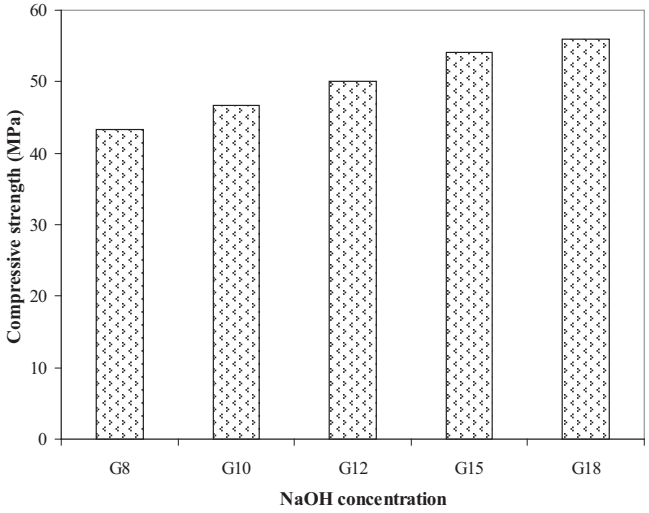


Fig. 2. Compressive strength of FAGP with various NaOH concentrations.

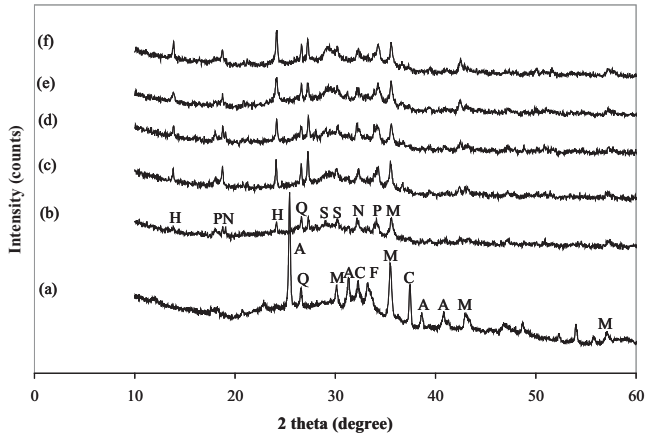


Fig. 3. XRD pattern of fly ash and FAGP with various NaOH concentrations (a) fly ash, (b) G8, (c) G10, (d) G12, (e) G15 and (f) G18.

For dielectric measurement, discs of 19 mm diameter and 2 mm thickness were cast and prepared in the same manner as the strength specimens. At the age of 7 days, the samples were

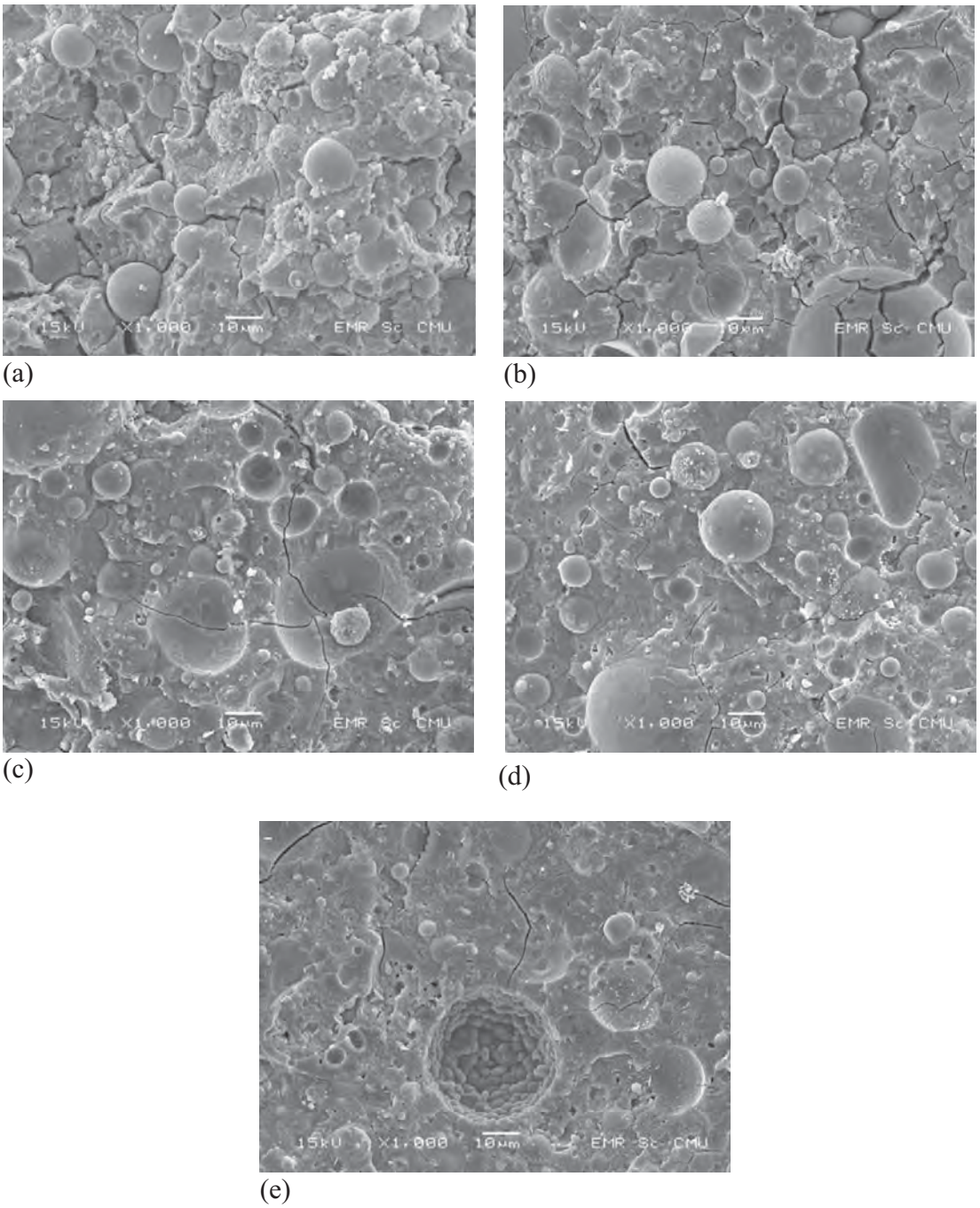


Fig. 4. SEM images of FAGP with various NaOH concentrations (a) G8, (b) G10, (c) G12, (d) G15 and (e) G18.

electroded by silver paint on both sides of the disk-shaped samples. The capacitance, dissipation factor, and electrical responses of the samples were measured with the use of a Hewlett Packard 4194A impedance gain phase analyzer over the frequency range of 102–106 Hz at room temperature and at oscillation voltage of 1.0 V. The relative permittivity or dielectric constant (εr) and dielectric loss (ε_r'') were calculated from Eqs. (1) and (2) [23,24]

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A} \tag{1}$$

where C is the capacitance of the sample, t is the thickness, ε_0 is the permittivity of free space constant (8.854×10^{-12}), and A is the electrode area;

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r} \tag{2}$$

where ε_r is the relative permittivity, ε_r'' is the dielectric loss, and $\tan\delta$ is the loss tangent.

3. Results and discussion

3.1. Setting time of geopolymer paste

The results of setting time are shown in Fig. 1. The initial and final setting times increased with an increase in NaOH concentration. The final setting times were 130, 160, 205, 245 and 260 min

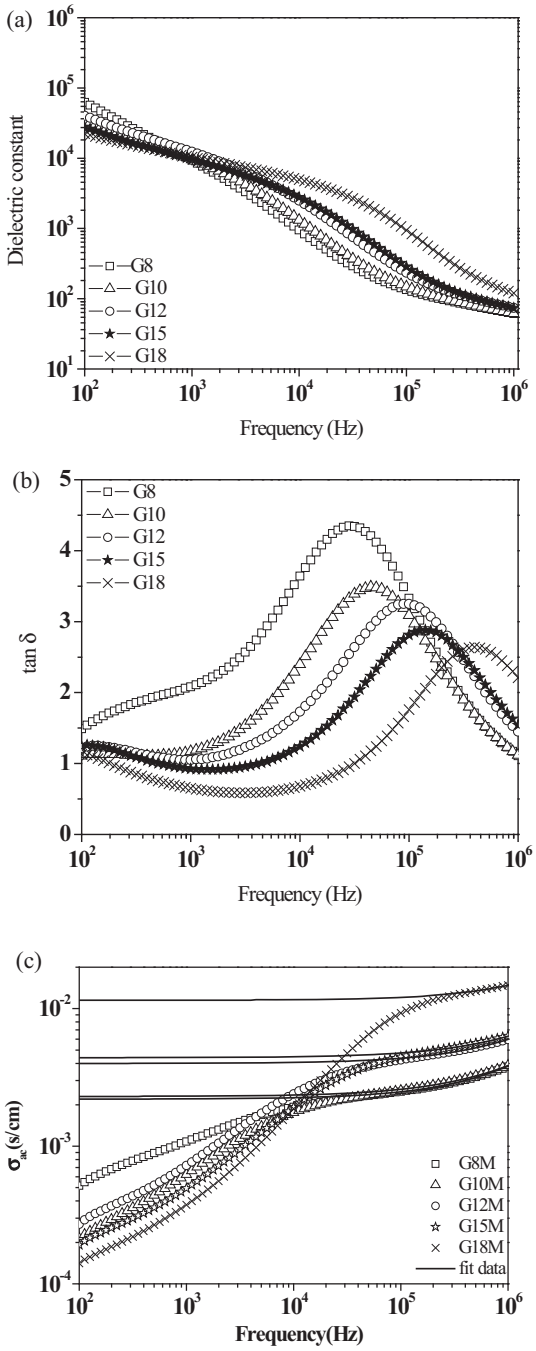


Fig. 5. Electrical properties of FAGP with various NaOH concentrations (a) dielectric constant, (b) tan δ, (c) AC conductivity (σ_{ac}).

Table 1
Parameters obtained from fitting universal power law curves of FAGP with various NaOH concentrations.

NaOH concentrations	σ_0 (S/cm)	A	n
8 M	0.0022	5.1×10^{-8}	0.75
10 M	0.0023	6.5×10^{-8}	0.73
12 M	0.0040	7.2×10^{-8}	0.74
15 M	0.0044	8.5×10^{-8}	0.72
18 M	0.0115	9.1×10^{-8}	0.76

for G8, G10, G12, G15, and G18 pastes, respectively. At low NaOH concentration, the leaching out of silica and alumina was low [20]. The leaching out of Ca^{2+} to the solution was not interrupted and the solution was thus filled with calcium. The amount of calcium was sufficient for the precipitation and reacted to form calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH). This resulted in the setting of paste and the setting time was thus short [25,26]. The setting time of geopolymer paste was thus related to the amount of the available calcium [27].

At high NaOH concentration, the leaching of silica and alumina was much better. The leaching out of calcium was hindered and the amount of calcium in the solution was limited. The setting of the paste was controlled by the normal geopolymerization process and the setting time was increased.

3.2. Compressive strength of geopolymer paste

The results of compressive strength are shown in Fig. 2. The compressive strength was increased with an increase in the NaOH concentration. They were 43.3, 46.7, 50.0, 54.1 and 56.0 MPa for the G8, G10, G12, G15, and G18 pastes, respectively. When the NaOH concentration was high, the dissolution of Si^{4+} and Al^{3+} ions from fly ash increased and the formation of sodium alumino-silicate was enhanced leading to an increase in strength [20,28,29].

The XRD patterns of fly ash and FAGP with various NaOH concentrations are shown in Fig. 3(a–f). The fly ash consists of an amorphous phase as indicated by the broad hump around 20–38° and crystalline phase as indicated by the sharp peaks of quartz (SiO_2), hematite (Fe_2O_3), anhydrite ($CaSO_4$), magnesioferrite ($MgFe_2O_4$) and calcium oxide (CaO). When the fly ash was activated with the alkali solutions, the glassy component was the first to dissolve and formed a new phase of alkaline aluminosilicate gel with apparent shift of broad hump around 25–38° [19,20,28,30]. Moreover, the peaks of quartz and magnesioferrite were still present from the remain of the unreacted or partially reacted fly ash with the disappearance of anhydrite. The new phases were portlandite ($Ca(OH)_2$), sodium sulfate (Na_2SO_4) and hydrosodalite ($Na_4Al_3Si_3O_{12}(OH)$). As discussed, the presence of $Ca(OH)_2$ affected the setting time of the paste. Moreover, the fly ash with high calcium oxide reacted with silicate compounds to form CSH similar to the hydration of Portland cement. The broad hump, therefore, included the geopolymeric gel and CSH gel [2,28]. A higher NaOH concentration had better ability to dissolve fly ash particles which resulted in better geopolymerization. The peaks of hydrosodalite and CSH increased with the increase in the NaOH concentration resulting in the increase in strength of paste.

Fig. 4(a–e) show the morphology of FAGP when activated by NaOH with various concentrations. The unreacted and/or partially reacted grains of fly ash and a continuous mass of alumino-silicate were easily detected. With increasing NaOH concentration, the unreacted fly ash particles were less abundant and the matrices looked rather dense. The findings were similar to the previously published results [31]. When the alumino-silicate source material came into contact with the alkali solution, the leaching of both silica and alumina started [32]. The increase in the NaOH concentration in the system resulted in the increase in leaching of silica and alumina from the fly ash particles to the solutions [20]. This resulted in a dense and strong geopolymer matrix which increased compressive strength of the paste.

Both the XRD and the SEM analyses reinforced the finding that the increase in compressive strength of high calcium fly ash ash geopolymer paste was due to the increase in NaOH concentration. The presence of calcium in substantial quantity in the system led to the formation of hydration products of CSH. At the same time, the high NaOH concentration of the system enhanced the leaching of silica and alumina and resulted in increased geopolymerization and formation of NASH gel. The CSH co-existed with NASH gel and increased the strength of paste [33].

3.3. Electrical properties of geopolymer pastes

Fig. 5 shows the electrical properties of FAGP with various NaOH concentrations. The results showed a decrease in dielectric constant (Fig. 5a) and increase in conductivity (Fig. 5b) with an increasing frequency which was indicative of a region of dispersion resulting from relaxation of a polarization process within the system [34]. For dielectric constant (Fig. 5a), the FAGP showed high dielectric constant values of 10^4–10^5at the low frequency range of 10^2–10^3 Hz which were the results of electrode/sample interfacial polarization and double-layer polarization on fly ash surface [33,34]. At the frequency of 10^3 Hz, the dielectric values of all samples were high at approximately 10^4. At the higher frequency, the dielectric values decreased and depended on the NaOH concentration. The dielectric values decreased less with the increase in NaOH concentration since the samples contained less unreacted fly ash and were denser than those of the low NaOH concentration mix.

For tan δ (Fig. 5b), the relaxation peaks of all samples were clearly observed and the trend of results was related to the dielectric constant values. The peak values of tan δ ranged between 2.5 and 4.5. When the NaOH concentration increased, the peak height decreased and the peak position shifted towards a higher frequency. This phenomenon was related to the denseness of structure. At high NaOH concentration, the leaching of alumina and silica was enhanced and the geopolymerization and formation of geopolymer gel increased [20] which led to a dense structure.

For the AC conductivity (Fig. 5c), the FAGP showed low conductivity in the range of 1.4×10^{-4}–5.2×10^{-4} at a low frequency as a result of electrode effect. At a high frequency, the conductivity increased with the increased frequency and NaOH concentration which was related to the increased geopolymerization. At 10^5–10^6 Hz, the AC conductivity values were 3.7×10^{-3}–1.5×10^{-2} S/cm. At a high frequency, the AC conductivity behavior follows the universal power law [35] as shown in Eq. (3).

$$\sigma(\omega) = \sigma_o + A\omega^n \tag{3}$$

where $\sigma(\omega)$ is the total conductivity, σ_0 is the DC conductivity, A is the pre-exponential factor, ω is the angular frequency, and n is the fractional exponent between 0 and 1.

The values of σ_0, A and n were obtained from Eq. (3) and shown in Table 1. The DC conductivity clearly increased with the increase in NaOH concentration which was due to the increase in geopolymerization.

4. Conclusions

Based on the results of the tests, the following conclusions can be made.

1. The NaOH concentration had significant influence on the physical and electrical properties of geopolymer paste. With an increase in NaOH concentration, the setting time and compressive strength increased resulting from a dense matrix with less unreacted fly ash in the microstructure.
2. The dielectric constant, loss and conductivity of geopolymer pastes were also affected by the NaOH concentration. At the low frequency range of 10^2–10^3 Hz, the geopolymer paste showed high dielectric constant values of 10^4–10^5. At the frequency of 10^3 Hz, all dielectric values of pastes were approximately the same at 10^4. At higher frequencies, the dielectric values decreased substantially and were related to the NaOH concentration. The decrease was less with the increases in NaOH concentration and strength of paste.
3. The relaxation peaks of tan δ of geopolymer paste ranged between 2.5 and 4.5, and were related to the dielectric constant values. When the NaOH concentration increased, the peak height decreased and the peak position shifted towards a higher frequency due to the increased denseness and strength of pastes.
4. For the AC conductivity, the geopolymer paste showed low conductivity of 1.4×10^{-4}–5.2×10^{-4}at a low frequency. At higher frequencies, the conductivity increased with the increased NaOH concentration. At 10^5–10^6 Hz, the AC conductivity values were 3.7×10^{-3}–1.5×10^{-2} S/cm. It was also found that the AC conductivity values of high calcium fly ash geopolymer pastes followed the universal power law.
5. It has been demonstrated that the physical and electrical properties of the high calcium fly ash geopolymer materials can be improved by using a suitable NaOH concentration.

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Short communication

Effect of particle size on the dielectric and piezoelectric properties of 0–3BCTZO/cement composites

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Abstract

0–3 $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZO)–cement composites were prepared by normal mixing and pressing of Ordinary Portland cement and BCTZO particles with average sizes of 569.8 and 8.9 μm. Three different composites were prepared with BCTZO to cement ratios of 30%, 50%, and 70% by volume. The effect of BCTZO particle size on the dielectric and piezoelectric properties of cement based 0–3 piezoelectric composites was investigated. The dielectric constant increases with both increasing BCTZO particle content and increasing BCTZO particle size. The piezoelectric properties were found to increase with the increasing BCTZO particle content and decreasing BCTZO particle size. It was found that a 70% BCTZO composite with an average particle size of 8.9 μm produced good dielectric constant, tan δ and piezoelectric properties of 107, 0.09 and 52 pC/N, respectively.
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Keywords: C. Dielectric properties; C. Piezoelectric properties; Cement composites; Particle size

1. Introduction

Recently, cement based-piezoelectric composites (0–3, 1–3, 2–2 etc.) have been of interest because of their promising applications in civil engineering structures such as sensors and actuators [1–5]. In particular, cement composites of 0–3 connectivity, cement–piezoelectric material composites, were first reported by Li et al. [1]. They fabricated the lead zirconate titanate (PZT)–cement composites using normal mixing and spreading methods and have shown that the composites have compatibility with cement and have potential to be used for sensor applications. Xin et al. [2] investigated 0–3 lead magnesium niobate (PMN)– sulphoaluminate cement composites using a ball milling and pressing method and found good performances of both piezoelectricity and electromechanical coupling. Chaipanich's group et al.[3–5] investigated the piezoelectric and dielectric properties of PZT–cement-based composites prepared by normal mixing and compressing. However, these piezoelectric–cement composites are made using PZT or PMN and are toxic on the environment. As an alternative, $BaTiO_3$ (BTO)–cement composites of 0–3 connectivity were fabricated using a normal mixing and compassing method by Rianyoi et al. [6]. However, the piezoelectric properties of these composites are lower than those of the PZT–cement composites. Therefore, they tried to form the piezoelectric–cement composites in 1–3 types [7], which have good piezoelectric properties than those of 0–3 type cement composites.

Today, $BaTi_{0.8}Zr_{0.2}O_3$–$Ba_{0.7}Ca_{0.3}TiO_3$ (BZT–BCT) piezoelectric ceramics, with a composition close to the morphotropic phase boundary (MPB), exhibit large piezoelectric response, large dielectric constant and high spontaneous polarization [8–11], and are replacing PZT in sensor applications. Therefore, it is expected that this piezoelectric will play a more active role than those of 0–3 lead free piezoelectric–cement composites.

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In this study, we report the $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZO)–cement composites with high piezoelectric coefficient, produced by the normal mixing and compressing of white cement and BCTZO ceramic particles. The dielectric and piezoelectric properties of these composites were investigated.

2. Experimental

$Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZO) ceramic particles were prepared by a solid state reaction method. $BaCO_3$ (99%), $CaCO_3$ (96%), TiO_2 (99%) and ZrO_2 (99%) were used as the

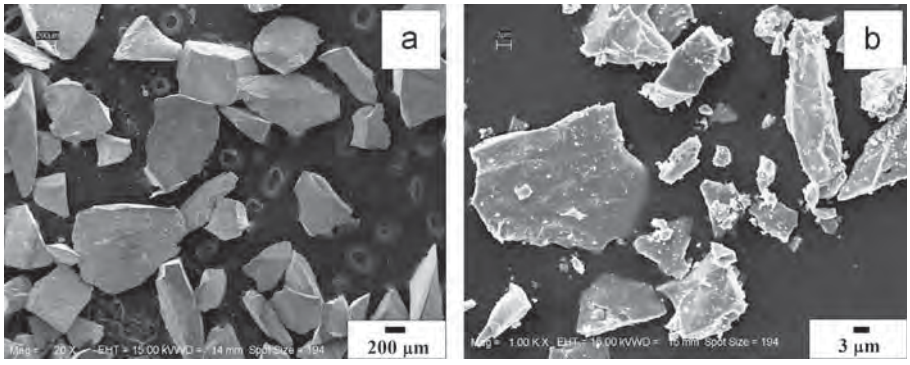


Fig. 1. The SEM images of BCTZO particles with the average particle size (a) 569.8 μm and 8.9 μm.

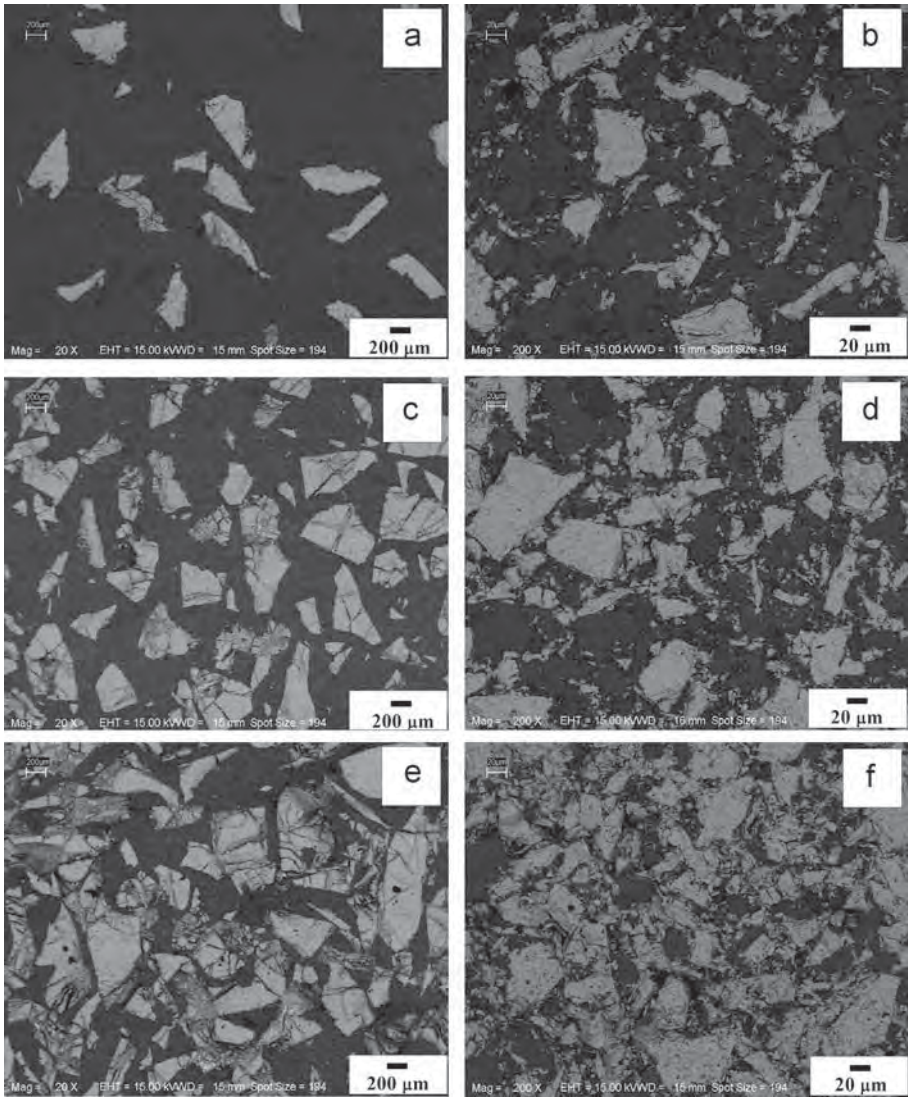


Fig. 2. The backscattered electrons SEM images of BCTZO–cement composites (a) 30%BCTZO, (b) 50%BCTZO and (c) 70%BCTZO for the average particle size as 569.8 μm, and (d) 30%BCTZO, (e) 50%BCTZO and (f) 70%BCTZO for the average particle size as 8.9 μm.

starting materials. Initially, all of these materials were mixed with 2-propanol and were ball milled for 24 h. After drying, the mixture precursor powders were calcined at 1300 °C for 3 h. The calcined BCTZO powders were compacted into disk-shaped pellets with a diameter of 13 mm and thickness of 1.5 mm with 221 MPa pressure. The green pellets were sintered at 1450 °C for 3 h. The sintered BCTZO ceramics were ground and sieved to select the size of BCTZO particles. To prepare the BCTZO–cement composites, the sintered BCTZO particles and Ordinary Portland cement were mixed and then pressed under a pressure of 146 MPa to form discs with a diameter of 16 mm and a thickness of about 2.5 mm. The disc specimens were cured in water vapor at 60 °C for 3 days and then dried.

The morphology of these samples was characterized by scanning electron microscopy (SEM, LEO VP1450, UK). Silver paint was used as the electrode and the dielectric properties of the composite discs were measured at room temperature by using an Agilent 4294A Precision impedance analyzer. The dielectric constant (ε_r) was calculated from the following equation:

$$\varepsilon_r = \frac{C_p t}{\varepsilon_0 A}$$

where C_p is the sample capacitance, t is the thickness, ε_0 is the permittivity of free space constant (8.854×10^{-12} F/m) and A is the electrode area.

The piezoelectric properties of composite discs were polarized at room temperature in silicon oil for 45 min under an electric field of 1 kV/mm. After being held for 24 h at room temperature, the piezoelectric strain factor (d_{33}) of the composite discs was measured by using a d_{33} meter (Model 90-2030, APD International, Ltd.).

3. Results and discussion

The morphology of the BCTZO particles was studied by SEM as shown in Fig. 1(a and b). The ground BCTZO particles have plate-like sharpness with sizes ranging from 294.8 to 1113.8 μm (Fig. 1(a)) or with sizes ranging from 1.6 to 36.9 μm (Fig. 1(b)). The average particle sizes of the ground BCTZO particles were evaluated to be 569.8 and 8.9 μm. SEM images of the composites, with 30%, 50% and 70% by volume of BCTZO particles, are shown in Fig. 2(a)–(f). In the backscattered electron SEM images, the black phase is cement and the white phase is BCTZO particles. It can be seen that using low content BCTZO particle results in their being isolated in the cement matrix, whereas using high content BCTZO particle results in their contact. However, with high content of BCTZO particles many cracks are observed, which are due to high compression during the formation of composite bulk.

The dielectric constants and tan δ, for the BCTZO–cement 0–3 composites of 30%, 50 %and 70% by volume and average particle size of 569.8 μm, are shown, respectively in Fig. 3(a)–(b). The dielectric properties were measured at 1 kHz and it was found that the dielectric constant increases with increasing BCTZO particle content. The values of dielectric constant were found to be 46.1, 80.7 and 154.0 and tan δ was found to be 0.12, 0.1 and 0.11 correspondingly. It was found that the dielectric constant of composites with the average particle size of 8.9 μm also increases with the increasing BCTZO particle content. The values of dielectric constant were found to be 38.7, 64.1 and 107.0 and tan δ was found to be 0.11, 0.12 and 0.09 correspondingly (Fig. 4). The dielectric constants and tan δ of the BCTZO–cement 0–3 composites, for the average particle size of 569.8 and 8.9 μm, are summarized in Table 1. From these results, it can be seen that all of the samples behave similarly to those in previous studies which show increasing dielectric constant with increasing piezoelectric particle content [1–6]. The dielectric constant increases with the increasing BCTZO particle size because of the influence of the dielectric constant of BCTZO bulks (4270 at 1 kHz), which is higher than that of cement bulk (19.7 at 1 kHz) and is explained by the composites model [1,6,12]. It was also found that the dielectric constant decreases with decreasing BCTZO particle size because of the low polarizations in small particles resulting in a lower dielectric constant in the samples.

The piezoelectric strain factor (d_{33}) values of the BCTZO–cement 0–3 composites of 30%, 50% and 70% by volume for the average particle sizes of 569.8 and 8.9 μm are also summarized in Table 1. It was found that the piezoelectric

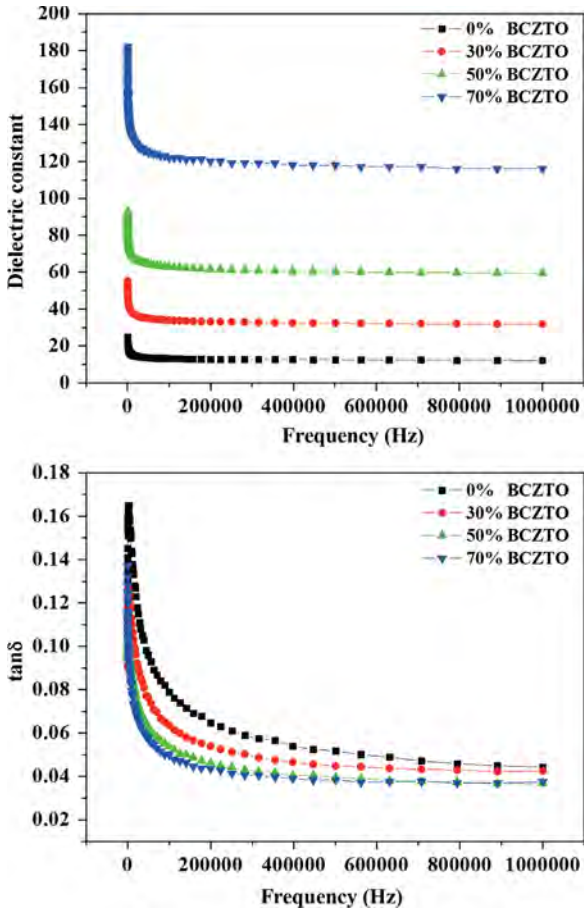


Fig. 3. Dielectric constant and tan δ of various BCTZO–cement composites with the average particle size as 569.8 μm measured at room temperature.

strain factor increases with increasing BCTZO particle content. In the composites with average particle size as 569.8 μm, the values of piezoelectric strain factor were found to be 4, 18 and 44 pC/N correspondingly. For composites with an average particle size of 8.9 μm, it was found that piezoelectric strain factor also increases with increasing BCTZO particle content. The values of piezoelectric strain factor were found to be 10, 32 and 52 pC/N. It is well known that cement is not piezoelectric and the incorporated BCTZO particles play an important role in the piezoelectricity of the composite. And then it can be seen that the piezoelectric strain factor of composites increases with decreasing BCTZO particle size

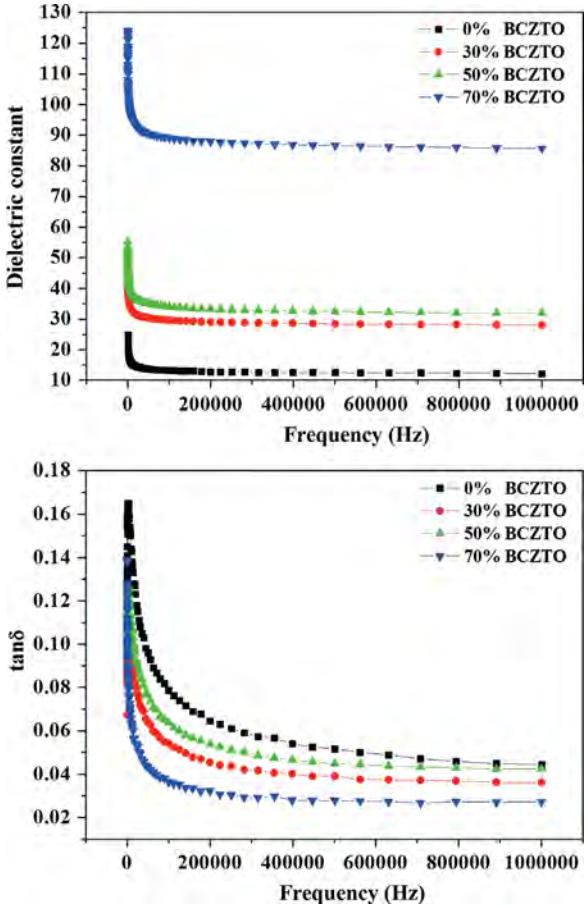


Fig. 4. Dielectric constant and tan δ of various BCTZO–cement composites with average particle size as 8.9 μm measured at room temperature.

[13,14]. Shifeng et al. [13] reported that piezoelectric properties decreased with decreasing ceramic particle size because the small ceramic particles (1.45–68.5 μm) have a high surface area and the volume ratio of lead lithium niobate to lead zirconate to lead titanate (PLN) leads to low piezoelectric properties or non-piezoelectric properties on the surface layer. On the other hand, because the chances for large ceramic particles (107.08–294.07 μm) to contact each other increase, the connectivity patterns change. In addition, Li et al. found that high piezoelectric properties can be obtained by using high crystalline nano-PZT particle (200 nm) cement composites [14] with a high d_{33} value of 52 pC/N. However, this study shows that smaller BCTZO particles have higher surface areas leading to lower interface space, resulting in better contact between the individual BCTZO particles. This is quite clear from the SEM results. The authors obtained quite good performances compared to those obtained by others at Composites with 70 vol% of piezoelectric particles, the BCTZO–cement composites, with average sizes of 569.8 and 8.9 μm have d_{33} values of 44 and 52 pC/N, respectively, which are higher than that of the BTO–cement composite (16 pC/N) [6] and the PZT–cement composite (43 pC/N) [3]. Therefore, the authors expect that 1–3 will play a more active role than 0–3 lead free piezoelectric–cement composites for sensors and actuators applications in civil engineering structures.

4. Conclusion

In this study, $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ particles were prepared by the solid state reaction method. The cement based 0–3 piezoelectric composites were fabricated by normal mixing and pressing of Ordinary Portland cement and BCTZO particles and curing in water vapor at 60 °C for 3 days. It was found that the dielectric constant and piezoelectric strain factor increase with increasing volume percentage of BCTZO particles. Good values for dielectric constant, dielectric loss and piezoelectric strain factor were obtained (107, 0.19 and 52 pC/N, respectively) for 70 vol% BCTZO particles with an average particle size of 8.9 μm. The piezoelectricity of the composites containing small BCTZO particles was high due to the high surface area and low interface space between the individual BCTZO particles, leading to good connection between those particles.

Table 1
Dielectric constant, tan δ and piezoelectric strain factor of various BCTZO–cement composites with the average particle size 569.8 and 8.9 μm measured at room temperature.

BCTZO particle content (vol%)	Dielectric constant ε_r measured at 1 kHz		tan δ, measured at 1 kHz		Piezoelectric charge constant, d_{33} (pC/N)	
	569.8 μm	8.9 μm	569.8 μm	8.9 μm	569.8 μm	8.9 μm
30	46.1	38.7	0.12	0.11	4	10
50	80.7	64.1	0.10	0.12	18	32
70	154.0	107.0	0.11	0.09	44	52

Acknowledgments

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Characterizations of FBC/PCC fly ash geopolymeric composites

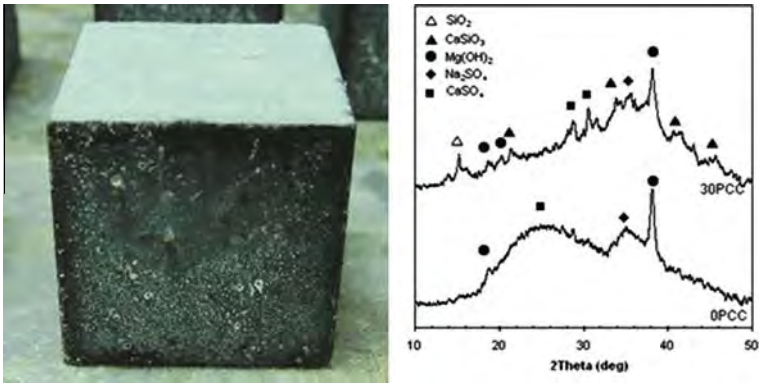
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HIGHLIGHTS

- FBC fly ash was used as a source material of geopolymeric composite.
- Grinding was applied to improve the physical property of FBC fly ash.
- PCC fly ash was blended with ground FBC fly ash to increase the glassy phase of source material.
- Results showed the changes in chemical compositions in the composite and physical performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluidized bed combustion (FBC) is a well-established coal burning process for small factories owing to energy efficiency and low environmental impact. Due to the low burning temperatures at 800–900 °C, FBC fly ash is not suitable for use as pozzolan in concrete mixture and requires proper improvement before utilization. This research proposed the use of FBC fly ash as a source material for geopolymeric composite. Grinding was applied to improve the physical property of FBC fly ash. In addition, the ground FBC fly ash was blended with pulverized coal combustion (PCC) high calcium fly ash to increase its glassy phase. The geopolymeric composites were then prepared using the blended powder mixed with alkali solutions, and thermally-cured to promote the reaction. The hardened specimens were subjected to chemical and physical tests. Resistance to acid and salt attacks of PCC/FBC fly ash composites was also investigated. Results showed the changes in chemical compositions and physical performances of geopolymeric materials. PCC fly ash helped enhance the properties of FBC fly ash based composite and the dense and homogeneous matrix was achieved. Additional C—S—H was formed resulting in the increase in strength of composites as a function of time. However, the durability was affected with the use of the high calcium PCC fly ash due to the presence of calcium and the associated hydration products.

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1. Introduction

Fluidized bed combustion (FBC) is an environmentally-friendly coal combustion process and is growing particularly in the small factories due to the low release of SO_2 and NO_x gasses in the flue gas. Combustion temperature of FBC unit is around 800–900 °C at which NO_2 cannot be generated and thus low-grade fuel can be efficiently burnt in the bed. SO_2 gas is effectively absorbed with ground limestone feeding resulting in no need of hi-tech flue gas desulfurization equipment [1]. Low combustion temperature

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results in a low glassy phase in FBC fly ash and hence it is not recommended to use as a cement replacement in concrete [2].

Alkali-activated composites have been widely studied owing to high strength gain in a short period of curing. Pulverized coal combustion (PCC) fly ash is a suitable alumino-silicate source and is effectively used as a source material for making an alkali-activated composite due to its pozzolanic property and availability. Aluminum and silicon ions are leached by alkali solutions (e.g. sodium hydroxide and sodium silicate solutions) from fly ash particles resulting in Al—O—Si geopolymerization chain [3–5]. The curing temperatures vary from ambient temperature to 90 °C. The resulting product is assigned as "geopolymer" [3]. PCC fly ash geopolymers possess excellent cementing, durability and thermal properties [4–8]. PCC fly ash consists of fine spherical particles of approximately 1–200 μm with high amorphous (glassy) phase content and high reactivity. It is widely use as pozzolanic material for partial replacement of Portland cement [9–11].

Numerous alumino-silicate source materials such as metakaolin [12,13], blast-furnace slag [14], rice husk ash [15], Al-rich waste [16] and red mud [17] have been used as source materials for the synthesis of geopolymer. Another alternative source material is FBC fly ash [18–20] as it contains silica and alumina and a large amount is produced annually. However, the use of FBC fly ash results in low strength geopolymer. Therefore, grinding and blending with PCC fly ash were applied to improve the mechanical properties of composites [19,20]. Proper grinding of FBC fly ash removed pores and cavities and increased the surface area [19].

The utilization of FBC fly ash is limited for making the geopolymer, non-cement binding, as it is a material with low reactivity. This research attempted to improve FBC fly ash as a starting material for geopolymer preparation. As the strength of FBC fly ash geopolymer was low, grinding was employed to increase its surface area and reactivity. In addition, the reactive PCC fly ash was used to blend with FBC fly ash to improve the properties of starting material. This was achieved without using Portland cement. Chemical and physical properties of FBC/PCC fly ash geopolymeric composites were characterized by XRD, SEM, FTIR, TGA techniques. Compressive strength tests of the cube specimens under normal curing condition and after immersion in 3% H_2SO_4 and 5% $MgSO_4$ solutions were performed in order to investigate the durability of composites.

2. Materials and methods

2.1. Materials

FBC and PCC fly ashes were obtained from two power plants in Thailand and used as alumino-silicate source materials. Bituminous coal was a feedstock of FBC unit, while lignite coal was a feedstock of PCC unit. Combustion temperatures of FBC and PCC units were 850 °C and 1200 °C, respectively. Particle shapes of fly ashes are shown in Fig. 1. FBC fly ash was irregular in shape owing to the low combustion temperature. High combustion temperature of PCC unit led to sintering of ash particle and thus resulted in a spherical shape fly ash. The median particle sizes (D_{50}) of FBC and PCC fly ashes as measured by the particle size analyzer (Malvern Mastersizer S) were 24 μm and 19 μm, respectively. Chemical oxides of PCC and FBC fly ashes were determined by X-ray fluorescence (XRF) spectrometer and shown in Table 1.

FBC fly ash had surprisingly low CaO and SO_3 contents of 8.2% and 2.3% owing to the high efficiency of bituminous FBC boiler. The use of bituminous coal reduced the retention time of fuel in combustion bed for any heat load and resulted in a relatively diluted calcium sulfate and residual lime content [21]. However, high calcium sulfate was detected in FBC fly ash when low grade lignite coal was used [19,20]. The FBC fly ash's loss on ignition (LOI) of 5.7% was substantially higher than 0.8% of PCC fly ash. The remaining residue decomposed at LOI heating temperature of 1000 °C. PCC fly ash had high CaO and Fe_2O_3 contents of 16.4% and 12.0% due to low grade lignite coal feedstock. XRD patterns of fly ashes are shown in Fig. 2. FBC fly ash had high crystalline phase with sharp peaks implying a low reactivity. Broad peak was present in PCC fly ash at 22–38° indicating a higher amount of amorphous phase than that of FBC fly ash. To enhance the reactivity with structural changes and increased surface area of FBC fly ash, grinding was performed on FBC fly ash with a laboratory ball mill for 2 h. A longer grinding time approached the grinding limit and did not significantly increase the fineness [22]. Ground FBC fly ash had a median particle size (D_{50}) of 6 μm.

In addition, sodium hydroxide solution (NaOH) and sodium silicate solution (Na_2SiO_3) with 9% Na_2O and 30% SiO_2 by weight were used as liquid activators. To increase Al and Si ions leachability from FBC fly ash particle and to control the ettringite formation, 15 M NaOH was used [23]. Graded-river sand with specific gravity of 2.65 and fineness modulus of 2.7 was used to prepare the mortar mixes. The 5-cm mortar cubes were used for compressive strength test in accordance with ASTM C109.

2.2. Mix preparation and experimental program

Ground FBC fly ash was replaced with as-received PCC fly ash at the dosages of 0%, 5%, 10%, 20% and 30% by weight. They were thoroughly mixed until uniform blend was obtained. Liquid mixture of 15 M NaOH and Na_2SiO_3 was then poured into the fly ash blend. NaOH helped the leaching of Al^{3+} and Si^{4+} ions from fly ash surface and the subsequent geopolymerization [24]. In addition, Na_2SiO_3 solution was used as the external source of dissolved SiO_2. A high proportion of Na_2SiO_3 in the mixture resulted in stiff paste, rapid setting and excess solid Na_2SiO_3 formation in the hardened-composite. Therefore, the Na_2SiO_3-to-NaOH ratio of 2.0 by weight was used [19,20] and the solid fraction was kept at 0.55 as high liquid content resulted in low strength mixes.

Pan mixer was used to prepare the geopolymeric paste. Mixing was performed for 5 min before paste was cast into 25 mm diameter × 25 mm height plastic cylinder molds. Specimens were vibrated for 10 s and subsequently cured in oven at 65 °C for 48 h. After that, the specimens were demolded and continuously cured at 25 °C in 80% RH chamber until the testing age. Mix proportion of geopolymeric pastes is tabulated in Table 2.

For strength test, 50 cm cube geopolymeric mortars were prepared. Powder and alkali solutions were mixed as described in the mixing of paste. The graded-river sand was then added to the mixture at final step with the sand-to-fly ash blend ratio of 2 (by weight), which 450 g of sand was added in the mixture in case of mortar preparation. Mixing was continued for another minute before casting into 5-cm cubic molds with the aid of vibration. The curing condition was the same as for the paste specimens.

The studies of morphology, microstructure, FTIR functional spectrometry and thermal properties were performed on the geopolymeric pastes at the age of 30 days. The compressive strengths of geopolymeric mortars under normal curing and after immersion in 3% H_2SO_4 and 5% $MgSO_4$ solutions were determined in order to investigate the durability of composites. The compressive strength tests were performed at the ages of 7, 30, 90 and 180 days and the reported results were the averages of three samples.

3. Results and discussion

3.1. Characterization of geopolymeric composites

The results of X-ray diffraction (XRD) pattern of geopolymeric composites are shown in Fig. 3. The XRD of composites showed the increase in broad peak and higher peak area starting from

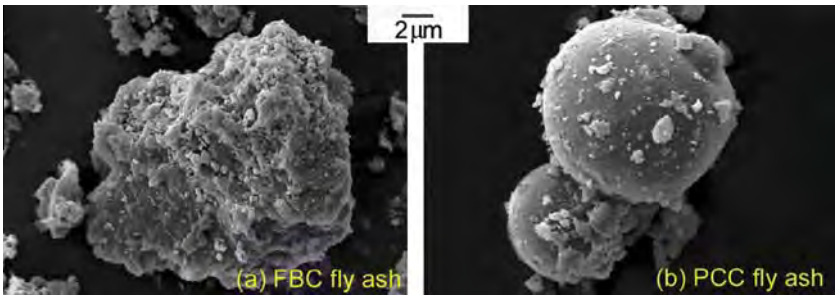


Fig. 1. Particle shape of the as-received fly ashes.

Table 1
Chemical composition and LOI of fly ashes.

Chemical compositions	FBC fly ash (wt%)	PCC fly ash (wt%)
SiO_2	47.1	36.1
Al_2O_3	22.6	25.0
CaO	8.2	16.4
Fe_2O_3	8.9	12.0
SO_3	2.3	3.3
MgO	2.7	2.2
K_2O	1.5	2.6
Na_2O	1.0	1.6
Loss on ignition (LOI)	5.7	0.8

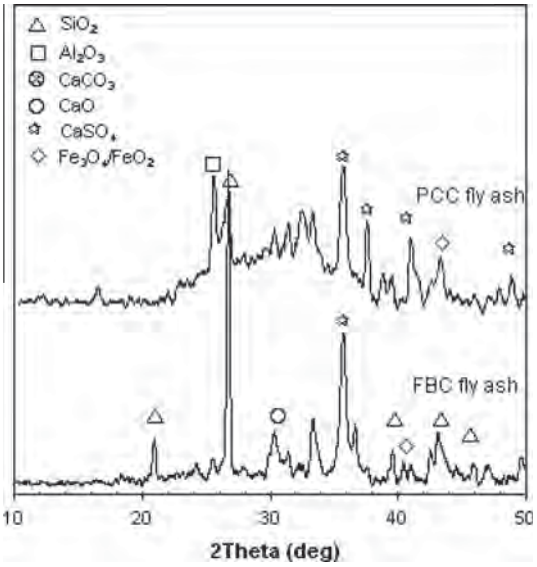


Fig. 2. XRD patterns of fly ashes.

20° to 38° compared with that of FBC fly ash. Broad peak of XRD pattern represented the amorphous phase of composite, and sharp peak was the crystalline phase. Composites consequently appeared as semi-crystalline with the highly disorder silicate glass phase [24]. Heat curing enhanced the geopolymeric reaction resulting in phase conversion with formation of glassy and crystalline phase products. Products consisting of aluminosilicate and calcium silicate hydrate (C—S—H) were also detected. The aluminosilicate compound was from the reaction between the alumina and silica in fly ashes and alkali solutions (i.e. NaOH and sodium silicate solution). In addition, C—S—H was obtained from the reaction between calcium and silicate compounds similar to the hydration reaction of Portland cement. However, unreacted oxide compounds of source material were also detected.

Blending FBC fly ash with PCC fly ash seemed to decrease the sharp peaks at 20° (SiO_2), 30.5° (CaO) and 37° (SiO_2). Increase in PCC fly ash content resulted in more reactive compound in reaction

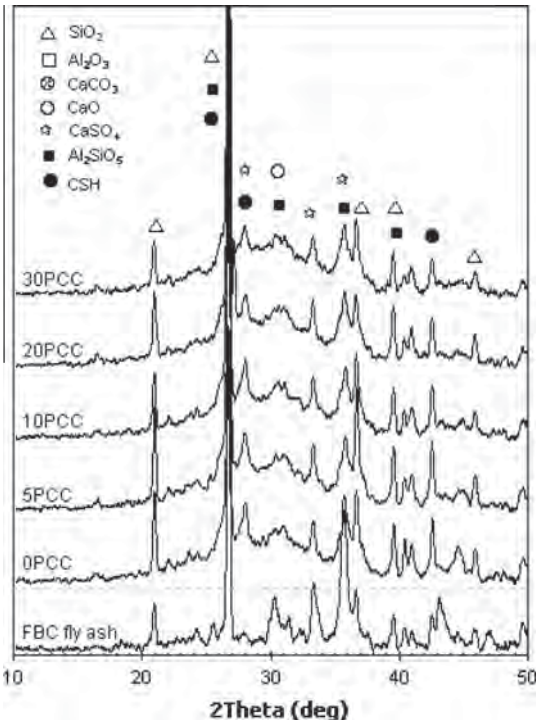


Fig. 3. XRD patterns of composites.

and low peak height of these compounds. As a result, the amorphous phase was increased with the increase in the amount of PCC fly ash.

Microstructural study of composites was conducted by SEM and the results are presented in Fig. 4. Ground FBC fly ash geopolymeric composite (sample 0PCC) showed the matrix with partially reacted-ash particles. Cracks and voids were easily observed throughout the matrix leading to the low physical properties of composite. Addition of PCC fly ash led to a dense and continuous matrix owing to the high glassy phase of fly ash. The high content of PCC fly ash resulted in the dense matrix compared with solitary FBC fly ash composite (0PCC). PCC fly ash was used to increase the reactivity and to develop the properties of geopolymeric matrix. Generally, fly ash consisted of glassy phase at the surface of the particles and crystalline phase in the interior [25]. This glassy phase played an important role in geopolymeric reaction and was easily leached out by alkali solutions to form the silica and alumina chain [24]. In the presence of alkali, alumina and silica in the source materials were leached out and resulted in aluminate ($Al(OH)_4^-$) and silicate (SiO_3^{2-}) species and consequent aluminosilicate formation. With high calcium in the source material, additional C—S—H was formed. Cracks were also seen due to the use of heat curing to accelerate the geopolymeric reaction and the evaporation of bound water in the alkali solution.

Table 2
Mix proportion of geopolymeric pastes.

Samples	Blended powder (g)		15 M NaOH (ml)	Na_2SiO_3 (ml)	Solid fraction
	FBC fly ash	PCC fly ash			
0PCC	225	0	61	123	0.55
5PCC	214	11	61	123	0.55
10PCC	202	23	61	123	0.55
20PCC	180	45	61	123	0.55
30PCC	157	68	61	123	0.55

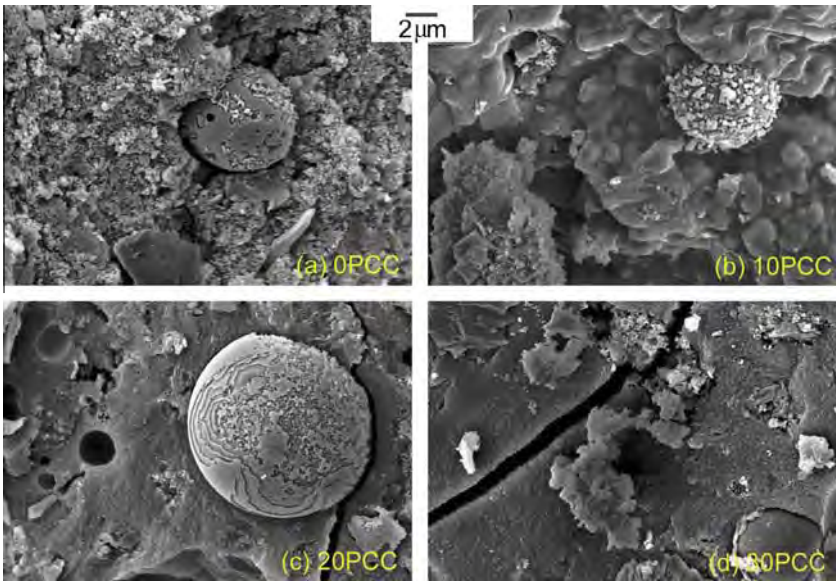


Fig. 4. Microstructure of composites.

Characterization of functional groups in geopolymeric composites was performed by Fourier Transform Infrared Spectroscopy (FTIR) at wavenumber between 3000 and 400 cm^{-1}. The results of spectrum bands are shown in Fig. 5. The vibration at a specific configuration of chemical bonding was related to the absorption band. Si—O and Al—O bonds were prominent in aluminosilicate geopolymer system. Spectrum of fly ashes and composites consisted of broad bands at 3450 cm^{-1} and 1600 cm^{-1} assigning to O—H stretching and O—H bending, respectively and C=O band (in CO_3^{2-} compound) at ~1460 cm^{-1} [26,27]. C=O band occurred in all fly ashes and composites due to the carbonation between alkaline solution (or moisture, in case of fly ash) and CO_2 in the environment. Si—O bending mode was observed near 460 cm^{-1}. The weak band at 575 cm^{-1} indicated Al—O stretching vibration. Si—O—Al and Si—O—Si stretching modes were recognized at the wavenumber range of 1100–1000 cm^{-1} assigning to the anti-symmetric stretching vibrations of the Si—O—Si in amorphous silica and Si—O—Al networks. Si—O—Al stretching mode was more noticeable than Si—O—Si bending mode. Si—O—Al stretching mode was therefore logically assigned to indicate the degree of geopolymerization [24,26,28].

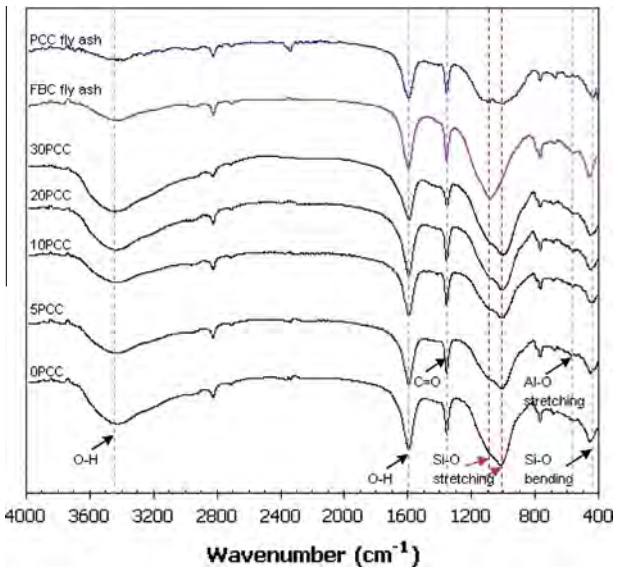


Fig. 5. FT-IR spectra of fly ashes and composites.

Addition of PCC fly ash in the composites resulted in a broader peak of Si—O stretching vibration at 1100–1000 cm^{-1} than that of the solitary FBC fly ash composite. This band was also found at 1100 cm^{-1} in FBC fly ash and shifted towards lower wavenumber of 1000 cm^{-1} as a result of a decrease in the average Si—O bond angle and increase in number of tetrahedral aluminum atoms [28]. This doublet peak probably resulted from asymmetry in the tetrahedral sites due to Al substitution [29] and indicated the —OH deformation for Al—OH leading to the possible assignment of a new type of Al—O bonds in the composite [30]. Shift of wavenumber also highlighted the structural disorder of the composite, breaking of interatomic bonds and formation of complex molecular units with strong bonding in composite. This implied that Si—O bond of SiO_2 in fly ashes was converted to new Si—O bond in composites.

Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were used to characterize the thermal property of composites by measuring the weight change of a sample as a function of temperature in a precisely controlled atmosphere. DTG presented the decomposition temperature of specific volatile components in composites. TGA/DTG curves of samples are shown in Fig. 6. FBC fly ash showed the weight change at 100, 400, 650 and 700 °C due to the moisture evaporation, and decompositions of $Ca(OH)_2$, CaO and $CaCO_3$, respectively. Weight loss of FBC fly ash was approximately 7% corresponding to its loss on ignition (LOI). The DTG curves of the composites displayed the same decomposition temperatures of compounds and therefore only one overlapped DTG curve (sample 0PCC) was presented. The weight losses of composites were higher than that of FBC fly ash since the composites consisted of alkali solutions and the free water remained in the geopolymer pore system. Weight changes of composites were detected at 100 and 600 °C implying the evaporation of bound water used in alkali solutions and decomposition of CaO. The peak of $Ca(OH)_2$ at 400 °C disappeared in the geopolymeric composites due to the conversion of $Ca(OH)_2$ to C—S—H or more stable calcium compounds. Addition of up to 10% PCC fly ash into composites resulted in low weight loss and the reaction was enhanced due to the high glassy phase of source material. This resulted in strong composites with good heat resistance and ther-

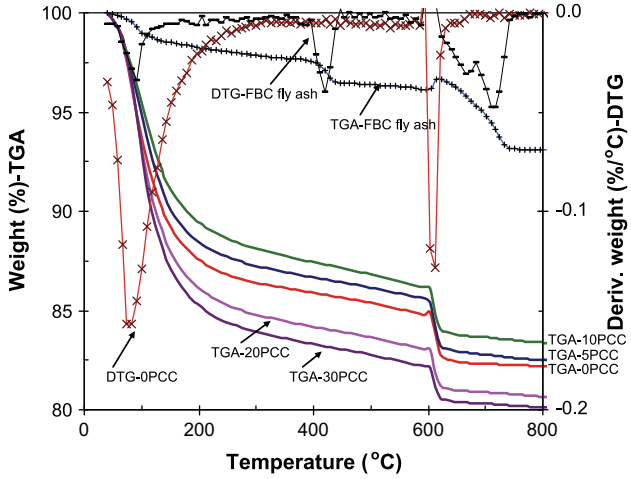


Fig. 6. TGA/DTG curves of fly ashes and composites.

mal stability at high temperature. However, the use of more than 10% PCC fly ash content resulted in the adverse effect on the weight loss of composites. The PCC fly ash contained high calcium content which decomposed during the TGA test. The remaining weights were 83% for the solitary FBC fly ash mix and 80% for the 30%PPCC mix. However, these remaining weights were significantly higher than OPC pastes with W/C ratios of 0.30–0.33 which was about 65% [31,32]. The result implied that geopolymeric composite had good heat resistance and thermal stability.

3.2. Chemical resistance

Chemical resistance of composites was presented as compressive strength of composite normally cured at 25 °C comparing with those immersed in 3% H_2SO_4 solution and in 5% $MgSO_4$ solution. Fig. 7 shows the compressive strength of composites cured at 25 °C. The control or FBC fly ash composite (0PCC) gave low strength of 10.0 MPa at the age of 180 days. FBC fly ash with high crystalline phase content was not reactive and thus the leaching out of Si and Al ions by alkali solutions was more difficult. Crystalline phases required high energy or temperature to break the strong bonding and orderly structure. Addition of PCC fly ash in the composites gave higher strengths of 11.0, 12.0, 12.5 and 18.0 MPa for composites with PCC fly ash contents of 5%, 10%, 20% and 30%, respectively. The glassy phases in PCC fly ash were conducive to the leaching of Si and Al ions to geopolymeric system and resulted in continuous aluminosilicate matrix as shown in the SEM images. This affected the strength of composites. The strength increased with age especially with PCC fly ash contained-composites since PCC fly ash had high calcium content. These calcium compounds reacted with alkali solutions resulted in $Ca(OH)_2$ compound. $Ca(OH)_2$ continued to react with silicon ions and formed C—S—H which contributed the strength of composites as curing continued. The reaction was similar to the hydration reaction of Portland cement. Compressive strength at 180 days of 24.0 MPa was achieved for 30PCC mix.

The results of strengths of composites after immersion in 3% H_2SO_4 and 5% $MgSO_4$ solutions are shown in Fig. 8. 3% H_2SO_4 was the acid solution and 5% $MgSO_4$ was salt solution representing the sewage water and saline soil environment. At 90 days, the immersion of composites in acid resulted in slightly higher compressive strengths than those of normal curing. However, 20–30% reductions in strengths after 180 immersion days for PCC fly ash content up to 20% compared with those of normal curing were obtained. With 30% content of PCC fly ash provided higher strength loss than all samples owing to the high content of calcium in composite. Calcium was easily dissolved in strong acid remaining the pores and cracks as shown in Eq. (1) [33].

$$Ca(OH)_2\ (s) + H_2SO_4\ (aq) \rightarrow CaSO_4 \cdot 2H_2O\ (s) \quad (1)$$

In addition, C—S—H also reacted with H_2SO_4 forming amorphous silica gel and calcium sulfate (Eq. (2)) which adversely affected the strength of composites [34].

$$3CaO \cdot SiO_2\ (s) + 3H_2SO_4\ (aq) + 3H_2O\ (l) \rightarrow 3CaSO_4 \cdot 2H_2O\ (s) + SiO_2\ (s) \quad (2)$$

Moreover, hydrogen ions (H^+) from H_2SO_4 ionization penalized the alumino-silicate network in composites at aluminum sites (—Al—O—Si—O—). The breaking of oxy-aluminum bridge (—Al—O—Si—O) weakened the composite in acid condition [35].

In case of 5 wt% $MgSO_4$ condition, the compressive strength of composites decreased more than those in acid solution. Low strength was observed for longer immersion time. With 30% content of PCC fly ash, the strength was not adversely affected. The deposit of white substance on the surface of composites was observed as shown in Fig. 9. XRD pattern indicated the occurrence of magnesium hydroxide ($Mg(OH)_2$), calcium sulfate ($CaSO_4$) and sodium sulfate (Na_2SO_4) for FBC fly ash composite (0PCC). The composite with 30% PCC fly ash (30PCC) gave many sharp peaks including the peaks of silica (SiO_2) and calcium silicate ($CaSiO_3$). The white powders were $Mg(OH)_2$ and $CaSO_4$ deposits obtained

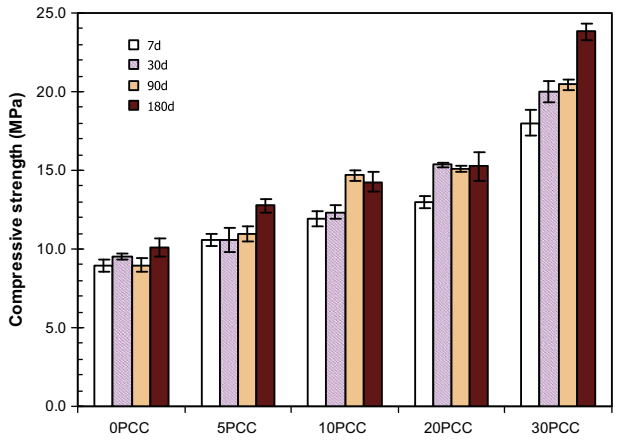


Fig. 7. Compressive strength of composites cured at 25 °C.

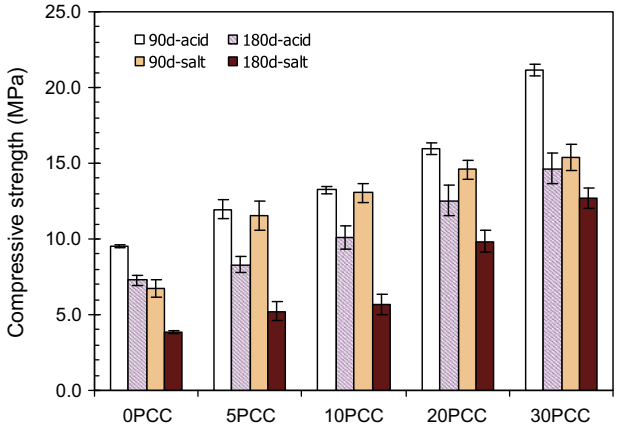


Fig. 8. Compressive strength of composites after immersion in 3% H_2SO_4 and 5% $MgSO_4$ solutions.

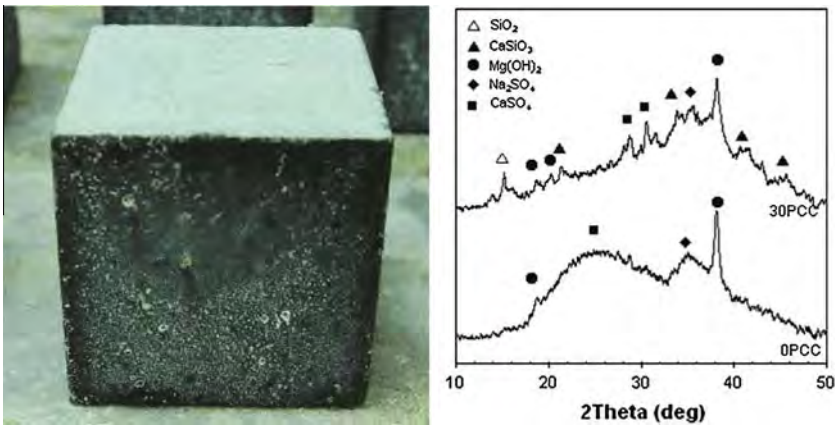


Fig. 9. White substance on composite surface and XRD pattern.

from the reaction between Mg^{2+}, SO_4^{2-} ion and hydroxyl ion (OH^-) from $Ca(OH)_2$ as shown in Eq. (3) [34].

$$Mg^{2+}\ (aq) + SO_4^{2-}\ (aq) + Ca(OH)_2\ (s) + H_2O\ (l) \rightarrow Mg(OH)_2\ (s) + CaSO_4 \cdot 2H_2O \quad (3)$$

C—S—H phase in FBC/PCC fly ash composites was attacked quite rapidly by $MgSO_4$ leading to the strength loss and forming of silica gel as detected in sample 30PCC. The equation is described as follows [34]:

$$3Mg^{2+}\ (aq) + 3SO_4^{2-}\ (aq) + 3CaO \cdot SiO_2\ (s) + 9H_2O\ (l) \rightarrow 3Mg(OH)_2\ (s) + 3[CaSO_4 \cdot 2H_2O]\ (s) + SiO_2\ (s) \quad (4)$$

The deterioration of composite in $MgSO_4$ solution seemed to be more severe than in H_2SO_4 solution. SO_4^{2-} ion was strongly absorbed on the alminosilicate composite due to the strong interaction between the ion and aluminol site (Al—OH) on the composite surface. This interaction led to high void ratio in the composite and resulted in low compressive strength [36].

4. Conclusions

The properties of FBC fly ash based-geopolymeric composite were enhanced by grinding of FBC fly ash and addition of high calcium PCC fly ash. The PCC fly ash had high glassy phase content and Si and Al ions were easily leached out by alkali solutions forming the linking network in geopolymeric composites. This resulted in dense and strong matrix. With high calcium PCC fly ash, additional C—S—H was formed and the strength of composites continued to develop with time. In addition, IR result showed that the Si—O bond shifted from 1100 cm^{-1} towards lower wavenumber of 1000 cm^{-1} implying the structural disorder, breaking of interatomic bonds and formation of molecular units with strong bonding of composite. This was supported by the DTG curve which showed the disappearance of $Ca(OH)_2$ peak at 400 °C in composites indicating the conversion of $Ca(OH)_2$ to C—S—H or more stable calcium compounds. The incorporation of PCC fly ash also improved the resistance of PCC/FBC fly ash composites to acid and salt attacks. However, the resistant properties were affected with the high calcium content and long period of immersion. FBC/PCC fly ash geopolymer can be used as alternative binding material with acceptable strength, durability and thermal properties.

Acknowledgements

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Improved Dielectric and Nonlinear Electrical Properties of Fine-Grained $CaCu_3Ti_4O_{12}$ Ceramics Prepared by a Glycine-Nitrate Process

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Pure $CaCu_3Ti_4O_{12}$ was successfully prepared by a glycine-nitrate process using a relatively low calcination temperature and short reaction time of 760°C for 4 h. Fine-grained $CaCu_3Ti_4O_{12}$ ceramics with dense microstructure and small grain size were obtained after sintering for 1 h. The nonlinear coefficient of a fine-grained $CaCu_3Ti_4O_{12}$ ceramic calculated in the range 1–10 mA/cm^2 was found to be very high of ~16.39 with high breakdown electric field strength of 1.46×10^4 V/cm. This fine-grained $CaCu_3Ti_4O_{12}$ ceramic also exhibited a very low loss tangent of 0.017 at 20°C with temperature stability over the range −55°C to 85°C. The grain growth rate of the $CaCu_3Ti_4O_{12}$ ceramics was found to be very fast after increasing the sintering time from 1.5 to 3 h, leading to formation of a coarse-grained $CaCu_3Ti_4O_{12}$ ceramic with grain size of about 100–200 μm. The dielectric permittivity of this coarse-grained ceramic was found to be as high as 1.03×10^5 with a low loss tangent of 0.054.

I. Introduction

Since the extremely high dielectric response (sometimes called the colossal dielectric response) of $CaCu_3Ti_4O_{12}$ (CCTO) was first discovered by Subramanian *et al.*,[1] CCTO polycrystalline ceramics have attracted considerable attention for two reasons. The first is due to the progressive development of small-sized multilayer ceramic capacitors. These devices require a dielectric material that can exhibit a very high dielectric permittivity (ε′) and temperature stability of ε′ as well as a low loss tangent (tanδ).[2] This type of capacitor can be miniaturized using a material with the so-called "giant" or "colossal" dielectric material, replacing materials used in recent years. It was also found that the current density-electric field strength (*J-E*) characteristic is nonlinear,[3] resulting from the formation of Schottky barriers at the grain boundaries (GBs) sandwiched between semiconducting grains. Such electrical behavior can potentially be used to develop CCTO polycrystalline ceramics in varistor applications if the nonlinear coefficient (α) and electric field breakdown strength (E_b) can be tuned to acceptable values.[4] The second reason is scientific elucidation. The origin of the giant dielectric response in CCTO ceramics is not yet clear. Many investigations have been performed to describe the exact giant dielectric response in CCTO ceramics. These were accompanied by the development of many models.[5–10] The internal barrier layer capacitor (IBLC) model of Schottky barriers at GBs is one of the most important models describing the giant dielectric response in CCTO polycrystalline ceramics. The IBLC model is based on the different electrical responses of grains and GBs investigated by using impedance spectroscopy and scanning Kelvin microprobe analysis.[3,5] It clearly shows that the microstructure of CCTO ceramics consists of an insulating component at the GBs and semiconducting component inside grains. The model predicts that dielectric and related electrical properties of CCTO ceramics can be modified by tuning their microstructure.

To study CCTO ceramics for use application in electronic devices, selection of the preparation method is one of the most important decisions, which largely determines the final bulk properties of CCTO ceramics. $CaCO_3$, CuO, and TiO_2 are usually selected as the starting raw materials to synthesize CCTO powder used to form a green body before sintering. This process is called the solid-state reaction (SSR) method. There are many disadvantages of the SSR fabrication method. The SSR method requires high temperatures and long reaction times to produce a pure CCTO phase. To best of our knowledge, to form a pure CCTO phase, CCTO powder prepared by the SSR method must be calcined at temperatures higher than 850°C using reaction times of more than 6 h.[11] Practically, sintered CCTO ceramics with fine-grained microstructure and with no pores are difficult to produce. Sintered CCTO ceramics prepared by the SSR method usually have microstructure with abnormal grain growth due to their high sintering temperatures and long sintering times.[12,13] Alternatively, CCTO ceramics with small grain size (<5 μm) may be obtained if the sintering temperature and sintering time are reduced. However, a large number of pores are usually formed in the resulting microstructure,[14] which is undesirable for all electronic device applications.

Syntheses of ceramic powder from chemical solutions offer the possibility of closer stoichiometric control compared to the SSR method. Low-temperature chemical reactions with short reaction times are usually sufficient used to produce a pure phase.[15,16] Recently, there have been many studies investigating preparation of CCTO ceramics by chemical methods.[15–27] Unfortunately, impurities such as CuO, $CaTiO_3$, and TiO_2 are usually residual in the resulting CCTO powders.[18–20,23,24,26,27] Although the impurities disappeared

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in final products due to high sintering temperatures, the residual impurities leave microstructural imperfections. These appear as pores and abnormal grain growth. Only some chemical methods can effectively produce a pure CCTO phase powder by calcination at temperature lowers than 800°C with short reaction times. These methods are pyrolysis of organic solutions,[15] combustion method using ammonia as a fuel,[16] ethylenediaminetetraacetic acid (EDTA) precursor,[25] and oxalate coprecipitation methods.[22] A pure CCTO phase was obtained by these methods and calcined at 700°C for 2 h, 800°C for 0.5 h, 800°C for 3 h, and 700°C for 1 h, respectively. Although there have been reports of successful chemical preparation of CCTO at relatively low temperatures and short reaction times, it is useful to develop new methods to increase the number of design options and to support a variety of applications in the future. Therefore, a new wet chemical solution route to prepare CCTO is worthy of study.

Among of these four primary methods as mentioned above, the combustion method using ammonia as a fuel[16] and EDTA route[25] are classified as the combustion process. Organic compounds like glycine, urea, citric acid, and EDTA have been widely used as fuels for gel combustion.[28] The glycine-nitrate process (GNP) is one of the most attractive methods. The GNP method was firstly reported by Chick *et al.*,[29] which can be used effectively to prepare homogeneous nanoparticles of ceramic powders by a self-ignited combustion process using glycine and metal nitrates. In this process, the amine ($-NH_2$) and carboxyl (–COO) groups can make complexes with metal ions, thus preventing the metal nitrates from segregating before the combustion reaction occurs.[29,30] The GNP process has the advantages of relatively low-cost, high-energy efficiency, fast heating rates, short reaction times, and high composition homogeneity.[31,32]

In this work, GNP was used to prepare CCTO ceramics. Pure phase of CCTO powder was successfully prepared using a relatively low calcination temperature and short reaction time. A fine-grained CCTO ceramic microstructure with good dielectric and nonlinear electrical properties was obtained.

II. Experimental Procedure

In this work, $Ca(NO_3)_2{\cdot}4H_2O$ (99%, Sigma-Aldrich, St. Louis, MO), $Cu(NO_3)_2{\cdot}4H_2O$ (99.5%, Carlo Erba, Strada Rivoltana, Italy), $C_{16}H_{28}O_6Ti$ (75 wt% in isopropanol, Sigma-Aldrich), deionized water, citric acid, and glycine were used as the starting raw materials. First, 1.2312 g of $Ca(NO_3)_2{\cdot}4H_2O$ and 3.7789 g of $Cu(NO_3)_2{\cdot}4H_2O$ were dissolved in 80 mL of aqueous solution of citric acid (2.5 wt%) with constant stirring at room temperature. Then, 10 mL of $C_{16}H_{28}O_6Ti$ solution was added into the metal ion solution above under constant stirring until a clear and transparent solution was obtained. Next, 1.0 g of glycine powder was added into the mixed solution with stirring at 150°C until a viscous gel was obtained. Finally, the gel was dried at 350°C for 30 min. Combustion was observed when the temperature was 200°C. The resulting dried porous precursors were ground and calcined at 700°C–760°C for 4 h. It was found that the CCTO powder calcined at 760°C for 4 h exhibited a CCTO phase with no impurities. A very small amount of CuO secondary phase was observed in the CCTO powders calcined at 720°C and 740°C for 4 h. The pure CCTO powder (calcined at 760°C) was selected for further investigation. The powder was pressed into pellets having dimensions of 9.5 mm in diameter and ~1–2 mm in thickness by uniaxial compression at 200 MPa. Finally, these pellets were sintered in air under various conditions. CCTO ceramics sintered at 1050°C for 0.5, 1.0, 1.5, and 3.0 h are referenced as the CCTO50-0.5h, CCTO50-1h, CCTO50-1.5h, and CCTO50-3h samples, respectively. CCTO ceramics sintered at 1035°C, 1050°C, 1065°C, and 1080°C for 1 h are referred to as the CCTO35-1h, CCTO50-1h, CCTO65-1h, and CCTO80-1h samples, respectively.

XRD (PW3040 Philips; Eindhoven, the Netherlands) and scanning electron microscopy LEO 1450VP; Cambridge, UK) techniques were used to characterize the phase compositions and surface morphologies of the sintered CCTO ceramics, respectively. Particle size and shape of the CCTO powders prepared by using various temperatures were revealed using transmission electron microscopy (TEM; FEI Tecnai G^2, Eindhoven, the Netherlands). Each pellet face was polished and sputtered with Au at a current of 25 mA for 8 min using a Polaron SC500 sputter coating unit. The dielectric measurement was performed by using an Agilent (Hayward, CA) 4294A Precision Impedance Analyzer over the frequency range from 10^2 to 10^7 Hz using an oscillation voltage of 500 mV. The dielectric properties were measured over the temperature range from −70°C to 220°C with step increases of 10°C. Each temperature step was held with an accuracy of ±1°C. Current-voltage measurements were done at room temperature using a high-voltage measurement unit (Keithley Model 247, Estado St Pasadena, CA). The breakdown electric field (E_b) was obtained at the current density of 1 mA/cm^2. The nonlinear coefficient (α) was calculated over the range 1–10 mA/cm^2 as the following:

$$\alpha = \frac{\log(J_2/J_1)}{\log(E_2/E_1)} \quad (1)$$

where E_1 and E_2 are the electric fields corresponding to J_1 = 1 and J_2 = 10 mA/cm^2, respectively.

III. Results and Discussion

Figure 1(a) shows the XRD patterns of CCTO powders calcined at different temperatures for 4 h. The main XRD peaks corresponding to CCTO crystal structure were observed in the samples that were calcined at 720°C, 740°C, and 760°C. It is likely that pure CCTO phase with no impurities can be achieved by calcination at a very low temperature and short reaction time, that is, 720°C for 4 h. However, as shown in Fig. 1(b), careful inspection revealed that a very small amount of CuO secondary phase was present as shown in the XRD patterns of the CCTO powders calcined at 720°C and 740°C. Pure phase of CCTO powder was obtained at 760°C for 4 h. It is worth noting that a GNP effectively produced a pure CCTO phase powder using a low temperature and short reaction time. Figure 2 shows the TEM images of CCTO powders calcined at different temperatures for 4 h. Particle sizes of CCTO powders prepared by a GNP were in the range 100–200 nm. The particles size tended to increase as the calcining temperature was increased.

Figures 3 and 4 show the XRD patterns of CCTO ceramics sintered under different conditions. The XRD results revealed that all of the sintered CCTO ceramic samples were pure phase just as their powder. Sintering time and temperature

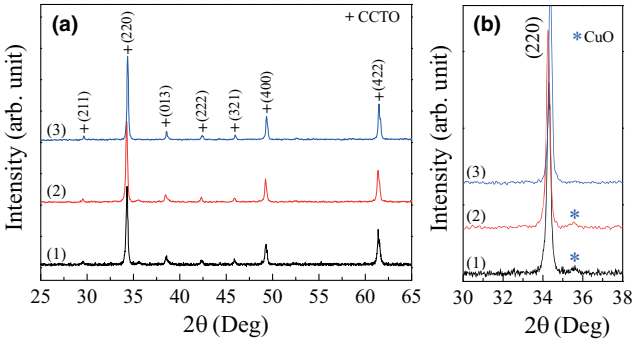


Fig. 1. XRD patterns of CCTO powders calcined at (1) 720, (2) 740, and (3) 760°C for 4 h. (a) and (b) represent the XRD patterns in a wide range scale of 2θ (25°–65°) and narrow range scale 2θ (30°–38°), respectively, revealing the existence a second CuO phase.

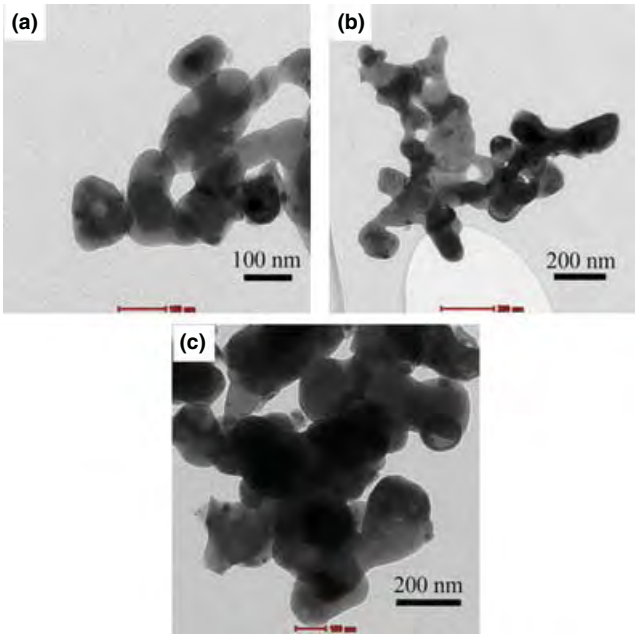


Fig. 2. Transmission electron microscopy images of CCTO powders calcined at (a) 720, (b) 740, and (c) 760°C for 4 h.

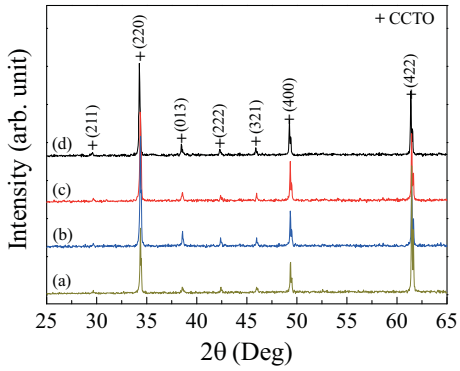


Fig. 3. XRD patterns of CCTO ceramics sintered at (a) 1035°C, (b) 1050°C, (c) 1065°C, and (d) 1080°C for 1 h.

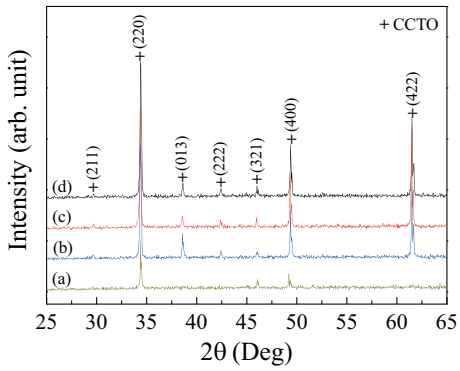


Fig. 4. XRD patterns of CCTO ceramics sintered at 1050°C for (a) 3.0 h, (b) 1.5 h, (c) 1.0 h, and (d) 0.5 h.

had no an effect on the phase formation of the CCTO ceramics in this study. This is due to the fact that CuO start to decompose at the sintering temperature of about 1100°C.[33]

Figure 5 shows the surface morphologies of the CCTO ceramics sintered in air for 1 h at various temperatures from 1035°C to 1080°C. All the samples had a fine-grained ceramic microstructure with grain sizes of about 2–4 μm. However, porosity in the form of large pores in the microstructure was still observed in the CCTO35-1h sample. Usually, a fine-grained CCTO microstructure with no pores is difficult to fabricate even when sintering at a low temperatures and/or using short reaction times. CCTO ceramic products with small grain sizes sintered at low temperatures and/or using short reaction times usually have residual pores in their microstructure.[14] In contrast, using high temperatures and/or long reaction times results in abnormal grain growth due to a liquid phase sintering mechanism that normally occurs in CCTO ceramics.[13] This is undesirable for many applications. Generally, residual impurities in ceramic powders used to prepare bulk sintered ceramics are a negative factor. They promote formation of large pores or results in a region of uncontrolled grain growth even when the ceramic was prepared from fine ceramic nanoparticles.[32] To overcome this problem, the use of high purity CCTO powder and proper powder compaction when forming the green body are good solutions. These can lead to fine-grained CCTO microstructure with no large pores in their microstructure. Therefore, high purity CCTO and fine nanoparticles used to form a green body may be important factors that contributed to the observed fine-grained ceramic microstructure of the CCTO50-1h, CCTO65-1h, and CCTO80-1h samples.

Figure 6 demonstrates the influence of sintering time on the microstructure of CCTO ceramics. It was found that grain growth rate in CCTO was very low when the ceramics were sintered at 1050°C for 0.5–1.0 h. The overall microstructures of the CCTO50-0.5h and CCTO50-1h samples are very similar. When sintering time was increased to 1.5 h, abnormal grain growth was observed. Some grains grew rapidly to very large sizes of about 100 μm within a fine-grained matrix having grain sizes of about 2–4 μm. The rapid grain growth observed in the CCTO ceramic sintered for 3 h is shown in Fig. 6(d). Grain sizes of the CCTO50-3h are about 100–200 μm, which is higher than those of the other three samples by a factor of 50. Pores are still observed in the grains of CCTO50-3h sample, which is indicative of abnormal grain growth.[32] The large grain size of the CCTO50-3h sample can be comparable to those of CCTO ceramics prepared by SSR methods sintered at relatively high temperatures and/or very long sintering times.[3,5,7,12,13] Comparing the grain growth rate of CCTO ceramics, it can be seen that grains of the CCTO50-3h sample grew faster than those of the samples prepared by an SSR method.

The fine-grained microstructure of CCTO ceramics shown in Figs. 5 and 6 was expected to have improved dielectric and nonlinear electrical properties. This is because CCTO polycrystalline ceramics are electrically heterogeneous, consisting of semiconducting grains enclosed by an insulating GB layer.[3,5] Thus, both the geometric and intrinsic properties of the GBs of CCTO ceramics are key factors determining their overall properties. Using the geometric approach, dielectric properties (especially tanδ) and the nonlinear electrical properties of CCTO prepared by a GNP should be significantly improved. The increase in the GB density due to the reduction in grain size can cause an increase in E_b and enhancement of the total resistance of GBs, leading to the reduction in tanδ in CCTO ceramics. The effect of the GB density (or the mean grain size) on the nonlinear electrical properties was also observed in commercial ZnO varistors.[4] Figure 7 shows the nonlinear electrical characteristics of all the ceramic samples. The E_b and α values of all the samples are summarized in Table I. The effect of geometric properties of the microstructure on the nonlinear properties of CCTO ceramics is clearly seen in Fig. 7(a). The CCTO50-0.5h and CCTO50-1h ceramic samples have closed grain size; therefore, these two ceramics have closed E_b. Comparing the microstructure of CCTO50-0.5h (or CCTO50-1h) sample to that of the CCTO50-3h sample, E_b strongly decreased by a factor of about 75 as the grain size increased from 2–5 μm to

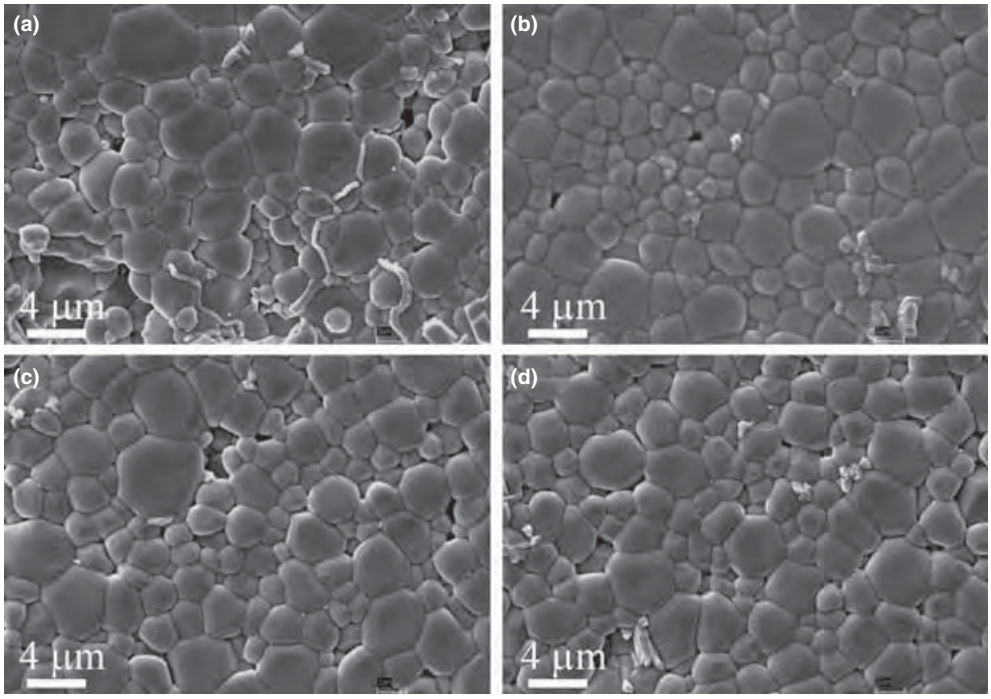


Fig. 5. Scanning electron microscopy images of polished surface morphologies of CCTO ceramics sintered at 1035°C, (b) 1050°C, (c) 1065°C, and (d) 1080°C for 1 h.

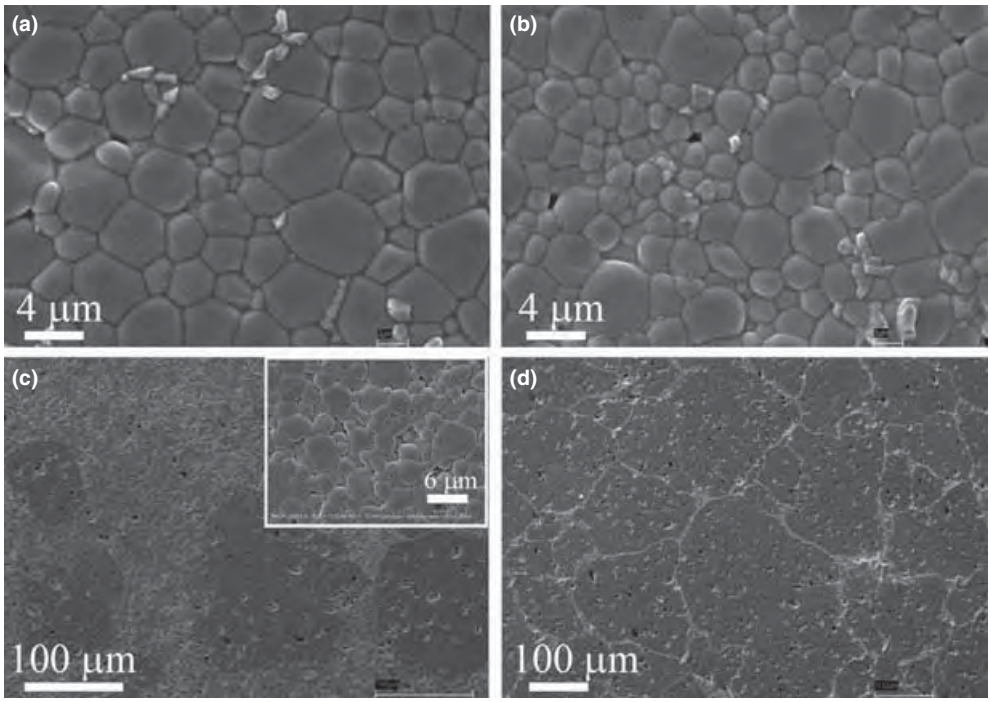


Fig. 6. Scanning electron microscopy images of polished surface morphologies of CCTO ceramics sintered at 1050°C for (a) 0.5 h, (b) 1.0 h, (c) 1.5 h, and (d) 3.0 h; the inset of (c) shows a high magnification image, revealing a fine-grained region.

100–200 μm. These results are consistent with the geometric approach if some GBs are considered to be electrically inactive boundaries. Furthermore, a strong decrease in E_b of the CCTO50-1.5h sample compared with that of the CCTO50-0.5h and CCTO50-1h samples was also observed. This result is attributed to detour of electric charge current within the ceramic arising as the current avoids the fine-grained regions. This is due to the impedance related to the high density of GBs in such regions.[34] More electric charge current can pass through the large-grain regions leading to a large drop in E_b. Furthermore, with fewer large grains in its microstructure, α of CCTO50-1.5h decreased by a factor of $\approx$2. This is attributed from the detour of the current, which can cause a drop in the voltage across an insulating interface (GBs) between fine grains. The CCTO50-1h ceramic sample exhibited the best nonlinear properties among all the samples with $\alpha = 16.39$ and $E_b = 14.6$ kV/cm. To our best knowledge, this α value is the highest value for undoped CCTO ceramics yet reported in the literature. This value is comparable to the value of $\alpha \approx 17$ (calculated over the range of 1–10 mA/cm^2) for the Sn-doped CCTO ($CaCu_3Ti_{3.8}Sn_{0.2}O_{12}$) ceramic.[35] However, α of the CCTO50-1h sample is lower than that of the Tb-doped CCTO ($Ca_{0.775}Tb_{0.15}Cu_3Ti_4O_{12}$) ceramic for which $\alpha = 29.67$.[36]

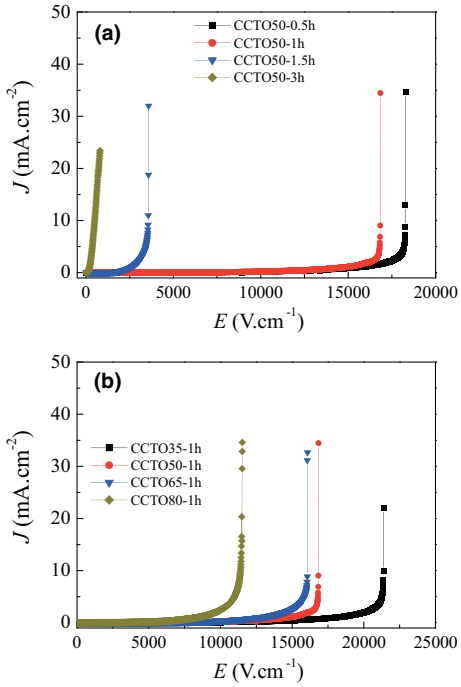


Fig. 7. *J-E* characteristics of (a) CCTO ceramics sintered at 1050°C for different times and (b) CCTO ceramics sintered at various temperatures for 1.0 h.

Table I. Dielectric Properties (ε′ and tanδ) at 1 kHz and 20°C and Nonlinear Electrical Properties (α and E_b) Measured at Room Temperature

CCTO sample	ε′	tanδ	α	E_b (V/cm^2)
CCTO35-1h	2932	0.019	13.24	17 991
CCTO50-1h	3045	0.017	16.39	14 640
CCTO65-1h	2645	0.024	9.71	12 685
CCTO80-1h	4108	0.017	7.45	8384
CCTO50-0.5h	2893	0.017	13.68	15 452
CCTO50-1.5h	4835	0.021	6.77	2539
CCTO50-3h	103 873	0.054	2.54	206

According to the results shown in Fig. 7(a), the geometric properties of the microstructure clearly show a strong effect on the nonlinear electrical properties of CCTO ceramics. Another factor that has an influence on the nonlinear properties of CCTO ceramics is the intrinsic properties of the GBs. Figure 7(b) shows *J-E* curves of CCTO ceramics sintered for 1 h at different temperatures as means control the fine-grain microstructure. E_b of the CCTO ceramics decreased significantly as the sintering temperature was increased even through their microstructures had very similar morphologies. This means that the intrinsic properties of GBs have an effect on the nonlinear properties of CCTO ceramics. In the traditional metal oxide non-Ohmic-based systems,[37] nonlinear electrical properties are related to oxygen enrichment at the GBs. Therefore, the decrease in E_b among these samples may have resulted from enhancement of oxygen vacancy concentration as the sintering temperature was increased. It was reported that E_b could be enhanced by annealing CCTO ceramics in O_2 atmosphere[38] or sintering in an O_2 atmosphere.[39] α values of the CCTO35-1h, CCTO50-1h, CCTO65-1h, and CCTO80-1h samples are of about 13.24, 16.39, 9.71, and 7.45, respectively.

Figures 8 and 9 demonstrate the frequency dependence of ε′ at 20°C of CCTO ceramics prepared by a GNP using different sintering conditions. Their insets show tanδ as a function of frequency at 20°C. The values of ε′ and tanδ at 20°C

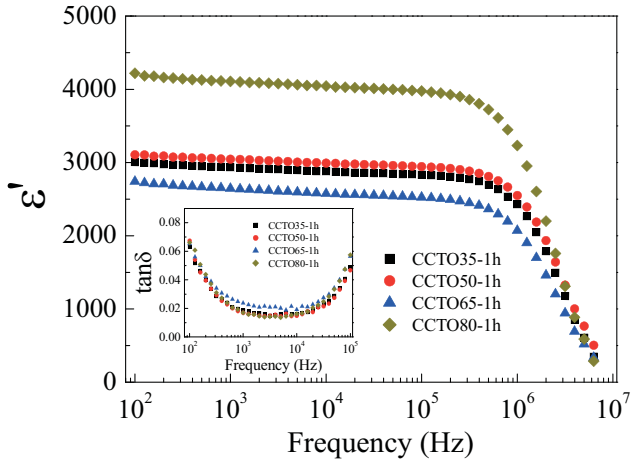


Fig. 8. ε′ as a function of frequency measured at 20°C of CCTO ceramics sintered at different temperatures for 1.0 h. The inset shows the frequency dependence of tanδ at 20°C.

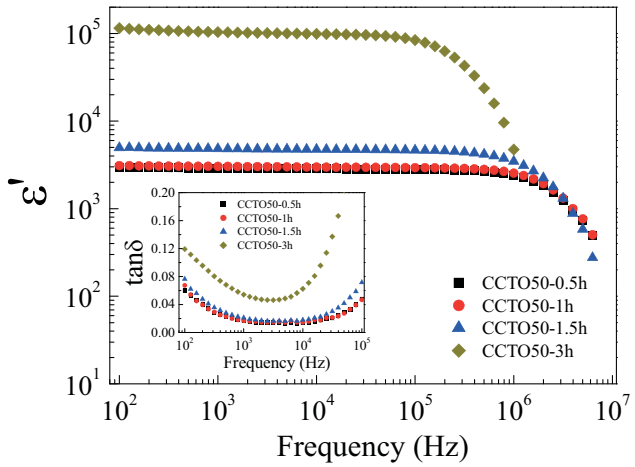


Fig. 9. ε′ as a function of frequency measured at 20°C of CCTO ceramics sintered at 1050°C for 0.5 h, 1.0 h, 1.5 h, and 3.0 h. The inset shows the frequency dependence of tanδ at 20°C.

and 1 kHz of all samples are summarized in Table I. ε′ values of the fine-grained ceramic microstructure were in the range 2893–4108. For these samples, tanδ values were very low, less than 0.024 at 1 kHz. These are acceptable values for ceramic capacitor applications. These values of ε′ and tanδ can be comparable to those observed in a CCTO/CTO composite system.[40] The CCTO50-3h sample with coarse-grained ceramic microstructure exhibited a very high ε′ of about 103,873; whereas, tanδ is still too low, 0.054 at 20°C and 1 kHz. As seen in Figs. 8 and 9, ε′ values for all the fine-grained CCTO ceramics are nearly independent of frequency over the range of 10^2–10^6 Hz. Furthermore, tanδ values of all fine-grained CCTO ceramics are lower than 0.08 over a wide frequency range from 10^2 to 10^5 Hz, as clearly seen in the insets of Figs. 8 and 9. The experimental results also revealed that the temperature coefficient of ε′ is less than ±15% (compared to the ε′ value at 20°C) over the temperature range −55°C to 85°C. Notably, CCTO ceramics prepared using a GNP have good dielectric properties and may be suitable for capacitor applications. Furthermore, their nonlinear electrical properties were improved, especially for the CCTO50-1h sample.

IV. Conclusion

Pure phase CCTO powder was successfully prepared at a relatively low temperature of 760°C and short reaction time for

4 h using a GNP. Fine-grained CCTO ceramics with few pores and small grain sizes were obtained by sintering the green body of compacted fine CCTO powders in air at temperatures of 1050°C–1080°C for 1 h. α of the fine-grained CCTO ceramic sintered at 1050°C for 1 h was extremely high of about 16.39. Furthermore, E_b was 1.46×10^4 V/cm, which is also high. For capacitor applications, all of the fine-grained $CaCu_3Ti_4O_{12}$ ceramics exhibited good dielectric properties. ε′ was higher than 2600 and tanδ ≈0.017 at 20°C and 1 kHz. Temperature stability of ε′ over the range −55°C to 85°C was <±15%. Very high ε′ (≈1.03×10^5) and low tanδ (≈0.054) were observed in the coarse-grained CCTO ceramics sintered at 1050°C for 3 h. This observation of a largely coarse-grained microstructure indicated a high grain growth rate over a narrow sintering time range.

Acknowledgments

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Original Research Paper

Strength and resistance to sulfate and sulfuric acid of ground fluidized bed combustion fly ash–silica fume alkali-activated composite

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ABSTRACT

Fluidized bed combustion (FBC) is an environmentally friendly process for burning of coal and is used in many small factories located in urban area. The FBC fly ash is an environmental problem and needs good disposal or utilization. This research studied the strength and resistance to sulfate and acid of alkali-activated FBC fly ash–silica fume composite. The FBC fly ash was interground with silica fume (at the dosage levels of 1.5%, 3.75% and 5.0%) to make the source material homogenous with increased reactivity. Addition of silica fume enabled the adjustment of SiO_2/Al_2O_3 ratios (6.55-7.54) of composite and improved the strength and resistance to sulfate and acid of composite. The composite with 3.75% silica fume showed the optimum strength with 28-day compressive strength of 17.0 MPa. The compressive strengths of composite with 3.75% silica fume immersed in 5% magnesium sulfate solution and 3% sulfuric acid solutions were substantially higher than the control. The strength loss was from the high calcium content of FBC fly ash and incorporation of silica fume thus increased the durability of the composite.

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1. Introduction

Fluidized bed combustion (FBC) is a promising environmentally-friendly coal combustion process with operating temperature of 800–900 °C comparing with pulverized coal combustion. The low temperature prohibits the nitrogen oxides (NOx) emission [1]. The amount of FBC fly ash has, therefore, increased significantly over the past few years owing to the rapid growth of FBC technology [1]. The fly ash has low glassy phase material and possesses very low pozzolanic property. Improvement on its reactivity can be obtained from an intense grinding to reduce the particle size [2]. In addition, it contains high amount of calcium compounds (CaO and $CaSO_4$) from the use of lime powder to capture SO_2. The use of FBC fly ash as a pozzolan to partially replace Portland cement is therefore not recommended [3].

Researches have focused on the utilization of fly ash as a source material in alkali-activated composite or "geopolymer" [4,5]. This composite is alumino-silicate compound and can be produced from the alumino-silicate source materials (e.g. fly ash or metakaolin) in alkaline solutions e.g. sodium hydroxide and sodium silicate solutions [6–8]. Heat curing (60–90 °C) is usually applied to accelerate the reaction. The aluminosilicate product with high early strength and stability up to temperature of 1400 °C could be obtained [9].

In addition, fly ash geopolymer is resistant to acid and sulfate solutions compared with OPC materials. Immersion of geopolymer in these solutions has small impact on the strength of material because of the nature of aluminosilicate gel in geopolymer [7,8]. The stability of materials depends on the type of activator and type of cation in the sulfate media [8]. For magnesium sulfate immersion, gypsum, $Mg(OH)_2$, SiO_2, and magnesium silicate hydrate can be formed. This caused the deterioration of materials and reflected in compressive strength loss [7].

Researchers have investigated the use of FBC fly ash as an alternative source material for preparation of alkali-activated composite [2,10,11]. However, as-received FBC fly ash provided both low strength and acid resistance owing to high calcium content in composite [2,10].

Due to high content of calcium compounds in FBC fly ash, additional pozzolanic reaction is possible in geopolymer which will lead to the formation of calcium silicate hydrate (C–S–H). Silica fume is a micro sphere of non-crystalline silica with very high surface area. It contains more than 78% SiO_2 in glassy form and is suitable for use as cement additive [12] with a large filler effect in concrete. In concrete application, the use of silica fume improves the strength and other physical properties of concrete [13,14]. It

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has also been shown that silica fume can also be used to prepare sodium silicate for geopolymer synthesis using sol–gel condensation reaction [15].

The use of silica fume as a silica source to enhance the properties of alkali-activated FBC fly ash composite is, therefore, promising. High calcium fly ash reacts and forms C–S–H and other calcium compounds e.g. $Ca(OH)_2$ in the presence of alkali solution [2,9]. This research has proposed that active silica fume should react with these calcium compounds (from FBC fly ash and products) forming the C–S–H in composite and contributing to the strength gain and good physical properties of alkali-activated composite. Owing to low reactivity and high pore volume of FBC fly ash, grinding of FBC fly ash was recommended to remove the void, refine the pore structure and increase surface area before using as source material for geopolymer preparation [2]. Therefore, grinding of the source materials was performed in this research.

2. Experimental procedure

2.1. Materials

The FBC-fly ash and silica fume were used as source materials for the synthesis of alkali-activated composite. This FBC fly ash mainly consisted of silica (SiO_2), alumina (Al_2O_3), lime (CaO) and sulfur trioxide (SO_3) determined by X-ray fluorescence (XRF) as tabulated in Table 1. High CaO content of 38.7 wt% was found in FBC fly ash owing to the addition of lime for sulfur absorption. SEM image of FBC fly ash showed that the particle shapes were irregular (Fig. 1) with the median particle size (D_{50}) of 24 μm. FBC fly ash contains low glassy material due to the low burning temperature. Three dosages of silica fume addition of 1.5%, 3.75% and 5% by weight were selected to intergrind with FBC fly ash. Intergrinding of materials helped to obtain the homogeneous blended powder. The blend was ground in a laboratory ball mill for 2 h as a longer milling time only marginally increased the fineness of the blend. The homogeneous blends with a median particle size (D_{50}) of 5–7 μm measured by particle size analyzer (Malvern Mastersizer S), which retention on sieve No. 325 (45 μm opening) of 3.5–4.0 wt% were obtained. XRD patterns of raw materials are presented in Fig. 2. Quantitative XRD analysis of source materials was performed to obtain the amorphous content by using α-Al_2O_3 (corundum) as an internal standard. It was found that the amorphous contents of FBC fly ash and silica fume were 37% and 97% respectively. Therefore, incorporation of silica fume into FBC fly ash resulted in more glassy phases of the blend as the broad peak was detected in the XRD curve.

In addition to the source materials, 15 M sodium hydroxide (15 M NaOH) and commercial grade sodium silicate solution (Na_2SiO_3) with 9 wt% Na_2O and 30 wt% SiO_2 were used as an alkaline activator. For mortar preparation, the river sand with specific gravity of 2.65 and fineness modulus of 2.8 was employed. The compressive strength of mortars was tested in accordance with ASTM C109 at the ages of 7, 28 and 90 days. The results were reported as the average of five samples.

Table 1
Chemical composition and FBC fly ash and silica fume.

Chemical composition	FBC fly ash (wt%)	Silica fume (wt%)
SiO_2	21.2	98.2
Al_2O_3	10.7	–
CaO	38.7	–
Fe_2O_3	7.0	–
SO_3	14.9	–
Na_2O	2.5	0.5
K_2O	0.9	0.6
TiO_2	1.1	–
MgO	1.9	0.7
P_2O_5	0.1	–
Loss on ignition (LOI)	1.0	–

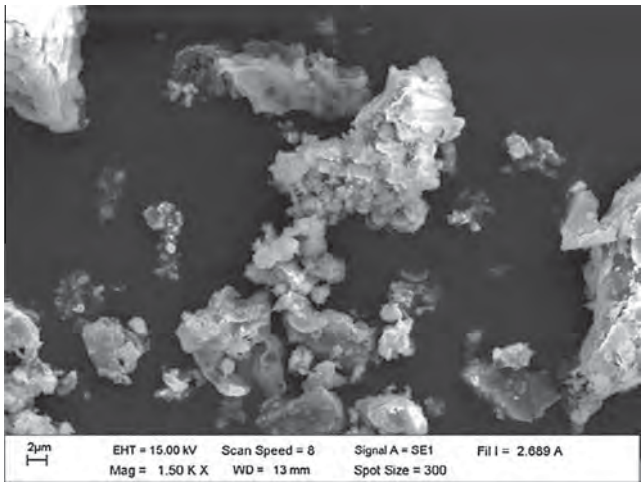


Fig. 1. Microstructure of FBC fly ash.

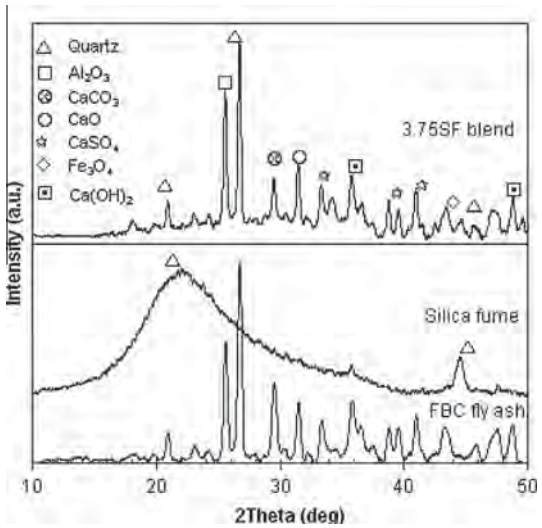


Fig. 2. XRD patterns of source materials.

2.2. Composite preparation

From a preliminary study, there was no ettringite formation in FBC geopolymer with NaOH concentration higher than 15 M [16]. The high NaOH concentration converted gypsum in the FBC fly ash system to calcium hydroxide ($Ca(OH)_2$) and aqueous sodium salt as shown in Eq. (1) and hindered the ettringite formation [17]. $Ca(OH)_2$, then, reacted with SiO_2 and resulted in C–S–H in the composite matrix.

$$CaSO_4 \cdot 2H_2O\ (s) + NaOH\ (aq) \rightarrow 4Ca(OH)_2\ (s) + Na_2SO_4\ (aq) \quad (1)$$

The Na_2SiO_3-to-NaOH mass ratio of 2 was used for the study as the higher ratio resulted in low strength composite as a result of excess silica gel and zeolite formation [18]. The blended powder-to-liquid mass ratio of 1.0 was employed. 15 M NaOH was thoroughly mixed with blended source material and Na_2SiO_3 was subsequently added to the mixture. The mix proportion is

tabulated in Table 2. The paste mixture was continuously mixed in a pan mixer for 2 min and was cast in the 5-cm cubic acrylic moulds. The casting was done in two layers with tamping in accordance with ASTM C109 with final compaction using a vibrating table for 10 s to remove the air bubbles. The specimens were then covered with clingfilm and cured at 65 °C for 24 h. After heat curing, the specimens were continuously cured in a 25 °C chamber (80% relative humidity) until the age of testing.

For the composite mortar, sand-to-blended powder mass ratio of 2 was employed. After mixing the paste, sand was added to the mixture and mixing was continued for another 2 min. The casting and curing conditions were the same as those of the paste preparation.

2.3. Sulfate and acid resistances

Composite mortars were tested for the durability in term of the strength loss after 3-month immersion in the 5 wt% $MgSO_4$ and 3 vol% H_2SO_4 compared with the room temperature (25 °C) cured mortars. One layer of specimens with 1-cm space were used for the storage of specimens in a plastic basket and immersed in closed 10-liter container which was filled with solution. Immersion was performed until the test date. The solutions were replaced every week for the first month and monthly thereafter.

2.4. Composite testing

Composite pastes were ground and used for the X-ray diffraction (XRD), and thermogravimetry (TGA) analyses. The amount of $Ca(OH)_2$ was calculated directly from TGA curves at its decomposition temperature of 400–450 °C using Eq. (2) [19].

$$\%Ca(OH)_2 = \%\text{weight loss}_{Ca(OH)_2} \cdot \frac{MW_{Ca(OH)_2}}{MW_{water}} \quad (2)$$

where $MW_{Ca(OH)_2}$ and MW_{water} are molecular weight of $Ca(OH)_2$ and water, respectively. For the scanning electron microscopy (SEM) analysis and pore size distribution/surface area determination with BET method, small pieces of pastes were employed. The condition for pore size distribution/surface area determination was as following; nitrogen gas was used as adsorbate with the out gas temperature of 120 °C. The samples were subjected to 99-point adsorption–desorption (BJH Theory) isotherms.

3. Results and discussion

3.1. Morphology of composites

The results of the XRD patterns of composites are shown in Fig. 3. Numerous sharp peaks of crystalline phases were presented in the control and blended FBC fly ash and silica fume composite. However, the heights of sharp peaks decreased in the blend composites compared with those of the control owing to the addition of a highly reactive silica fume. The broad hump around 30° 2θ for the composite pastes indicated the converted amorphous phases of the composite and the geopolymerization reaction

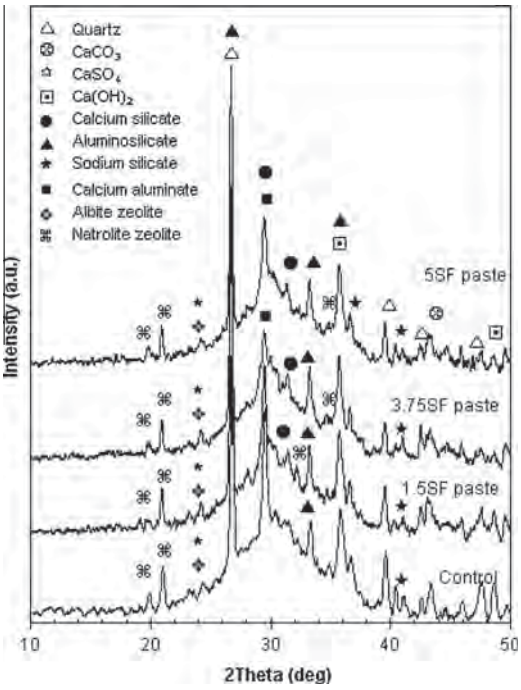


Fig. 3. XRD pattern of control and blend composite.

[20–22]. This led to the highly disorder material in the form of amorphous phases and some crystalline products. The main products consisted of the aluminosilicate and calcium silicate compounds. Due to the use of high concentration sodium hydroxide (15 M NaOH), sodium silicate, calcium aluminate and zeolites (i.e. albite and natrolite) were also formed.

Addition of silica fume (SiO_2) in composite mixture led to the formation of the calcium silicate ($3CaO{\cdot}2SiO_2{\cdot}3H_2O$, C–S–H) as shown in Eqs. (3) and (4) [23].

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2\ (aq) \quad (3)$$

$$3Ca(OH)_2\ (aq) + 2SiO_2\ (s) \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O\ (s) \quad (4)$$

Aluminosilicate and calcium silicate were important products in the composite and contributed to the good physical properties of the composite matrix. However, the increase in silica fume content in the mixture could lead to a high SiO_2/Al_2O_3 ratio and resulted in the composite with lower strength [24].

3.2. Compressive strengths of composites

The results of compressive strengths of blend composite mortars are shown in Fig. 4. The compressive strength of control mortar was comparatively low at all ages. The compressive strengths at the ages of 7, 28 and 90 days were 10.5, 10.8 and 12.0 MPa, respectively. The increase in strength with curing age was low due to the low reactive of FBC fly ash. On the one hand,

Table 2
Mix proportion of composite.

Samples	Blend (g)		15 M NaOH (g)	Na_2SiO_3 (g)	Molar ratio	
	FBC fly ash	Silica fume			SiO_2/Na_2O	SiO_2/Al_2O_3
Control	100	0	33	67	0.39	6.55
1.5SF	98.5	1.5	33	67	0.38	6.83
3.75SF	96.25	3.75	33	67	0.36	7.28
5.0SF	95.0	5.0	33	67	0.35	7.54

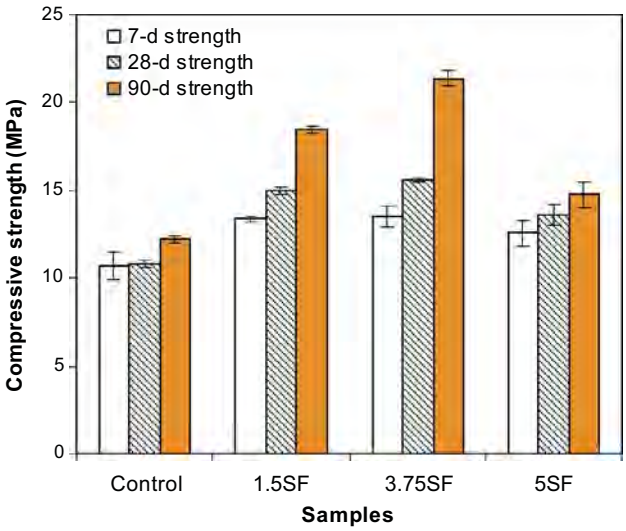


Fig. 4. Compressive strengths of composite mortars at 7, 28 and 90 days.

the increase in strength with curing age could be noticed with the blend composite mortars. The strengths at the age of 7, 28 and 90 days of 3.75SF mortar were 13.0, 15.5 and 22.0 MPa, respectively. The strength at 90 days of 3.75SF mortar was almost double that of the control. In addition to aluminosilicate compound, silica fume in FBC geopolymer matrix reacted with calcium hydroxide and formed calcium silicate hydrate (C–S–H) as confirmed by the XRD results. For the system with substantial amount of calcium, C–S–H was formed and co-existed with the geopolymer products and the strength of composite developed with curing age [25,26]. The strength at 90 days of 1.5SF mortar was also significantly improved to 18.0 MPa.

For the use of 5% silica fume (5SF sample), the compressive strength also developed with curing age due to the pozzolanic reaction. However, gradual improvement in strength was obtained in this case. This was the result of sodium silicate and zeolites (i.e. albite and natrolite) formation which was detected on the XRD pattern. The presence of crystallized zeolite resulted in the composite with lower strength [18]. The excess silica fume acted as the filler in composite matrix. The increase in the silica resulted in a high SiO_2/Al_2O_3 ratio of composite mix with low strength [24].

3.3. Microstructural study

Fig. 5 showed the microstructure of the control and 3.75SF mortar specimens. In addition to the composite matrix and other compounds, the unreacted fly ash particles were found. Reaction occurred at the surfaces of fly ash and silica fume and resulted in the binding property of the geopolymer. The control paste contained a relatively loose matrix and several microcracks since FBC fly ash had low reactivity and high content of calcium compounds. This caused the low strength of geopolymer mortar. Owing to the high reactivity of silica fume and intergrinding of FBC fly ash, dense matrix was formed in the 3.75SF geopolymer paste. High NaOH concentration of 15 M helped the leaching of Si^{4+} and Al^{3+} ions from fly ash surface and the subsequent geopolymerization [27]. The dissolution of calcium sulfate was also enhanced and this led to calcium hydroxide formation as previously presented in Eq. (1). Subsequently, the pozzolanic reaction between calcium hydroxide and silica fume formed more C–S–H in the matrix as shown in Eq. (4) and this enhanced the strength development of the geopolymers.

3.4. Thermal property of composites

Physical changes in materials were presented by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) as shown in Fig. 6. TGA/DTG was use to determine a thermal stability of geopolymer and its fraction of volatile components by monitoring the weight change during heating of specimen. FBC fly ash showed the weight loss at approximately 100, 400 and 700 °C due to the evaporation of water (from sodium hydroxide and sodium silicate solution), and decompositions of portlandite ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) into CaO and CO_2, respectively [28] (Fig. 6a). At 600 °C, increase in weight was found on the TGA curve due to the carbon oxidation (carbonation). This led to an upward swing of the TGA curve prior to the bulk of the weight loss, which made the definition of onset temperature (T_{onset}) even more difficult and ambiguous [29].

The DTG curves of the composite pastes were similar and they are shown as one overlapped curve in Fig. 6b. The control FBC composite showed the highest weight loss among the composite pastes. The loss was greatest between 50 and 150 °C indicating the loss of water. The blended composite pastes gave lower weight loss compared with that of the control FBC composite at the same temperature. With low range heating temperature of 200–500 °C, weight of blend geopolymer paste was approximately 5% higher than the control. The addition of silica fume resulted in the additional C–S–H. The water molecules were consumed and the calcium silicate became the integral part of the C–S–H gel [23]. Thermal resistant product was obtained as indicated by low weight loss compared with that of the control. This was due to more binding materials (i.e. aluminosilicate and calcium silicate compounds) and calcium silicate hydrate formed in matrix. Weight loss of the blend samples slightly reduced with the increase in the silica fume content. The remained weight of the control and 1.5SF pastes were 66.5% and 68.0% respectively and were similar to those of OPC pastes with W/C ratio of 0.30–0.33 conformed with other findings

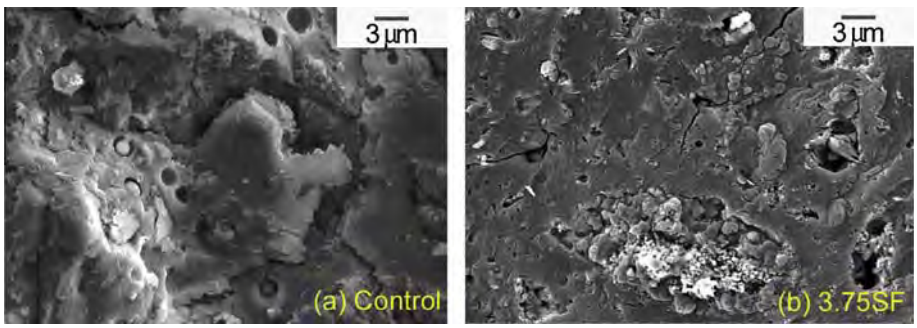


Fig. 5. SEM micrographs of composite pastes at the age of 28 days.

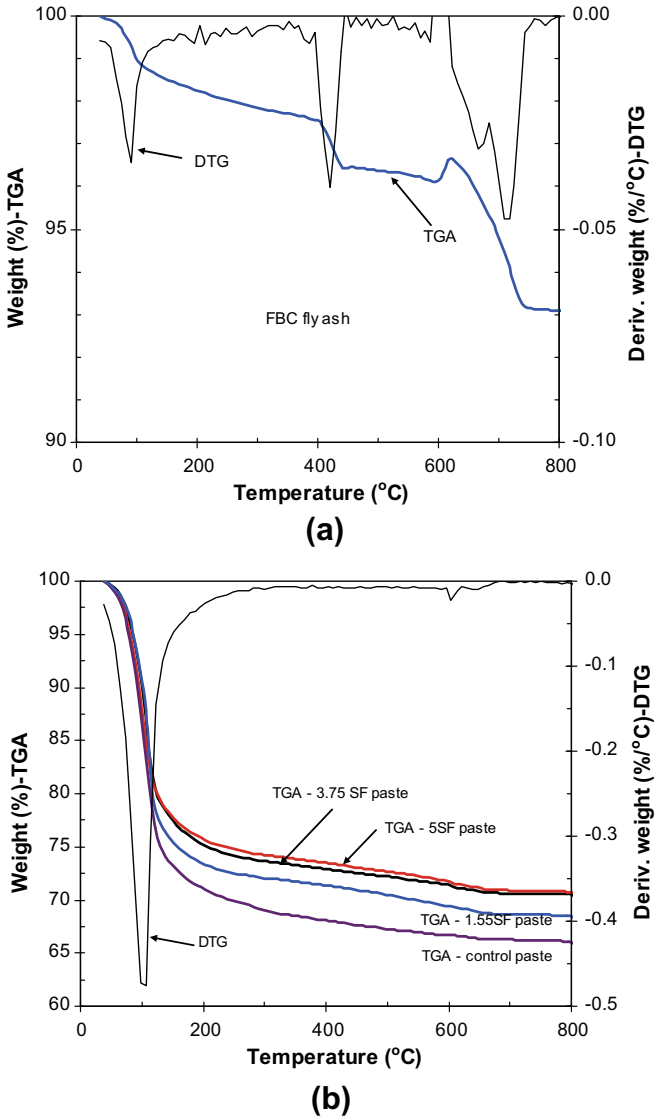


Fig. 6. TGA/DTG curves of FBC fly ash and composite pastes.

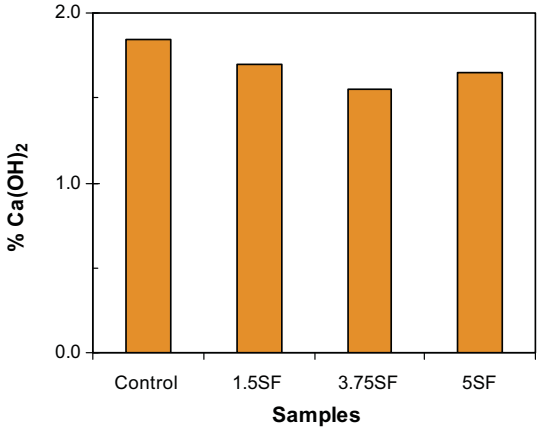


Fig. 7. $Ca(OH)_2$ content of composite pastes.

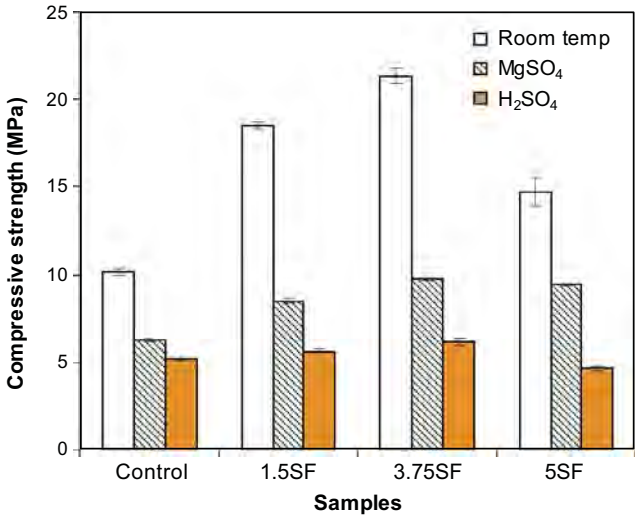


Fig. 8. Compressive strengths of composite under $MgSO_4$ and H_2SO_4 attack.

[30,31]. The increases in silica fume to 3.75% and 5% by weight of FBC fly ash achieved the lower weight loss.

For the derivative thermogram (DTG) profile of geopolymers, a peak corresponding to maximum weight loss at around 100 °C was observed resulting from evaporation of bound water. A small peak was also found at 400 °C indicating the decomposition of $Ca(OH)_2$ formed as a result of reaction between an alkaline solution and calcium from FBC fly ash. Amounts of $Ca(OH)_2$ are presented in Fig. 7. It was found that the $Ca(OH)_2$ contents reduced with the addition of silica fume indicating its conversion to calcium silicate hydrate.

In addition, low decompositions at 400 and 700 °C were found which was due to the conversion of calcium compounds in high calcium FBC fly ash to the thermal stable products in presence of alkali solutions. The reduced $Ca(OH)_2$ and the associated formation of additional C–S–H supported the results of the compressive strength.

3.5. Durability of composites

The results of the durability test of composite mortars in term of the strength loss after 3-month immersion in 5 wt% $MgSO_4$ and 3 vol% H_2SO_4 are shown in Fig. 8. The strength of composite significantly decreased after immersion in both 5 wt% $MgSO_4$ and 3 vol% H_2SO_4 solutions. The high calcium content of FBC fly ash was possibly the cause of this strength loss. For immersion in 5 wt% $MgSO_4$, the strength of control and blend composite mortars reduced to 6 MPa and 10 MPa, respectively. The sample surfaces were deposited with white substance of magnesium hydroxide ($Mg(OH)_2$), silica (SiO_2), magnesium silicate and calcium magnesium silicate compounds [7,32]. Mg^{2+} ion reacted with hydroxyl ion (OH^-) from $Ca(OH)_2$ and NaOH in geopolymer matrix yielded the insoluble $Mg(OH)_2$ leading to the deposition on material surface. In addition, C–S–H phase was attacked and decomposed in the present of $MgSO_4$ resulting in low stability C–S–H and strength loss [32,33]. It was also reported that the hydrated magnesium silicate had no binding capacity which adversely affected the physical property of composite [33].

For immersion in H_2SO_4, higher strength losses were detected compared with the immersion in $MgSO_4$ solution due to the attack of calcium compound with strong acid solution. High calcium fly ash is very susceptible under acid condition. This adversely affected the leaching of calcium and resulted in physical and chemical damages.

The remaining strengths of blend geopolymer mortars were not still significantly higher than that of the control. The strength of 3.75SF blended was only slightly higher than the others. For instant, the compressive strengths of mortars with 0, 1.5%, 3.75%

Table 3
BET results of composite pastes.

Samples	Specific pore area (m^2/g)	Pore volume (cm^3/g)
Control	39.2	0.118
1.5SF	40.1	0.130
3.75SF	52.9	0.167
5SF	72.2	0.217

and 5% SF after 90 days immersion in magnesium sulfate were 6.5, 8.5, 9.5 and 9.0 MPa respectively, whereas those immersed in sulfuric acid were 5.5, 6.0, 6.5 and 4.5 MPa, respectively. In the acid environment, in addition to calcium compound dissolution, C–S–H reacted with H_2SO_4 and formed $CaSO_4$ and amorphous silica gel [33,34]. It was also reported that H^+ (from H_2SO_4 ionization) could destroy the alumino-silicate network in geopolymer and yielded silicic acid ($Si(OH)_4$) and aluminum ions (Al^{3+}) [32,34]. The breaking of oxy-aluminum bridge caused the deterioration of geopolymer in acid condition. With high silica fume content of 5%, the remaining strength of immersed mortar was lower than that of the control. The high strength loss was due to the low initial strength of mortar and the favorable dissolution of excess silica in acid solution.

3.6. BET pore areas and pore volumes of composites

The BET pore areas and pore volumes of composite pastes at the age of 30 days were measured by N_2 adsorption and are given in Table 3. Both pore area and volume increased with the increase in the silica fume content. The pore distributions of composite pastes are presented in Fig. 9. The pores mainly distributed between 200 and 30 nm which corresponded to the gel pores. The addition of silica fume increased the average pore of the samples due mainly to the increase in the C–S–H gel. The main peak of the pore of the control was around 7 nm and those of the pastes containing silica fume were approximately 9 nm. The increase in the C–S–H was mainly responsible for the strength improvement of the sample with addition of up to 3.75% silica fume. Addition of silica fume could refine the pore size resulting in higher amount of small pore than that of the control. This also contributed to the higher cumulative pore volume.

At high silica fume content of 5%, the strength dropped as the silica content was too high and the composite gel consisted of high free SiO_2 resulting in a paste with low strength and also high pore area and volume. The presence of silica fume in composites divided the large pores into smaller pores [23]. It also acted as filler due to its fineness and filled into spaces between fly ash grains. This improvement in pore structure was reflected in the higher strength. Pore diameter in the range of 10–50 nm mainly affected the strength of the material while the smaller pore diameter affected the shrinkage [35]. The refinement of pore structure led to a reduction in the diffusion of harmful ions, a reduction in calcium hydroxide content and a conversion of lime in high calcium fly ah through pozzolanic reaction. This behavior resulted in a high resistance to sulfate attack which also indicated by the durability results. However, magnesium sulfates had a more damaging effect than sodium sulfates [36].

4. Conclusions

The interground FBC fly ash and silica fume can be used as a source material for making alkali-activated composites. The

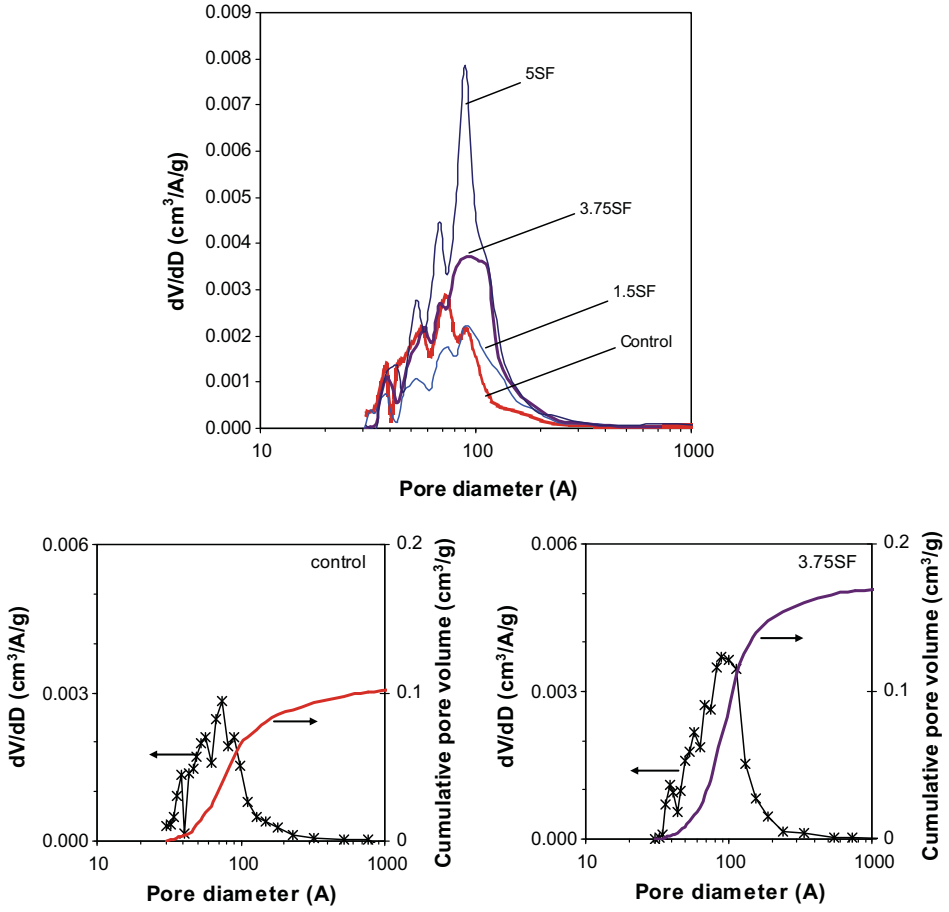


Fig. 9. Pore size distribution of composite pastes.

grinding improved the reactivity of FBC fly ash and the presence of reactive silica fume also helped to increase the reactivity of the system. Silica fume reacted to form aluminosilicate and additional calcium silicate compounds in the composite matrix. These compounds enhanced the physical properties of composite. However, high content of silica fume in geopolymer mixture increased the SiO_2/Al_2O_3 ratio beyond the optimum and adversely affected the strength of composite. The optimum silica fume content was 3.75% for both strength and durability of the composites. Incorporation of silica fume also increased the resistance to magnesium sulfate and sulfuric acid attack of the composite. This is due to the increase in the C–S–H which resulted in the increased strength and reduction of calcium as a result of C–S–H formation. Higher SiO_2/Al_2O_3 ratio resulted in a low strength composite as a result of excess silica gel and zeolite formation. Addition of silica fume resulted in thermal resistant product with low weight loss as calcium hydroxide was converted to calcium silicate compound which was more stable at high temperature up to 800 °C.

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Effect of sodium hydroxide concentration on chloride penetration and steel corrosion of fly ash-based geopolymer concrete under marine site

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HIGHLIGHTS

- The long term durability of geopolymer concrete under marine site was investigated.
- The findings provide valuable data for a practice guide line of geopolymer concrete.
- The findings could help select for fly ash geopolymer concrete used in marine site.

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ABSTRACT

In this research, the effect of sodium hydroxide (Na(OH)) concentrations on chloride penetration, steel corrosion and compressive strength of fly ash-based geopolymer concretes under marine environment were studied. The geopolymer concrete were prepared from class C fly ash with sodium silicate (Na_2SiO_3) and sodium hydroxide (Na(OH)) solutions. The concentrations of Na(OH) of 8, 10, 12, 14, 16 and 18 molar, and the constant molar ratio of SiO_2/Al_2O_3 were used. The $200 \times 200 \times 200\ mm^3$ concrete cube specimens with steel bar embedded at coverings of 20, 50 and 75 mm were investigated. The specimens were air-cured in laboratory for 28 days and then were exposed to tidal zone of marine environment in the Gulf of Thailand. After 3-year exposure, the specimens were tested for compressive strength, chloride penetration and corrosion of embedded steel bar. The results showed that the chloride penetration and corrosion of embedded steel decreased with the increasing of Na(OH) concentration. The steel corrosion was related to the compressive strength of geopolymer concrete. The corrosion is high with the concrete of low compressive strength. In addition, increasing the Na(OH) concentration in geopolymer concrete resulted in a decrease in the chloride binding capacity.

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1. Introduction

The high performances materials (low cost, high durability and high strength) needed to be achieved in the new construction. The new materials from industrial wastes are an interesting possibility for sustainability and economically use of resource. An industrial waste is generally used as pozzolanic materials to partially replace Portland cement for a high performance concrete (good mechanical and durability properties) [1–3]. However, they cannot totally replace Portland cement since silica (SiO_2) and alumina (Al_2O_3) in pozzolanic materials still need $Ca(OH)_2$ from hydration process for its pozzolanic reaction to produce calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) which is primarily responsible for the concrete strength [4]. Recently, it was found that pozzolanic materials containing SiO_2 and Al_2O_3 could be activated with alkaline solution at room temperature to produce a cementitious material called geopolymer [5]. Previous research had studied the effect of various factors such as alkalinity concentrations, curing condition and types of source materials on the microstructure and mechanical properties of geopolymer paste or mortar [6–10]. However, there are only a few reports concerning the durability properties of geopolymer concrete in real exposure which is significant for practical used, especially, the deterioration of geopolymer concrete caused by severe environment.

Current researches on geopolymer concrete are mainly focused on geopolymer properties such as mechanical properties, paste properties [6–10] and durability properties in laboratory [11–13]. However, no specific publications are available concerning the durability of geopolymer concrete in the actual marine site which is mainly due to sulfate attack and the corrosion of steel under chloride attack [14,15]. However, all of these mechanisms are the

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combination of many influences, such as moisture, temperature, impact force and abrasion by sand in sea water. The combined destruction of chemical and physical aggressive of actual environment are complicated. Consequently, the long term durability study in marine site was needed for the development of good practice guide line on selection and design for fly ash geopolymer concrete in marine environment. Thus, the goal of the study was to study the fly ash-based geopolymer concrete under the marine environment in order to achieve the good mechanical and durability properties for marine structure. The effect of sodium hydroxide (NaOH) concentrations on compressive strength, chloride penetration profile, chloride binding capacity and steel corrosion of fly ash-based geopolymer concretes under 3-year exposure in tidal zone of marine environment were carried out.

2. Experimental program

2.1. Materials and specimens

The geopolymer concrete mixtures were prepared from Mae Moh class C fly ash with a 30-μm median particle size (by sieve analysis), sodium silicate (Na_2SiO_3, NS) solution with 9% Na_2O and 30% SiO_2 by weight, NaOH solution, graded sand, and crushed limestone with a maximum size of 19 mm. The chemical compositions of fly ash are shown in Table 1. The NaOH concentrations were varied at 8, 10, 12, 14, 16 and 18 molar and the molar ratio of SiO_2/Al_2O_3 was kept constant. The liquid to binder ratio (L/B) was kept constant of 0.60. Mixture proportions of fly ash-based geopolymer concrete are shown in Table 2. For the mixture procedure, the fly ash and aggregates were dry-mixed with a power mixer, the alkaline liquids (NaOH and sodium silicate solutions) were sequentially added and the wet-mixing was continued for 1 min. These were similar to the mixing of normal concrete. Concrete cylinder having 100-mm in diameter and 200-mm in height were prepared for compressive strength test. For chloride penetration and steel corrosion tests, the $200 \times 200 \times 200\ mm^3$ geopolymer concrete cube specimens were cast and the steel bars (12-mm in diameter and 50-mm in length) were embedded at the corners of concrete specimens with the covering depths of 20, 50, and 75 mm. The embedded steel bars which is commonly used for reinforced concrete construction were cut from 12-mm diameter round bar graded SR24 (yield strength of 240 MPa). Geopolymer concrete specimens preparations are shown in Fig. 1(a). The geopolymer concrete specimens were removed from the molds at the age of 1 day and then were air cured until the age of 28 days. Consequently, the geopolymer concrete specimens were transferred to the tidal zone of the marine site in the Gulf of Thailand as shown in Fig. 1(b). The ranges of annual temperature at this site are between 26 and 35 °C, and based on chemical analysis of the seawater, chloride and sulfate compositions range from 16,000 to 18,000 and 2200 to 2600 mg/l, respectively. The geopolymer concrete specimens were exposed to two wet–dry cycles of seawater daily.

2.2. Tested program

2.2.1. Compressive strength

The compressive strengths of geopolymer concretes at 28 days and at 3 years exposure in marine environment were investigated in accordance with ASTM C39/39M [16]. The compressive strength was collected based on the average of values obtained from three samples.

2.2.2. Chloride penetration

After being exposed to seawater for 3 years, the top surface of concrete cube specimens were cored to obtain 75-mm diameter cylinders. The core specimens were dry-cut from the surface to obtain a series of 10-mm thick slices, and then were ground into small powdery particles. The powder sample from each slice was selected for chloride tests by acid-soluble and water-soluble to determine the total and free chloride contents in geopolymer concrete, respectively. The acid-soluble and water-soluble chloride tests were conformed to ASTM C 1152 [17] and ASTM C1218 [18], respectively. The specimens preparation for chloride penetration test are shown in Fig. 2(a).

Table 1
Chemical composition of fly ash.

Chemical composition (%)	
Silicon dioxide, SiO_2	32.10
Aluminum oxide, Al_2O_3	19.90
Iron oxide, Fe_2O_3	16.91
Calcium oxide, CaO	18.75
Magnesium oxide, MgO	3.47
Sodium oxide, Na_2O_3	0.69
Potassium oxide, K_2O	2.38
Sulfur trioxide, SO_3	2.24
Loss on ignition, LOI	0.07

Table 2
Mixture proportions of fly ash-based geopolymer concrete.

Mix	Mixture proportion (kg/m^3)				
	Fly ash	Fine aggregate	Coarse aggregate	NaOH	NS
8-M	390	585	1092	67	167
10-M	390	585	1092	67	167
12-M	390	585	1092	67	167
14-M	390	585	1092	67	167
16-M	390	585	1092	67	167
18-M	390	585	1092	67	167

2.2.3. Steel corrosion and chloride content at the position of embedded steel

The embedded steel corrosions were measured in terms both of the percentage of rusted area (RA) and percentage of weight loss (WL). After 3-year exposure in marine site, the geopolymer concrete specimens were broken, and then the embedded steel bars were removed. An image of each visible surface of rusted steel was recorded. For the percentage of rusted area, transparent paper with a grid composed of 1 mm-squares was then wrapped around each embedded steel bar. The visible surface of the rusted steel was marked on the paper and evaluated (Fig. 2(b)). The corrosion of the embedded steel bars was measured in terms of the percentage of rusted area by comparing the surface rusted area to the total surface area of the embedded steel. Also, the percentage of weight loss of embedded steel bar were determined by comparing the amount of steel weight loss due to corrosion (the decrease in embedded steel weight during the exposed time period) to the initial steel weight (the steel weight before embedding in geopolymer concrete). In addition, mortar debris was collected from the position of the embedded steel–concrete matrix interface and ground to powder. Its water-soluble chloride content was determined and represented the free chloride content at the position of the embedded steel.

3. Results and discussions

3.1. Compressive strength

Table 3 shows the compressive strength results for fly ash-based geopolymer concretes after 28-day curing in air and 3 years exposure in the tidal zone of marine site. Also shown is the strength at 3 years as a proportion of the 28-day strength in order to present the degree of strength loss or strength gain. The 28-day compressive strength of geopolymer concretes increases with the increase in NaOH concentration. All geopolymer concretes recorded no strength loss between 28 days and 3 years, especially in geopolymer concrete with high strength grade. The increasing compressive strength of geopolymer concrete between 28 days and 3 years tended to be high with the increase of Na(OH) concentration and the highest increase was in geopolymer concrete with sodium hydroxide concentration of 18 molar. For instance, geopolymer concrete with Na(OH) concentration of 8, 10, 12, 14, 16 and 18 molar had percentage compressive strength at 3 years as compared to 28 days of 107.3%, 112.8%, 117.7%, 125.2%, 125.2% and 126.1%, respectively. During exposure period, the compressive strength gain of geopolymer concrete with higher strength grade (higher NaOH concentration) was larger than the lower strength grade (lower NaOH concentration). The high concentration of NaOH resulted in the leaching of a larger amount of Si and Al from fly ash [8] and thus produced a better degree of polycondensation and resulted in a high development of long-term compressive strength of geopolymer concrete [19–21]. However, some previous research [9] found that the leaching of Si and Al from fly ash tend to decrease at a high concentration of Na(OH). This may be caused by an increase in the viscosity and density of NaOH solution result in a high viscosity and low flow ability. Consequently, lower pore surface-solution interaction is expected. This trend was consistent

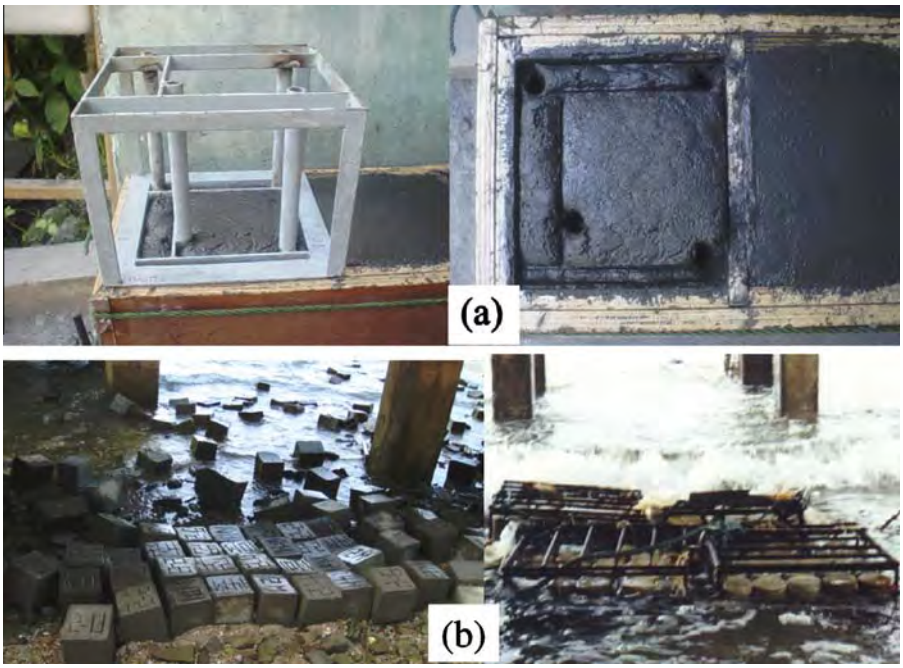


Fig. 1. (a) Geopolymer concrete specimens preparation and (b) geopolymer concrete specimens at a tidal zone of marine site.

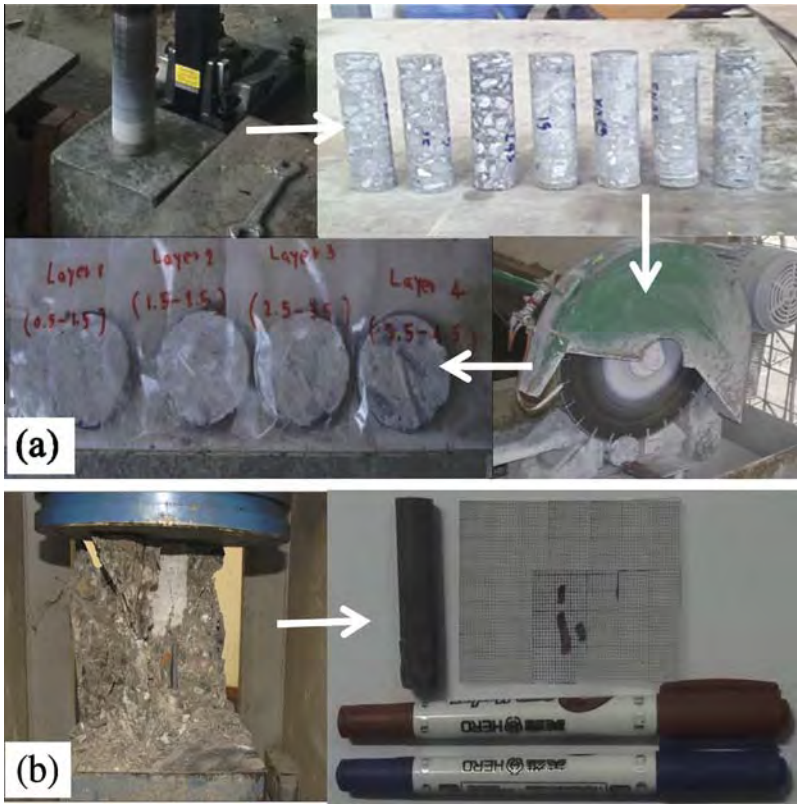


Fig. 2. Specimens preparation for (a) chloride penetration test and (b) corrosion of embedded steel bar.

with the results from this study that the compressive strength of geopolymer concrete (at 28 days and 3 years exposure) increase with NaOH concentration but they were found to slightly decrease when the NaOH concentration was high (up to 18 molar). Besides, previous research showed that the strength loss of cement based concrete due to seawater was caused from a complex combination of physical (such as abrasion, temperature, moisture) and chemical processes (sulfate attack) [14,22]. The sulfate ions in seawater (about 0.22–0.27% by weight of seawater, for marine site in this study) caused deterioration from expansive reactions which also produced non-cohesive products and resulted in strength loss of concrete. Similar to normal Portland cement concrete, the

Table 3
Compressive strength of fly ash-based geopolymer concrete after 28 days and 3 years of exposure in a marine environment.

Mix	Compressive strength (MPa)		
	28-Day curing	3-Year exposure	3-Year/28-day (%)
8-M	23.4	25.1	107.3
10-M	25.0	28.2	112.8
12-M	28.2	33.2	117.7
14-M	31.8	39.8	125.2
16-M	32.2	40.3	125.2
18-M	30.3	38.2	126.1

geopolymer concrete exposed to an external source of sulfate deteriorated by expansive reactions with products such as magnesium hydroxide ($Mg(OH)_2$) and calcium sulfate ($CaSO_4$) [11,12] which resulted in the loss of cohesion of paste matrix. The high early strength of high NaOH concentration geopolymer concrete in this study resulted in a low porosity paste leading to reduce amount of sulfate ions ingress into concrete and thus showed a low strength loss (high strength gain) when compared with a low NaOH concentration geopolymer concrete. Also, the increase of NaOH concentration (increased compressive strength) helped to resist the physical attack which strongly affected the surface layers of geopolymer concrete [23].

3.2. Chloride penetration

The total and free chloride penetration profiles of fly ash-based geopolymer concrete at 3-year exposure in a tidal zone of marine environment are shown in Fig. 3(a) and (b). The chloride penetration in geopolymer concretes decreased with the increasing of NaOH concentration. For instance, geopolymer concrete with NaOH concentration of 8, 10, 12, 14, 16 and 18 molar had total chloride (Fig. 3(a)) and free chloride (Fig. 3(b)) concentrations at 35-mm cover depth of 0.30%, 0.16%, 0.15%, 0.12%, 0.11%, 0.09% and 0.22%, 0.12%, 0.11%, 0.08%, 0.07%, 0.04% by weight of concrete, respectively. The reduction in chloride penetration found in concrete with high concentration NaOH could be attributed to the refinement of the pore structures as a result of polycondensation reaction and filler effect. The relatively high concentration of NaOH enabled the leaching of more Si and Al from fly ash, produced a better degree of polycondensation and resulted in a decrease of geopolymer concrete porosity.

This result is consistent with several other researches [24,25] which indicated that the polycondensation reaction of ash-based geopolymer concrete with a higher concentration of NaOH produced lower permeability and higher strength, thus leads to lower chloride ingress than those with lower NaOH concentration. In addition, $Ca(OH)_2$ (the product from a reaction between calcium from fly ash and alkaline activated in geopolymer) reacted with Si and resulted in calcium silicate hydrate (CSH) which is primarily responsible for the strength in cement based materials [4,25,26].

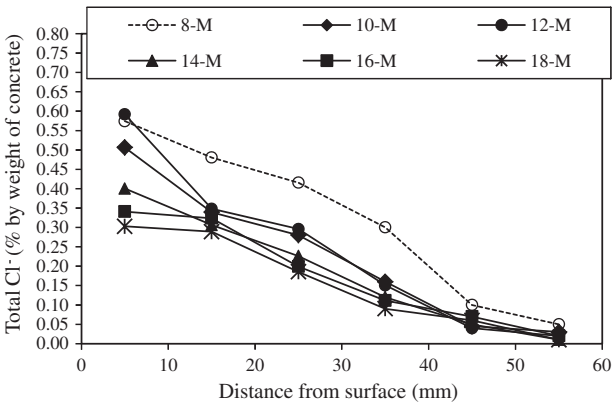
3.3. Chloride diffusion coefficients (D_c)

In this study, D_c was evaluated based on Fick's second law of diffusion as given by Eq. (1) [27].

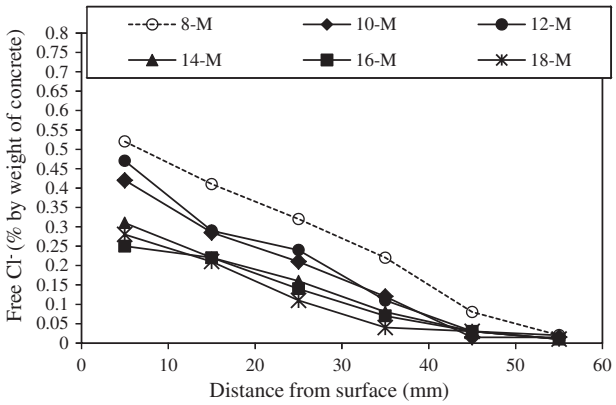
$$\frac{\partial C}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2} \quad (1)$$

If D_c in this equation is a constant at a specific exposure time, a general solution of Eq. (1) is given in Eq. (2)

$$C_{x,t} = C_o\left[1 - erf\left(\frac{x}{2\sqrt{D_c t}}\right)\right] \quad (2)$$



(a) total chloride penetration



(b) free chloride penetration

Fig. 3. Chloride penetration profiles of fly ash-based geopolymer concrete at 3-year exposure in a tidal zone of marine environment.

where $C_{x,t}$ = chloride concentration (% by weight of concrete) at the position x and exposure time t, x = distance from concrete surface (mm), t = exposure time (s), C_o = chloride concentration at concrete surface (% by weight of concrete) at exposure time t, D_c = diffusion coefficient (mm^2/s) at exposure time t, erf = error function.

The general solution in Eq. (2) provides the chloride concentration at any depth and at any exposure time under the constant of D_c and C_o. Consequently, the value of D_c by this equation can be obtained when the value of D_c is a constant at a specific exposure time. Also, the value of C_o can be determined by extrapolation of the chloride penetration profile to depth $x = 0$. The determination of D_c in geopolymer concrete can be evaluated by fitting the Fick's second law on chloride penetration profile from experiment. Fig. 4 shows the fitting curve of general solution of Fick's second law on total chloride penetration profile in fly ash-based geopolymer concrete with difference NaOH concentration at 3-year exposure in a tidal zone of marine environment.

The effect of NaOH concentrations on chloride diffusion coefficient of fly ash-based geopolymer concrete are shown in Fig. 5. The results showed that the increase of NaOH concentrations in geopolymer concrete clearly reduced the rate of chloride ingress into geopolymer concrete. For instance, geopolymer concretes with NaOH concentration of 8, 10, 12, 14, 16 and 18 molar had the D_c at 3-year exposure in marine environment of 6.2×10^{-6} mm^2/s, 4.1×10^{-6} mm^2/s, 3.9×10^{-6} mm^2/s, 3.7×10^{-6} mm^2/s, 3.5×10^{-6} mm^2/s and 2.9×10^{-6} mm^2/s, respectively. This is due to the high NaOH concentrations resulted in geopolymer concretes with high compressive strength as mentioned in Section 3.1. This is similar to cement based concrete that the higher

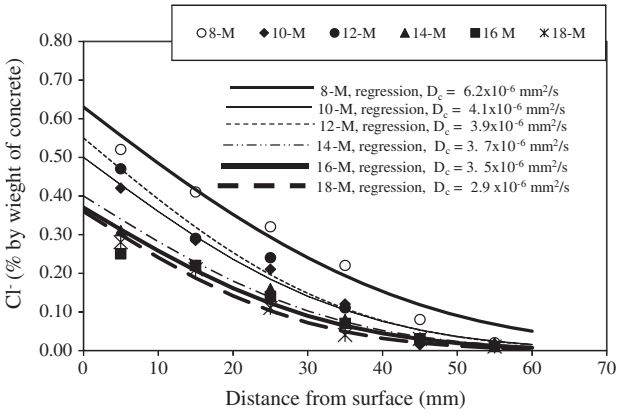


Fig. 4. The fitting curve of general solution of Fick's second law on chloride penetration profile in fly ash-based geopolymer concrete at 3-year exposure in a tidal zone of marine environment.

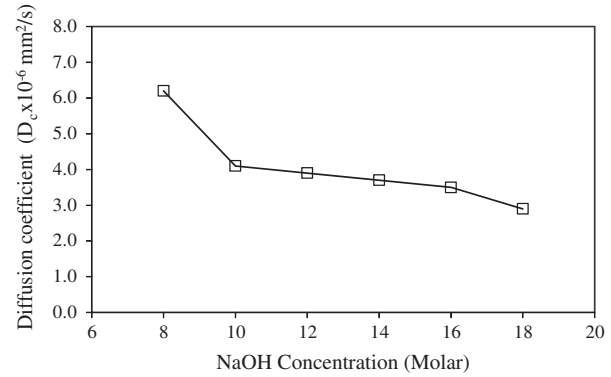


Fig. 5. The effect of sodium hydroxide (Na(OH)) concentrations on chloride diffusion coefficient of fly ash-based geopolymer concrete.

compressive strength lead to lower water permeability and lower chloride ingress [28,29]. In addition, a high concentration of NaOH enhances the leaching of Si and Al from fly ash to produce the higher degree of geopolymerization than that of concrete with low NaOH concentration. This leads to dense matrix and increased ability to resist chloride ions penetration in geopolymer concrete [24]. The SEM were also used to characterize the geopolymer concrete with NaOH concentration of 8 and 18 molar (after exposed to marine site for 3 years) as shown in Fig. 6(a) and (b), respectively. It was found that the geopolymer concrete with high concentration of NaOH solution was denser than that of geopolymer concrete with low NaOH concentration. This result is also consistent with that of chloride diffusion coefficient in geopolymer concrete.

Previous researches [2,30] studied chloride diffusion coefficient of Portland cement type I concretes with W/B ratios of 0.45, 0.55, and 0.65 after 3-year exposure in the gulf of Thailand, the same location where fly ash-based geopolymer concrete specimens in this study were placed. Relationships between compressive strength at 28 days and chloride diffusion coefficients of fly ash-based geopolymer concretes obtained from this study were generated and compared to those of Portland cement type I concretes obtained from previous researches as shown in Fig. 7. According to the figure, chloride diffusion coefficients of fly ash-based geopolymer concretes were lower than those of Portland cement type I concretes even though their compressive strength at 28 days were lower than those of Portland cement type I concrete. As a result, if the compressive strength of fly ash-based geopolymer concrete were improved to be as high as that of Portland cement type I concrete, fly ash-based geopolymer concrete tended to provide a higher resistance to chloride diffusion than Portland cement type I concrete does.

3.4. Chloride binding capacity

The chloride binding capacity in cement based concrete can be calculated by subtracting the free chloride content from total chloride content. For the geopolymer concrete in this study, the chloride binding capacity was evaluated similarly to cement based concrete in terms of percentage chloride binding capacity compared to the total chloride content (P_{cb}). The findings are similar to previous research [31]. Fig. 8 illustrates the relationship between free chloride (C_f) and total chloride content (C_t) in geopolymer concretes at 3-year exposure in marine site. Consequently, the linear regression is used to determine their relation and to produce the equation for C_f in terms of C_t as shown in Fig. 8. According to the relationship between C_f and C_t, the percentage chloride binding capacity (P_{cb}) as compared to the total chloride content can be determined from Eq. (3):

$$P_{cb} = \frac{[(C_t - C_f) \times 100]}{C_t} \quad (3)$$

By substituting C_f in terms of C_t in Eq. (3), the percentage chloride binding capacity (P_{cb}) of fly ash-based geopolymer concrete with NaOH concentration of 8, 10, 12, 14, 16 and 18 molar are 14.3%, 19.0%, 19.8%, 25.8%, 30.2% and 30.8%, respectively.

Fig. 9 presents the effect of NaOH concentration on chloride binding capacity (P_{cb}). The results show that the chloride binding capacity in terms of P_{cb} clearly increased as the NaOH concentration increased. Generally, chloride binding capacity of cement based concrete depends on the physical binding and chemical

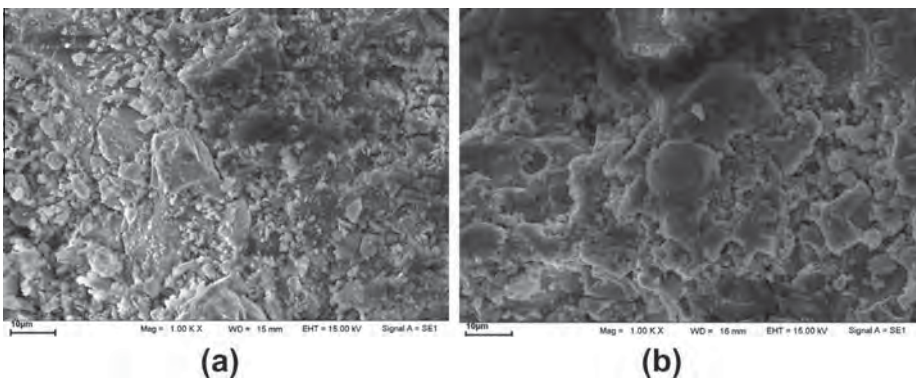


Fig. 6. SEM analysis of fly ash geopolymer concrete with NaOH concentration of (a) 8 molar and (b) 18 molar after exposed to marine site for 3 years.

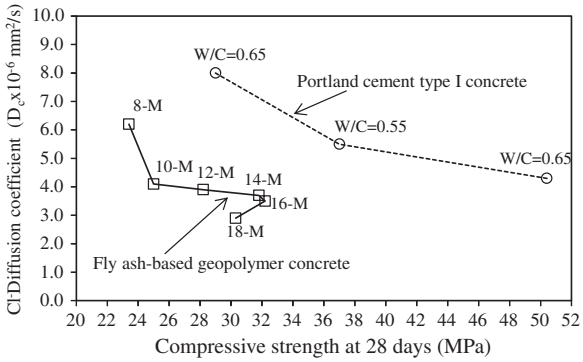


Fig. 7. Relationship between compressive strength at 28 days and chloride diffusion coefficient of Portland cement type I and fly ash-based geopolymer concretes at 3-year exposure.

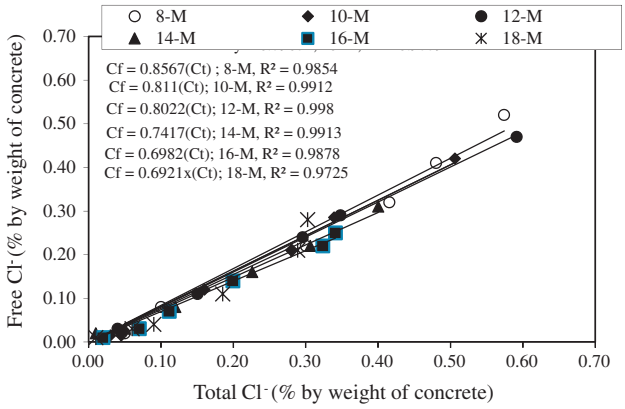


Fig. 8. Relationship between the free and total chloride contents of fly ash-based geopolymer concrete at 3-year exposure in a tidal zone of marine environment.

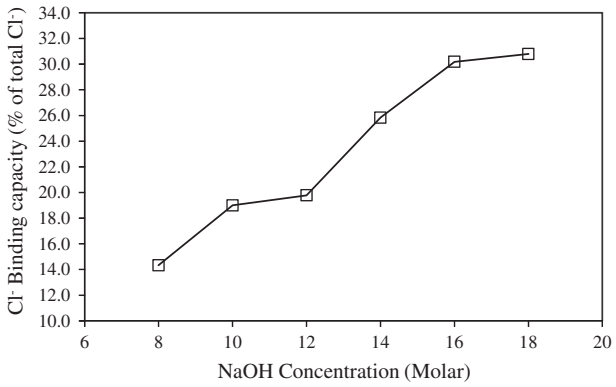


Fig. 9. The effect of sodium hydroxide (Na(OH)) concentrations on chloride binding capacity of fly ash-based geopolymer concrete.

binding [32,33]. The chemical chloride binding can take place only as a result of hydrated calcium aluminate derived from C_3A, produces calcium chloroaluminate hydrate (Friedel's salt). Thus, more chloride ions should be bound when cement contains higher C_3A. Besides, the physical binding, chloride can be physically adsorbed on the surface of hardened gel from the hydration process, such as calcium silicate hydrate (the main product of the hydration reaction which possess cementitious properties) and calcium aluminate hydrate. Previous research had reported that more chloride ions are bound in cement based concrete with higher strengths than those with lower strengths [34]. This confirmed the fact mentioned above. In this study, more chloride ions was bound in geopolymer concrete with higher NaOH concentration than that with lower NaOH concentration due to the physical binding of chloride ions in geopolymer concrete. Since, the use of high NaOH concentration in geopolymer concrete resulted in increased compressive strength, this implied that the hardened gel products from polycondensation reaction was increased. Besides, the fly ash with high calcium oxide can be reacted with silicate compounds to form calcium silicate hydrate, which was the cement gel similar to the hydration reaction of Portland cement concrete [20]. As a result, chloride ions were more physically adsorbed on the surface of hardened gel when compared with the low strength geopolymer concrete. Moreover, the decrease of both total (C_t) and bound chlorides ($C_t - C_f$) in a high NaOH concentration geopolymer resulted in the decrease of P_{cb}, due to a large reduction of C_t as compared with bound chloride. For instance, geopolymer concrete with Na(OH) concentration of 8, 10, 12, 14, 16 and 18 molar had P_{cb} of 14.3%, 19.0%, 19.8%, 25.8%, 30.2%, and 30.8%, respectively.

3.5. Steel corrosion

In this study, the steel corrosion of geopolymer concrete with different concentrations of NaOH was investigated in terms of percentage weight loss (WL) and percentage rusted area (RA). The embedded steel bars at covering depth of 20, 50 and 75 mm at 3-year exposure in a tidal zone of marine environment are shown in Fig. 10(a)–(c). The result indicated that the steel corrosion of geopolymer concretes tended to decrease with the increasing of NaOH concentration. It is consistent with the proposed results in this study that the higher NaOH concentration produces a lower chloride diffusion coefficient and a higher compressive strength. For instance, geopolymer concretes with NaOH concentration of 8, 10, 12, 14, 16 and 18 molar, the percentage of rusted area and weight loss of embedded steel bar at the covering depth of 20 mm were 76.7%, 62.0%, 56.1%, 46.9%, 27.8%, 23.8% and 2.07%, 0.23%, 0.21%, 0.13%, 0.12%, 0.11%, respectively. Also, the same trend of steel corrosion in geopolymer concrete were found at the deeper covering depths of 50 mm and 75 mm. The use of high NaOH concentrations of 16 and 18 molar in geopolymer concretes clearly reduced the embedded steel corrosion at all covering depth when compared with other lower NaOH concentrations. Although, geopolymer concretes were exposed to marine site up to 3 years, it presented low steel corrosion at any depth of concrete and did not show the corrosion of embedded steel bar at 75-mm covering depth.

Generally, the corrosion of steel in cement based concrete in seawater has deteriorated due to the incompatibility of the mix constituents. Both physical characteristics (i.e. pore distribution, pore size, connectivity of pores, shrinkage and movement cracks) [35,36] and chemical characteristics (i.e. chloride binding capacity, alkalinity) [37,38] of cement paste significantly affect the corrosion rates of steel in concrete. In this study, the reduction in steel corrosion was greater in geopolymer concretes with higher NaOH concentrations than that with lower NaOH concentrations. It was due to a lower permeability of a high NaOH concentration geopolymer concrete improved the physical characteristics of paste and led to a lower chloride ingress and steel corrosion in geopolymer concrete. Besides, the improved chemical characteristics of geopolymer paste for protecting the steel corrosion was produced by the increase in the chloride binding capacity of concretes. Thus, the use of a high NaOH concentration solution in geopolymer concrete in this study resulted in increased chloride binding capacity (as mentioned in Section 3.4) and led to a lower free chloride content in pore solution and lower steel corrosion.

By considering the free chloride content at the position of embedded steel bar (Fig. 11), the result also indicated the

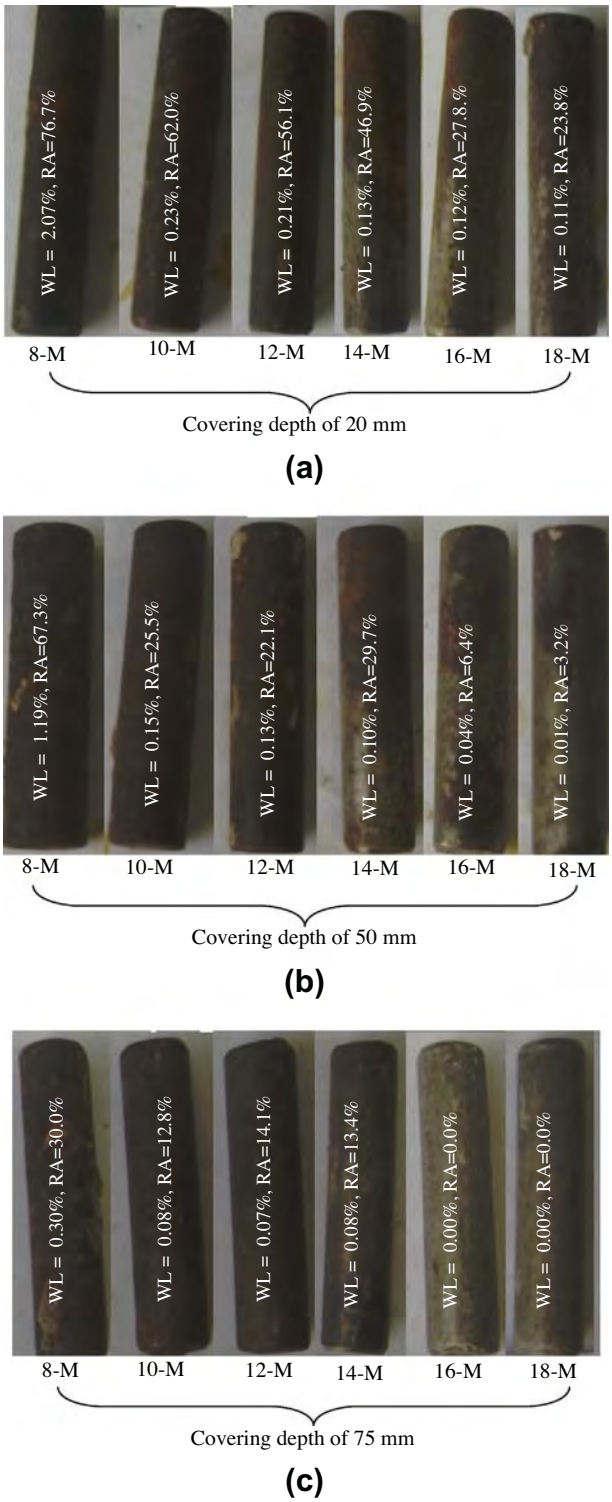


Fig. 10. Corrosion of embedded steel bars at covering depth of (a) 20 mm (b) 50 mm and (c) 75 mm in fly ash-based geopolymer concrete at 3-year exposure in a tidal zone of marine environment.

consistent trend of steel corrosion that the higher chloride content in geopolymer concrete resulted in the higher corrosion of embedded steel bar. The use of 16–18 molar NaOH concentration solutions in geopolymer concrete significantly reduced the free chloride content and increases its durability. For instance, geopolymer concretes having NaOH concentrations of 8, 10, 12, 14, 16 and 18 molar were found to have free chloride contents at 50 mm

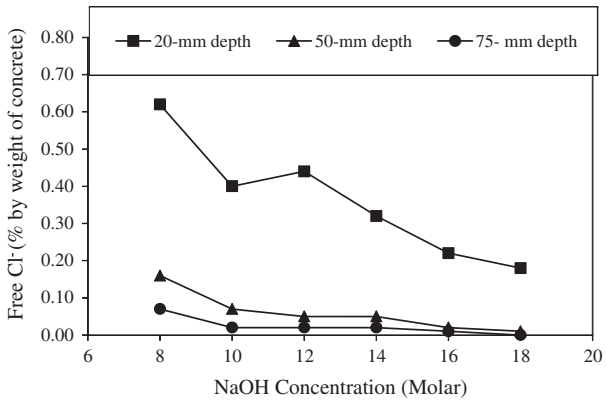


Fig. 11. The effect of sodium hydroxide (Na(OH)) concentrations on chloride contents at the position of embedded steel bars of fly ash-based geopolymer concrete.

depth of 0.16%, 0.07%, 0.05%, 0.05%, 0.02% and 0.01% by weight of concrete, respectively.

4. Conclusions

Based on the results and discussions for the high calcium fly ash-based geopolymer concrete, the following conclusions are made.

(1) During 3-year exposure in seawater, fly ash-based geopolymer concrete with a high NaOH concentration continuously gain strength faster than that with a low NaOH concentration.
(2) Evidently, higher NaOH concentration in fly ash-based geopolymer concrete resulted in lowering of both of free and total chloride ingresses in geopolymer concrete.
(3) The increase in NaOH concentration in geopolymer concrete resulted in the decrease of chloride diffusion coefficient (D_c) and steel corrosion in geopolymer concrete.
(4) Increasing the NaOH concentration in geopolymer concrete resulted in a decreasing the percentage of chloride binding capacity (P_{cb}) as compared to the total chloride content.

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Research paper

Lime-calcined clay materials with alkaline activation: Phase development and reaction transition zone

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ABSTRACT

The research aim was to investigate phase development and reaction transition zone of alkaline activated lime-calcined clay materials. Locally available china clay mainly supplied metakaolin (MK) after calcination. MK and calcium hydroxide (CH) were used to supply SiO_2 and CaO, respectively. The CH to MK ratio of 0.4 with CaO/SiO_2 of 1.18 was selected to coincide with the theoretical CaO/SiO_2 of calcium silicate hydrate in tobermorite group ($Ca_5Si_6O_{16}(OH)_2$). Phase development was investigated using X-ray diffraction and Fourier transform infrared spectroscopy. Compressive strength and density were also investigated to confirm binding properties of the pozzolanic reaction products. The reaction of mixture was dependent on the NaOH concentration. At low concentration of NaOH (<1 M), the pozzolanic reaction was dominant while the zeolitic reaction and geopolymerization became dominant at medium NaOH concentration (>1 M) and at high NaOH concentration, respectively. The activations of CH:MK mixtures with 0.01 and 0.1 M NaOH promoted semicrystalline calcium silicate hydrate (CSH (I)) and crystalline calcium aluminosilicate hydrate (CASH) formations. The mixture with 0.01 M NaOH gave the highest compressive strength of 19.0 MPa. With 3 and 5 M NaOH activations, sodium aluminosilicate hydrate (NASH) and sodium calcium silicate hydrate (NCSH) compounds were formed instead of CSH (I) gel and crystalline CASH phase. At 10 M NaOH, NCSH disappeared and only NASH was formed and resulted in a relatively low compressive strength of 6.7 MPa.

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1. Introduction

Pozzolans have been receiving high attention as their use as supplementary cementing material to react with calcium hydroxide (CH), so called "pozzolanic reaction" to form compounds possessing binding properties resulting in concrete strength enhancement (ASTM C125, 2011). Uses of pozzolans as supplementary cementing material from various sources such as volcanic ash, clay minerals, and coal ashes aim to reduce cost and overall environmental impact according to CO_2 emission. Calcium silicate hydrate (CSH) gel is a pozzolanic reaction product for strength improvement together with porosity reduction (Chindaprasirt and Pimraksa, 2008; Frías et al., 2000; García et al., 2009 and García et al., 2009; Kakali et al., 2001; García et al., 2009; Siddique and Klaus, 2009; Sabir et al., 2001). The CSH gel formed at ambient temperature exists in both amorphous and semicrystalline phases at which a distorted semicrystalline phase referred as CSH (I) is normally found as hydration product. Its composition varies considerably depending on parameters such as the component materials (CaO/SiO_2 ratio) and the pH of the surrounding medium (Chen et al., 2004; García et al., 2008; Yip et al., 2005). CSH gel has been found to be compatible to other hydrated products such as sodium aluminosilicate hydrate gel (NASH) which is a new family of aluminosilicate polymers (geopolymers) (García et al., 2008, 2010; Yip et al., 2005). However, CSH and/or calcium aluminosilicate hydrate (CASH) compounds could also precipitate as well-crystalline solids. Geopolymers are usually precipitated by reacting active aluminosilicate materials such as metakaolin (MK) and fly ash, with an appropriate proportion of alkali metals (Na, K, Ca) under very high alkalinity conditions in which the water content is limited (Davidovits, 1989, 1991; Khale and Chaudhary, 2007; Steveson and Sagoe-Crentsil, 2005; Verdolotti et al., 2008).

The mechanism of alkaline activated CH and MK materials are quite close to geopolymer cement (Khale and Chaudhary, 2007; Yip et al., 2005). Geopolymer cement is formed by 2 main steps; dissolution of reactive starting materials and polycondensation of reaction products. For alkaline activated CH and MK materials, the second step includes the precipitation of the pozzoalnic reaction products in addition to the polycondensation. Therefore, chemical structures of alkaline activated CH and MK materials compose of several forms of products ranging from highly alkaline products such as geopolymer, zeolite material

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and hydration gel products of CSH and CASH. Not many works explored the relation between CSH and CASH/MASH gels (M = alkali metals) by alkaline activation, to their mechanical properties (Alonso and Palomo, 2001a,b; Yip et al., 2005). However, the coexistence of geopolymeric and CSH gels obtained from using ground granulated blast furnace slag and MK as starting material is responsible for the strength enhancement as geopolymeric binder works as micro-aggregate, thus resulting in the homogeneous and dense structures (Yip et al., 2005). In synthesizing CSH gel including pozzolanic reaction and sol–gel procedures, the CSH gel was produced cooperating with alkaline aluminosilicate product at high alkalinity (Alonso and Palomo, 2001a,b; Bondar et al., 2011; Granizo et al., 2002; García et al., 2008, 2010). Sol–gel procedure was used to synthesize both CSH and NASH gels. pH level was found to play a determinant role as pH >11 and >12 resulted in CSH and NASH gels, respectively (García et al., 2008).

This study, therefore, proposed an investigation of alkaline activated CH and MK materials in terms of their phase development and reaction transition zone. The attention to explore pozzolanic reaction of MK was due to the advantages of abundantly local availability and its highly reactive nature. Locally available clay is used as starting material to obtain MK in this study. Not only does such clay contain kaolinite (Kaol), but also muscovite and quartz. With calcination during 500–800 °C, Kaol is transformed to MK by dehydroxylation at which bound hydroxyl groups located at octahedral sites of Kaol are dispelled resulting to a disruption of Kaol structure (Sabir et al., 2001; Siddique and Klaus, 2009; Vizcayno et al., 2010). However, some clay minerals are much less reactive although they undergo dehydroxylation due to their crystallinity are not all disrupted, for example, illite or muscovite and montmorillonite (Fernandez et al, 2011). Quartz is also inert to pozzolanic reaction (Carroll and Starkey, 1971; Deschner et al., 2012; Fennis et al., 2009; Mechti et al., 2012; Yock, 2009). Many researchers reported some inert minerals also influenced on mechanical properties of material structure due to filling effect (Deschner et al., 2012; Fennis et al., 2009; Jaturapitakkul et al., 2011; Mechti et al., 2012). With alkaline activation, such inert minerals have been found to be dissolved. For example, the findings from dissolution of aluminosilicate minerals in alkaline solutions at low and high concentrations, found that minerals composed of crystalline phases (cristobalite, feldspar, K-alunite, quartz, Kaol, illite, zeolite) could be dissolved to be aluminate and silicate ions in high concentration of alkaline activation (Panagiotopoulou et al., 2007). The pozzolanic reaction of MK under alkaline activation was, therefore, studied in term of mineralogical development in order to figure out the reaction transition zone of the formation between calcium based hydrate products and sodium based hydrate products using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) spectroscopy and the related mechanical properties. The reaction of secondary minerals such muscovite and quartz was also investigated. This finding would no doubt lay a solid ground work to explain the uses of locally available clay instead of pure MK.

2. Materials and experimental methods

2.1. Raw materials

Kaolin in this study was obtained from Ranong Province in southern Thailand supplied by Sibelco Mineral (Thailand) Co., Ltd. Its chemical composition characterized by X-ray Fluorescence (XRF) using a Horiba Mesa-500W with principle of energy dispersive XRF Analyzer and XEROPHY high-purity silicon used as detector, the results are shown in Table 1. Mineralogical composition was identified by XRD using a Rigaku Miniflex with CuKα radiation and Kb-filter (λ = 1.540 Å), the current and voltage intensity applied to the generating X-ray tubes were 15 mA and 30 kW, the analysis was performed over the diffraction angle range $5° \le 2\theta \le 70°$ with a 12 degree min^{-1} and step width of 0.015°, as shown in Fig. 1 and in Table 1. The calcination temperature of kaolin was investigated by thermal differential analysis and thermal gravimetric analysis (DTA/TGA) using a Seiko SSC-5000 analyzer with temperature range of room temperature to 1000 °C and heating rate of 10 °C/mim. The DTA/TGA curves are shown in Fig. 2. From the DTA/TGA result, kaolin was calcined at 750 °C for transforming Kaol into MK phase (dehydroxylation). XRD was used to confirm phase formation of MK. The mineralogical compositions of Kaol were quantitatively calculated by Rietveld method refinement using X'pert high score plus software to report the degree of Kaol structure disorder.

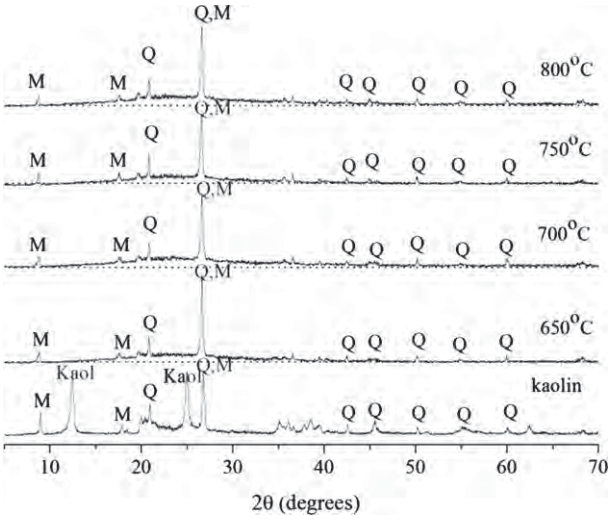
Table 1
Chemical and mineralogical compositions of kaolin.

Characteristics	
Chemical composition (mass %):	
SiO_2	53.08
Al_2O_3	30.69
Fe_2O_3	1.51
CaO	0.08
K_2O	2.46
MnO	0.11
Y_2O_3	0.07
LOI	12.00
Mineralogical composition (mass %)	
Kaolinite	53.70
Muscovite	14.70
Quartz	31.60
Volume mean diameter, D[4,3] (μm)	20.01
Specific surface area (m^2/g)	21.07
Specific gravity	2.62
SiO_2/Al_2O_3 molar ratio	2.93

Particle sizes and specific surface areas of clays were measured by Laser diffraction and by Brunauer–Emmett–Teller method (BET), respectively. The results are shown in Table 1. A commercial grade CH and analytical grade sodium hydroxide (NaOH) were used in this study.

2.2. Solubility of kaolin and MK in alkaline solutions

The solubility of amorphous phase contained MK due to phase transformation from Kaol to MK was studied using 0.500 g of kaolin and MK mixed with 20 mL of NaOH solutions at various concentrations (0.01, 0.1, 1, 3, 5 and 10 M). The solutions were filtrated by Whatman filter paper (no. 5) and 5 mL of solutions were diluted into 250 mL and adjusted to pH < 1 by hydrochloric acid. Atomic absorption spectrometer (AAS, SHIMADZU AA-6200) was used to analyze the dissolved Si and Al ion concentrations (Panagiotopoulou et al., 2007).



M = muscovite, Kaol = kaolinite, Q = quartz

Fig. 1. XRD patterns of kaolin and calcined kaolin at 650–800 °C.

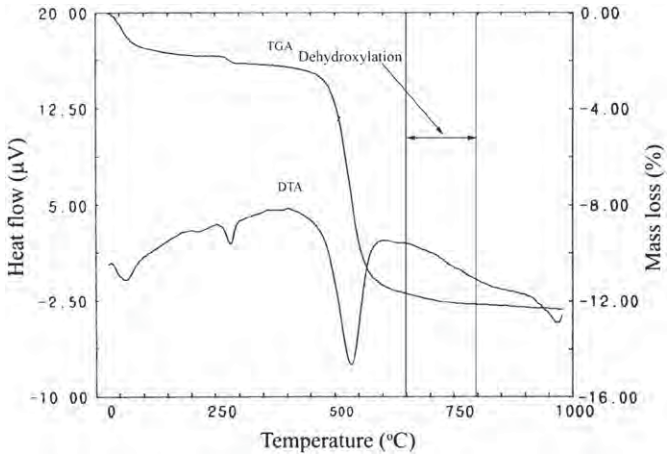


Fig. 2. DTA and TGA graphs of kaolin.

2.3. Pozzolanic reactivity of MK under various NaOH concentrations

The samples were prepared by using 750 °C MK and CH at CH:MK ratios of 0.2, 0.4, 0.6, 0.8 and 1 by mass with corresponding CaO/SiO_2 molar ratios of 0.59, 1.18, 1.76, 2.35 and 2.94, respectively. The same consistency of paste as measured by Vicat apparatus was used by controlling the liquid to solid ratio (L/S) as shown in Table 2.

The mixture was cast into cylinder molds with 20 mm in diameter and 40 mm in height. The samples were placed in the 98% RH and 25 °C chamber. The strength was performed at the age of 28 days using 3 samples. The broken samples were used for the investigation of mineralogical composition by XRD, molecular structure by FTIR, Nicolet 6700 FT-IR Spectrometer, Thermo Fisher Scientific, with attenuated total reflection mode (ATR) and microstructure by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Prior to the characterizations, the hydration reaction of the samples was stopped by soaking in acetone for 48 h and dried before the tests (Poon et al., 2001).

The CH:MK of 0.4 with CaO/SiO_2 of 1.18 was selected to study the effect of alkaline activation. The mixtures were blended with 0.01, 0.1, 1, 3, 5 and 10 M NaOH solutions at the same liquid (NaOH solution) to solid ratio as shown in Table 2.

3. Results and discussions

3.1. Characteristics of kaolin and MK

Chemical compositions and mineralogical compositions of kaolin are shown in Table 1 and Fig. 1. The major chemical compositions were approximately 53.08% of SiO_2 and 30.67% of Al_2O_3. The calculated Kaol was about 53.70%. Some quartz and muscovite were also found in the kaolin sample. Dehydroxylation temperature was about 450–650 °C from DTA-pattern while TGA showed the major mass loss at the same temperature as shown in Fig. 2. The degree of dehydroxylation (D_{TG}) of Kaol was around 650–800 °C as indicated by high D_{TG} value (Bich et al., 2009; Shvarzman et al., 2003) at which $DT_G = 1 - (M/M_{max})$, where M and M_{max} were residual and maximum mass loss, respectively. Therefore, the calcination temperature of 650–800 °C was selected which was slightly higher than the evidence obtained from DTA. The XRD of MK showed the transformation of Kaol to MK and crystalline phases such quartz and muscovite did not change. The broad diffuse halo reflection was found in the range of major diffraction reflection in the crystalline state of Kaol with 650–800 °C of calcinations as shown in Fig. 1. At 650 °C, there was no Kaol contained in kaolin sample.

Table 2
Compositions of mixtures.

CH:MK ratios	Composition of mixtures				
	CH (mass)	MK (mass)	Ca/Si	NaOH (M)	L/S
0.2	0.2	1	0.59	No	0.63
0.4	0.4	1	1.18	No	0.62
0.6	0.6	1	1.76	No	0.61
0.8	0.8	1	2.35	No	0.61
1	1	1	2.94	No	0.60
0.4, 0.01 M	0.4	1	1.18	0.01	0.60
0.4, 0.1 M	0.4	1	1.18	0.1	0.60
0.4, 1 M	0.4	1	1.18	1	0.60
0.4, 3 M	0.4	1	1.18	3	0.60
0.4, 5 M	0.4	1	1.18	5	0.60
0.4, 10 M	0.4	1	1.18	10	0.60

Ca is the mole of CaO calculated from the CH content. Si is the mole of reactive SiO_2 calculated from the kaolinite content

3.2. Solubility of kaolin and MK

The concentration of dissolved Si and Al ions of kaolin and MK in 0.01, 0.1, 1, 3, 5 and 10 M are shown in Table 3. The results showed that high alkaline concentration resulted in high solubility of Si and Al from kaolin sample. In addition to alkalinity, the calcination temperature played a role on the solubility of Si and Al ions. MK was more reactive than kaolin as indicated by higher solubility in alkaline solution to produce Si and Al ions. The calcinations temperatures for providing high concentration of Si and Al ion were at 700–800 °C due to complete transformation of Kaol to MK (amorphous). At 750 °C, the highest amount of Si ions was obtained with the use of 10 M NaOH. The maximum content of Al ions was obtained at 700 °C calcined temperature. 750 °C MK was chosen for next experiments and MK was stand for the 750 °C calcined kaolin.

3.3. Characteristics and properties of CH–MK samples

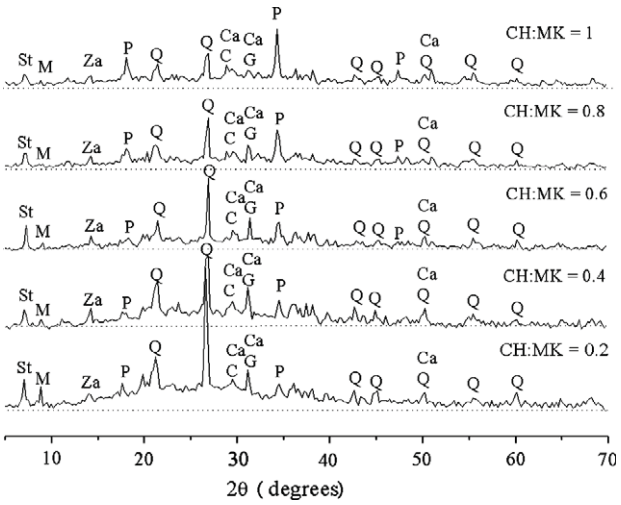
3.3.1. Mineralogical compositions from XRD patterns

XRD patterns of the pozzolanic reaction products made of CH and MK are shown in Fig. 3. The alteration of spectra clearly observed at 26.75° and 34.25° 2θ were assigned as quartz (Q) (SiO_2, 88-2302) and Portlandite (P) ($Ca(OH)_2$, 87-0673), respectively. The available CH left behind after the pozzolanic reaction at 28 days curing was maximum

Table 3
Silicon and aluminum ion concentrations in sodium hydroxide solution after leaching tests.

NaOH solution	Si ion (ppm)				
	non-calcine	650 °C	700 °C	750 °C	800 °C
0.01 M	2.52	5.46	6.80	6.13	6.00
0.1 M	5.86	7.87	7.60	8.94	11.61
1 M	10.68	29.00	28.20	28.73	29.00
3 M	20.47	116.70	149.99	151.14	149.32
5 M	29.94	188.16	191.03	244.11	230.44
10 M	52.61	193.89	232.54	247.37	241.15
NaOH solution	Al ion (ppm)				
	non-calcine	650 °C	700 °C	750 °C	800 °C
0.01 M	n.a.	n.a.	n.a.	n.a.	n.a.
0.1 M	n.a.	0.05	0.05	0.29	0.06
1 M	1.40	11.21	11.32	10.65	10.99
3 M	8.89	90.66	82.59	80.97	82.95
5 M	31.95	109.83	166.86	162.71	156.45
10 M	42.99	103.38	160.83	153.91	158.16

n.a. is not available.



C = calcite, Ca = CSH (I), G = gehlenite, M = muscovite, P = portlandite, Q = quartz, St = stratlingite, Za = zeolite A

Fig. 3. XRD patterns of pozzolanic reaction products with different CH:MK ratios.

at CH:MK of 1.0 and minimum at 0.2. It was shown that CH was required in the reaction at the certain amount. Muscovite and quartz were higher reactive with an increase in CH content resulting in the reduction of their reflection intensity. Calcium silicate hydrate in a form of CSH (I) gel was found. The previous research reported the formation of poorly crystalline CSH (I) in lime--pozzolan system with hydrothermal activation and suitable curing time corresponding to around 7.82°, 29.35°, 32.05° and 50.08° of 2θ (Hong and Glasser, 2004). In addition, the occurrence of tobermorite like C-S-H (I) with CaO/SiO_2 of ~0.67–1.5 was reported in several works (Richardson, 2004, García et al., 2009; Zhang et al., 2009). In this study, semicrystalline CSH (I) was found in every varied ratio. Calcium aluminosilicate hydrate (CASH) compounds composed of stratlingite ($Ca_2Al_2SiO_78H_2O$; C_2ASH_8, 29-0285), gehlenite ($Ca_2Al_2SiO_78H_2O$; C_2ASH_8, 19-0210) and zeolite A ($((Si_4Al_8Ca_2)_{24}(H_2O)_{12}$,86-2218). As shown in Fig. 3, the high contents of zeolite and gehlenite were at CH:MK of 0.4. Therefore, the amount of CaO and SiO_2 significantly affected on the phase formation of both CSH (I) gel and CASH compounds.

3.3.2. Microstructure from FTIR

The FTIR spectra of CH:MK = 0.2–1.0 pastes are shown in Fig. 4. The spectra exhibited the presence of typical O–H stretching vibrations (ν).

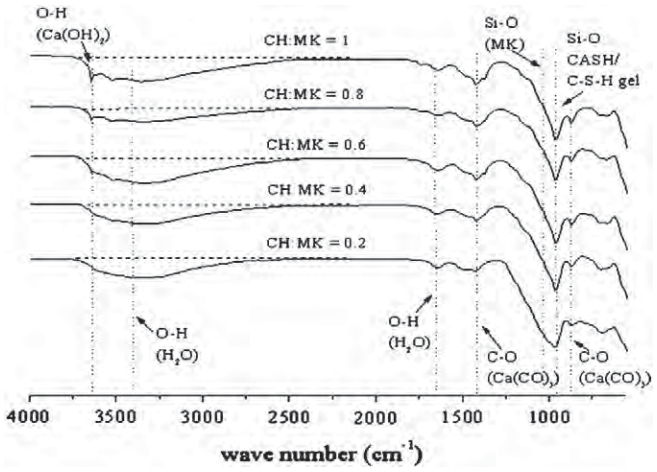


Fig. 4. FTIR spectra of pozzolanic reaction products with different CH:MK ratios.

A broad transmission around 3400 cm^{-1} corresponded to CSH (I) gel. A sharp band at 3630 cm^{-1} corresponding to O–H in calcium hydroxide (Panagiotopoulou et al., 2007) was clearly seen in the mixtures with CH:MK of 0.6–1.0. This indicated the high content of CH remained after pozzolanic reaction and was consistent with the XRD results. The spectra were deconvoluted at the range of 1800–550 cm^{-1} to identify the overlapping peaks at the same frequency with computer software that fits the theoretical curve to the original spectrum (García et al., 2008) as shown in Fig. 5. At CH:MK of 0.2, broad peaks of 1030 cm^{-1} (g) corresponded to the stretching vibration (García et al., 2008) of Si–O in the residue MK after the pozzolanic reaction. Peak at 975 cm^{-1} (h) corresponding to Si–O in CSH gel phase (García et al., 2008, 2010) was detected with the highest content at CH:MK of 0.6. High CH:MK of 0.4–1.0 increased the peak areas around 630 cm^{-1} (l) of Si–O (Si–O–Si, Si–O–Al) bending vibration (δ). In addition, calcite ($CaCO_3$) with C–O stretching vibration around 850–700 cm^{-1} (i, j) and around 1500–1420 cm^{-1} (c, d) (García et al., 2008, 2010) was found in every mixture. Peaks around 1640 cm^{-1} (b) corresponded to O–H bending vibration of H_2O. The results showed that CH:MK of 0.4 contained small residue of CH with the higher CH:MK ratios and was consistence with the XRD result.

3.3.3. Mechanical properties and density

The results of compressive strength and bulk density are shown in Table 4. The highest compressive strength of 17.0 MPa were obtained from samples with CH:MK 0.4 and 0.6. While, the lowest strength (11.0 MPa) was obtained from CH:MK of 1.0 due to the excess hydrated lime. The CH:MK of 0.2 also gave low strength of 12.0 MPa due to

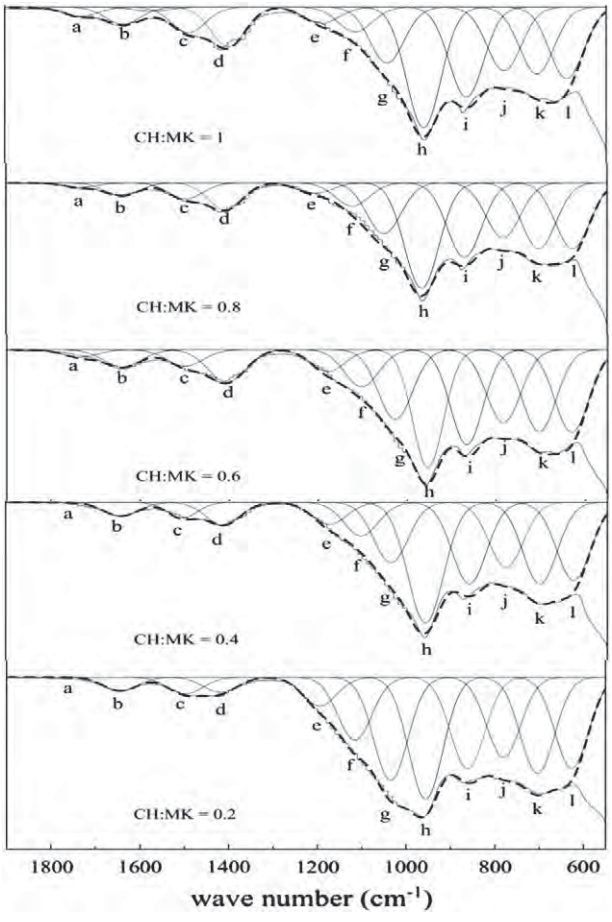


Fig. 5. Deconvolution of FTIR spectra of pozzolanic reaction products with different CH:MK ratios.

Table 4
Compressive strength and density of CH–MK products with different CH:MK ratios.

Samples CH:MK	Properties of products	
	Compressive strength (MPa)/Std.	Density (g/cm^3)
0.2	12.0/0.52	1.05
0.4	17.0/0.21	1.06
0.6	17.0/0.76	1.12
0.8	15.0/0.12	1.11
1.0	11.0/0.62	1.10

Std. = standard deviation.

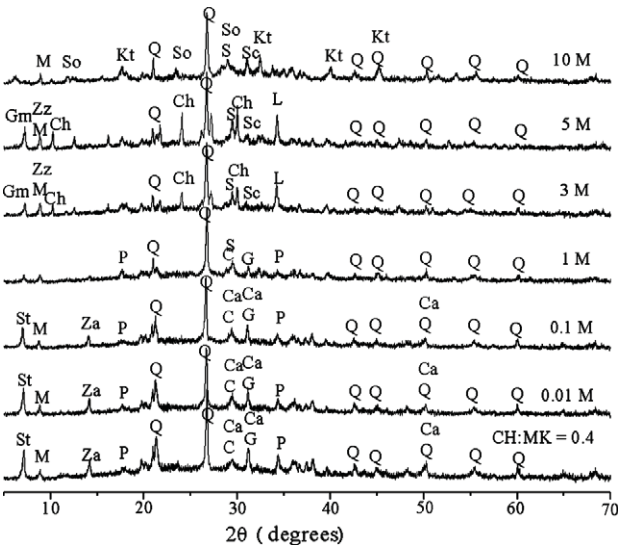
insufficient CH content for the pozzolanic reaction. The highest density of 1.12 g/cm^3 was obtained with the CH:MK of 0.6 and was in good agreement with the highest compressive strength and CSH gel contents confirmed by XRD and FTIR results. However, the density of sample made of CH:MK of 0.4 (1.06 g/cm^3) was slightly lower than that sample made of CH:MK of 0.6 (1.12 g/cm^3), while their strengths were similar. The difference in the density could be from the difference in the secondary phase resulting in different packing behaviors of samples.

3.4. Characteristics and properties of CH and MK mixed product in NaOH solution with different concentration

3.4.1. Mineralogical compositions from XRD patterns

Fig. 6 shows XRD-patterns of the pozzolanic reaction products using CH:MK of 0.4 (CaO/SiO_2 of 1.18) with various alkalinities of 0.01, 0.1, 1, 3, 5, 10 M NaOH solutions. Portlandite was found in samples activated with low NaOH concentration representing incomplete chemical reaction between CaO and SiO_2 and/or Al_2O_3. $CaCO_3$ was also found in samples both with and without alkaline activation. However, muscovite and quartz were still left behind under alkaline activation. At low NaOH concentrations (0.01 and 0.1 M), poorly crystalline CSH (I) and crystalline CASH compounds of stratlingite, gehlenite and zeolite could be observed. At higher NaOH concentration (1 M), stratlingite, zeolite and poorly crystalline CSH (I) disappeared. At 3 M NaOH, sodium aluminosilicate hydrate (NASH) compounds were formed corresponding to chabazite ($Na_{3.16}Al_{3.72}Si_{8.28}O_{24}(H_2O)_{9.68}$, 88-1261) together with the formations of gmelinite ($Na_2Si_4Al_2O_{12}(H_2O)_5$, 75-1682) and zeolite ZK-14 (84-0695). Moreover, some part of Na^+ ions was found in a form of Na_2CO_3. The NASH compound was found around 7.15° 2θ corresponding to gmelinite ($Na_2Si_4Al_2O_{12}(H_2O)_5$, 75-1682) with the presence of lawsonite, ($CaAl_2(Si_2O_7)(OH)_2(H_2O)$, 76-1808). At 5 M NaOH, the phase formation was similar to that of 3 M NaOH. In addition, the combination of sodium and calcium ions could be found in a form of sodium calcium silicate hydrate ($Na_2CaSi_2O_6(H_2O)_2$, NCSH) due to a substitution of Na^+ ion in Ca^{+2} site of CSH compounds (Hong and Glasser, 2004). At 10 M NaOH, NASH, NCSH and katoite (calcium aluminium silicate hydroxide, $Ca_3Al_2(SiO_4)(OH)_8$), 38-0368) occurred with the disappearance of Portlandite. Poorly crystalline CSH (I) and CASH compounds disappeared at the high alkaline activation and NASH was developed in significant quantity. Calcium ions, therefore, precipitated favorably as $CaCO_3$ in a great quantity. At high alkalinity (>1 M) sodium ions from NaOH solution played an important role both in dissolution and precipitation stages.

For alkaline activated CH–MK with CaO/SiO_2 of 1.18, the boundary of phase transformation from no sodium bearing compounds to sodium bearing compounds was at 1 M NaOH. From the above results, pozzolanic reaction products (poorly crystalline CSH (I) and CASH compounds) were found at 0.01 M NaOH, but at 1 M NaOH, pozzolanic reaction products disappeared and NASH was formed and played a role on the obstruction of pozzolanic reaction product formation. The alkaline aluminosilicates viz., NASH in the forms of zeolitic and geopolymeric products were formed rapidly within 24 h (Khale and Chaudhary, 2007) rather than pozzolanic reaction product formation in form of CSH gel and crystalline CASH phases (more than 24 h) (Cabrera and Rojas, 2001; Sabir et al., 2001; Siddique and Klaus, 2009). At the same time of building up geopolymer structure via polymerization, crystalline zeolite could also be formed (Chindaprasirt et al., 2009). Moreover, the [OH^-] species impeded $Ca(OH)_2$ dissolution and resulting in insufficient Ca^{2+} ions existed to achieve saturation and no CSH gel was formed (Alonso and Palomo, 2001b). At 3–5 M NaOH, a large amount of zeolitic products was found as compared with that of 1 M NaOH. For 10 M NaOH



C = calcite, Ca = CSH (I), Ch = chabazite, G = gehlenite, Gm = gmelinite, Kt = katoite, L = lawsonite, M = muscovite,P = portlandite, Q = quartz, S = sodium carbonate, Sc = sodium calcium silicate hydrate, So = sodium alumino silicate hydrate, St = stratlingite, Za = Zeolite A, Zz = zeolite ZK-14

Fig. 6. XRD patterns of alkaline activated CH–MK with 0.4 of CH:MK ratio at various alkaline concentration activations (0.01, 0.1, 1, 3, 5 and 10 M NaOH).

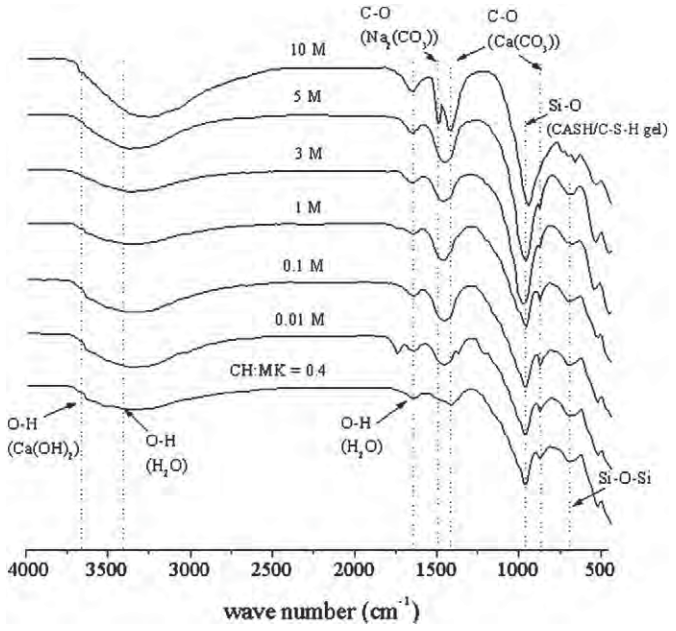


Fig. 7. FTIR spectra of alkaline activated CH–MK with CH:MK of 0.4 at various NaOH concentrations.

activation, both pozzolanic reaction products and zeolitic products disappeared due to the presence of very large amount of [OH^-] species which affected the formation of CSH gel, and the structural rearrangement to form crystalline zeolite was also obstructed. However, geopolymer gel could be formed (Davidovits, 1989, 1991) but was very difficult to be identified by XRD.

3.4.2. Microstructure from FTIR

The FTIR spectra of the mixture at 0.4 CH:MK with 0.01–10 M NaOH are shown in the Fig. 7. Peak around 3630 cm^{-1} corresponded to O–H in calcium hydroxide at 0.01 M, 0.1 and 1 M NaOH activations, but disappeared at 3 M, 5 M and 10 M NaOH activations. The wave number around 550–1800 cm^{-1} represented phase transformation. The spectra in this range were deconvoluted to identify the overlapped peaks as shown in Fig. 8. Si–O stretching vibration peaks around 960–950 cm^{-1} (García et al., 2008, 2010) of CSH gel, and crystalline CASH, NASH and NCSH compounds were found. Peaks around 1030–1073 cm^{-1} of Si–O of quartz (García et al., 2008, 2010) were also found in every NaOH concentration. In addition, the other phase observed in the sample activated by 0.01–5 M NaOH was around 1500–1400 cm^{-1} and 870 cm^{-1} corresponding to C–O vibration of CO_3^{-2} in $CaCO_3$. At 10 M NaOH, the spectrum showed different character from the other NaOH concentrations with two sharp spectrums at around 1500–1400 cm^{-1} and disappeared at 870 cm^{-1}. This suggested that $CaCO_3$ was transformed to the other phase. Moreover, the spectrum around 1070–950 cm^{-1} corresponded to Si–O indicated three categorizes of structures at low 0.01–1 M, medium 3–5 M and high at 10 M NaOH. At 0.01–1 M, sharp peaks around 960–955 cm^{-1} corresponding to Si–O stretching vibration of CSH gel (tobermorite-like structure) (García et al., 2008, 2010) could be observed. At 3–5 M NaOH, peaks around 960–955 cm^{-1} corresponding to Si–O stretching vibration of zeolitic products could be detected. Peaks around 1070–1000 cm^{-1} corresponding to Si–O stretching vibration of quartz and Si–O of geopolymer gel were found. At 10 M NaOH, the height of peaks of around 1000–950 cm^{-1} decreased due to the reduction of zeolitic products. This indicated that the alkalinity affected on phase transformation of samples made of CH:MK ratio of 0.4.

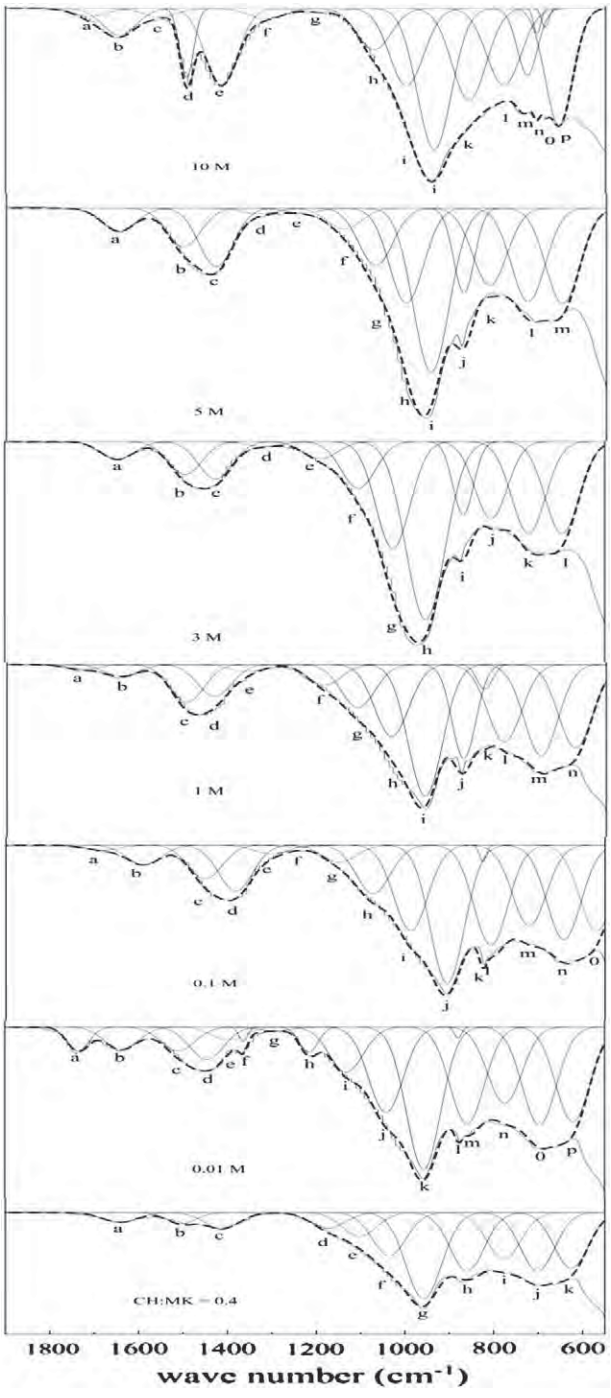


Fig. 8. Deconvolution of FTIR spectra of alkaline activated CH–MK with CH:MK of 0.4 at various NaOH concentrations.

At low concentration of NaOH (<1 M), the pozzolanic reaction was dominant. While the zeolitic reaction and geopolymerization became dominant at medium NaOH concentration (1 M < NaOH < 5 M) and at high NaOH concentration (>5 M), respectively as shown in the following equation.

$$\underset{}{MK + CH + H_2O} \overset{NaOH<1M}{=>} \text{Pozzolanic reaction} \overset{1M<NaOH<5\ M}{=>} \text{Zeolitic reaction} \overset{NaOH>5\ M}{=>} \text{Geopolymerization}$$

3.4.3. Microstructure from SEM

SEM-photomicrographs and EDS spectrum of CH:MK mixture under NaOH activation are shown in Fig. 9. The structure of CH:MK activated with 0.01 and 0.1 M as shown in Fig. 9(b, c) did not change comparing to non-activation system. At 1 M activation as shown in Fig. 9(d), the structure was deformed to have very small particles and fragment. At 3 and 5 M activation as shown in Fig. 9(e, f), the small content of CSH gel (A) and of NASH gel (B) were found as confirmed by EDS. In addition, very small crystalline NASH (C) was found. At the medium range of concentration, microstructures of samples showed highly interconnected phases of CSH and NASH gels. At 10 M as shown in Fig. 9(g), NASH phase was found in form of particulates with particle size around 1 μm. At high NaOH concentration, the development of NASH particles resulted in the disruption of interconnecting phase and the porosity of matrix was thus high.

3.4.4. Mechanical properties and density

The result of compressive strength and density of samples made of 0.4 CH:MK ratio with various NaOH concentrations are shown in Table 5. The highest strength of 19.0 MPa was obtained with 0.01 M NaOH activation due to the formations of both CSH (I) gel and CASH compounds. The strength of 0.1 M NaOH sample slightly decreased to 18.0 MPa. From the microstructure of low alkaline activated products, the CSH gel network was found which affected on the high strength. The strength decreased significantly to 12.0 MPa with an increase in NaOH concentration to 1 M due to the disappearance of CSH (I) gel phase as the pozzolanic reaction was obstructed by [OH^-] species. At 3 M and 5 M NaOH, the compressive strength increased to 13.0 and 17.0 MPa, respectively because zeolitic products viz., chabazite and gmelinite and new CASH compound were formed as the cause of

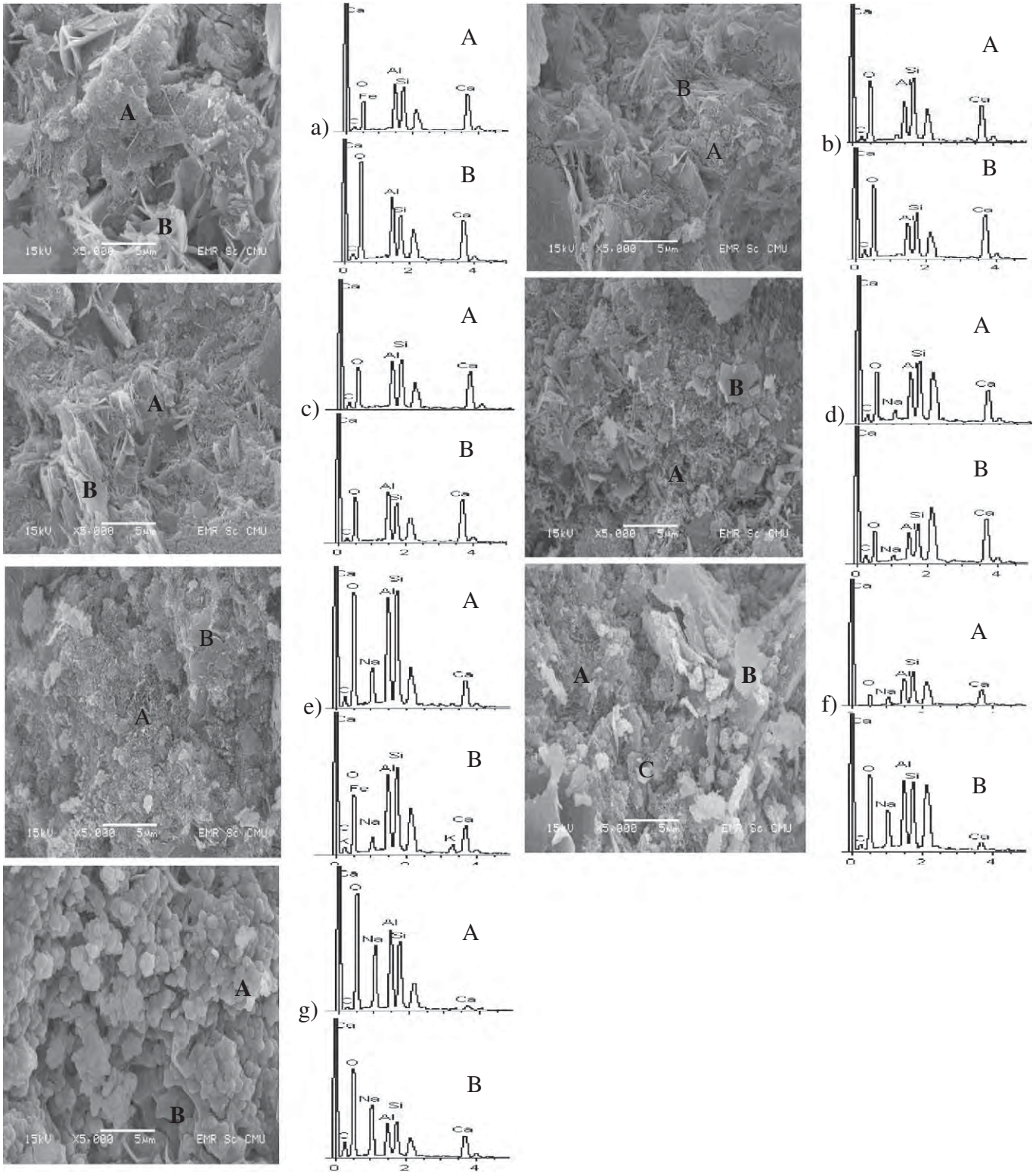


Fig. 9. SEM photomicrographs of CH:MK of 0.4 (a) and CH:MK of 0.4 with NaOH activation at various concentrations, 0.01 M (b), 0.1 M (c), 1 M (d), 3 M (e), 5 M (f) and 10 M (g).

dense microstructure. At 10 M NaOH, the compressive strength greatly decreased to 7.0 MPa due to the structure rearrangement and the formation of zeolitic products was hindered. NCSH compound and geopolymeric gel with a little amount of zeolitic phases was not as strong as CSH gel, CASH compound and zeolitic structures. In addition, the small particles were found in microstructure which implied that as the reason of decreasing of the strength in this product. The results also revealed that density tended to increase with an increase in NaOH concentration.

However, the curing of samples was done at low temperature of 25 °C. The strength of the samples especially at high NaOH concentration could be further improved with moderate temperature curing (45–70 °C) (Boonserm et al., 2012; Chindaprasirt et al., 2012; Hewlett, 1988).

Table 5
Compressive strength and density of alkaline activated CH–MK products with CH:MK of 0.4 at various NaOH concentrations.

Alkaline activation of CH:MK of 0.4	Properties of products	
	Compressive strength (MPa)/Std.	Density (g/cm^3)
Non-activation	17.0/0.52	1.06
0.01 M	19.0/0.60	1.06
0.1 M	18.0/0.23	1.08
1 M	12.0/0.43	1.03
3 M	13.0/0.18	1.11
5 M	17.0/0.89	1.16
10 M	7.0/0.65	1.35

Std. = standard deviation.

4. Conclusions

This study investigated the phase development due to pozzolanic reaction of MK and CH with alkaline activation. The conclusions were as follows;

1. The CH:MK ratios of 0.4 and 0.6 with CaO/SiO_2 (amorphous SiO_2) of 1.18 and 1.76 were the proper conditions to complete the pozzolanic reaction of MK as indicated by the higher pozzolanic reaction product contents of CSH gel and crystalline CASH compounds than those at the other ratios. This resulted in the high compressive strength of lime calcined clay materials.
2. The strength of CH:MK of 0.4 with alkaline activation at low NaOH concentration (0.01 and 0.1 M NaOH) was higher due to the formation of CSH (I) gel. At slightly higher NaOH concentration (1 M), the strength was significantly reduced due to the reduction of CSH (I) gel phase. At moderate NaOH concentrations (3 and 5 M), CSH (I) gel disappeared while zeolitic products, and NASH and NCSH compounds were formed and strength improved to be slightly less than those at the low NaOH concentration. A high NaOH concentration (10 M), the zeolitic products disappeared and alkali aluminosilicate hydrate was formed and adversely affected the strength.
3. The reaction of the mixture was dependent on the NaOH concentration. At low concentration of NaOH (<1 M), the pozzolanic reaction was dominant. The zeolitic reaction was dominant at medium NaOH concentration (1 M < NaOH <5 M) and geopolymerization became dominant at high NaOH concentration (>5 M).

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Investigation of Properties of Lightweight Concrete with Calcined Diatomite Aggregate

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Abstract

This paper reports the investigation of the properties of Lightweight Concrete (LWC) made from Portland cement and diatomite aggregate. The chemical and physical properties of diatomite and the mechanical properties of LWC with regard to the effects of calcined temperature and gradation were studied. The uncalcined diatomite was crushed and calcined at 400, 600, and 800°C for 4 hours and used as lightweight aggregate. A constant Water to Cement ratio (W/C) of 2.0 and Aggregate to Cement ratio (A/C) of 1.6 were used for all mixes. The 28-day compressive strength of LWC of 6.4-11.9 MPa, porosity and water absorption of 34.0-49.4%, modulus of elasticity of 2.0-4.3 GPa, thermal conductivity of 0.166-0.192 W/mK, and unit weight of 1170-1300 kg/m^3 were obtained. The results indicated that the strength of concrete increased when the calcined temperature of diatomite and the amount of small-size aggregate were increased. The increase in temperature ridded the burnable elements and improved the properties of diatomite. The small-size aggregate produced good matrix-aggregate bonding and enhanced the strength of concrete. The calcined diatomite could, therefore, be used as good aggregate in making lightweight concrete.

Keywords: *lightweight aggregate, concrete, diatomite, compressive strength, unit weight, porosity, modulus of elasticity*

1. Introduction

Diatomite is a soft sedimentary rock and composed of fossil skeletons of phytoplankton, also known as diatom. It originated in fresh and salt water since the Eocene period and the main composition is amorphous silicon dioxide (SiO_2) (De Rojas *et al.*, 1999). Its beneficial characteristics includes lightweight due to high porosity and attractive dark-yellow shade due to high content of ferrous compound and semi-crystalline siliceous phase (Owen and Utha-aroom, 1999; Pimraksa and Chindaprasirt, 2009). The diatomite could, therefore, be used as lightweight aggregate for Lightweight Concrete (LWC).

LWC is a concrete with unit weight less than normal concrete and not exceeding 1840 kg/m^3 (ASTM C330-89, 1989). The purpose is to reduce the dead load of structure resulting in smaller and lighter structures and also with reduced cement content. The production of cement is an energy intensive operation and accounts for about 7% of the green house gas produced annually (Malhotra, 2002). Lightweight aggregate are popular for use in concrete because they offer some improved physical properties such as high insulating coefficient and superior sound-dampening quality (Jo *et al.*, 2007). The production of LWC is expanding and now includes all types of no-fines concrete of low density of 300-1200 kg/m^3 for block production (Chandra, 2002).

This research aims to use diatomite as lightweight aggregate in making LWC with improved physical properties. The knowledge of the use of diatomite in producing LWC would be beneficial to future applications of this material in the construction industry.

2. Experimental Program

2.1 Materials and Preparation

2.1.1 Materials

Materials consist of Ordinary Portland Cement (OPC) and Diatomite (DE) from Lampang province in northern Thailand.

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Table 1. Chemical Composition of DE (by Weight)

Chemical compositions (%)	25DE	400DE	600DE	800DE
SiO_2	74.30	76.09	78.40	78.29
Al_2O_3	8.07	7.98	8.18	9.43
Fe_2O_3	5.35	5.46	5.19	7.08
CaO	0.48	0.43	0.47	0.54
K_2O	1.76	1.89	1.99	2.21
TiO_2	0.11	0.43	0.51	0.51
Na_2O	0.15	0.13	0.12	0.17
P_2O_5	0.11	0.08	0.09	0.11
BaO	0.04	0.04	0.04	0.04
MgO	0.47	0.43	0.47	0.56
LOI	9.10	7.00	4.50	1.00

Table 2. Physical Properties of DE

Materials	FA	MA	CA
Particle size (mm)	0.001-1.18	1.18-4.75	4.75-12.5
Fineness modulus	1.33	4.02	5.75
Unit weight (kg/m^3)	600	425	417
Water absorption (%)	61	102	112

The uncalcined DE was crushed and then classified as Fine Aggregate (FA), Medium Aggregate (MA), and Coarse Aggregate (CA). The DE aggregates were calcined and kept in the dry condition and used for the mix for ease of control and comparison. They were then calcined at 400, 600, and 800°C for 4 hours (Pimraksa and Chindaprasirt, 2009). The chemical compositions are shown in Table 1 and the physical properties are shown in Table 2. The DE consisted of a high content of SiO_2 with some Al_2O_3, Fe_2O_3, and SO_3. The other compounds viz., CaO, MgO, K_2O, and TiO_2 are also presence in a small quantity.

2.1.2 DE Aggregate Series

Three DE aggregate series were used for the preparation of LWC. As the effect of small aggregate portion is larger than that of large portion (Unal *et al.*, 2007), the CA portion was kept constant and the FA and MA portions were varied. A total of three aggregate series viz., series A, B, and C with FA:MA:CA ratios of 0:70:30, 30:40:30, and 70:0:30, respectively were used as shown in Table 3.

2.2 Mix Details

2.2.1 Mix Proportion

All mixtures were made with Water to Cement ratio (W/C) of 2.0 and Aggregate to Cement ratio (A/C) of 1.6. From trial mixes, the W/C of 2.0 was needed as the DE aggregates were porous. The A/C of 1.6 was selected as higher A/C produced very dry mixes and the casting was difficult. The details of the mixes are given in Table 3. The uncalcined DE (25°C), DE calcined at 400, 600, and 800°C are denoted by 25DE, 400DE, 600DE, and 800DE, respectively.

Table 3. Mix Proportions of Lightweight Concrete

DE	Series	Aggregate			W/C	A/C
		FA (%)	MA (%)	CA (%)		
25DE	A	0	70	30	2.0	1.6
	B	30	40	30		
	C	70	0	30		
400DE	A	0	70	30	2.0	1.6
	B	30	40	30		
	C	70	0	30		
600DE	A	0	70	30	2.0	1.6
	B	30	40	30		
	C	70	0	30		
800DE	A	0	70	30	2.0	1.6
	B	30	40	30		
	C	70	0	30		

2.2.2 Mixing

The OPC and DE were firstly mixed until the mixture was homogenous which took approximately 1½ minutes. Afterward, water was added and the mixing was done for another 1½ minutes. The fresh concretes were immediately cast in 50 × 50 × 50 mm cube molds in accordance with ASTM C109 (2002), and in 100 × 100 × 100 mm cube molds, and 150 × 300 mm cylindrical molds in accordance with ASTM C39 (2001). The specimens were covered with damp cloth and plastic sheet to prevent moisture loss and stored in a 25°C controlled room.

2.3 DTA and TGA, XRD, and SEM

The Differential Thermal Analysis (DTA) and Thermal Gravitation Analysis (TGA) were performed on DE to investigate its physical and chemical changes during heating (Kroehong *et al.*, 2011). Mineralogical compositions of as-received DE were determined using X-Ray Diffraction (XRD) and morphological composition using Scanning Electron Microscope (SEM) (Pimraksa and Chindaprasirt, 2009).

2.4 Compressive Strength

The 50 × 50 × 50 mm cube specimens were tested to determine the compressive strength at the age of 28 days in accordance with ASTM C109 (2002). The reported results were the average of three samples.

2.5 Porosity and Water Absorption

The 100 × 100 × 100 mm cube specimens were tested for the porosity and water absorption at the age of 28 days in accordance with ASTM C642 (2006). The porosity was calculated using Eq. (1) whereas, Eq. (2) was used for the calculation of water absorption. For porosity measurement, the specimens were boiled for 5 hr and then allowed to cool for not less than 14 hr to a final temperature of 20 to 25°C. The surface moisture of the specimen was then removed with a towel and the mass of specimen determined.

The methods for measuring porosity and absorption were used

successfully in a number of researches (Chindaprasirt and Rukzon, 2008; Rukzon and Chindaprasirt, 2008; Thokchom *et al.*, 2009). The reported results were the average of three samples.

$$\text{Porosity}(\%) = [(C-A)/(C-D)] \times 100 \quad (1)$$

$$\text{Absorption}(\%) = [(B-A)/A] \times 100 \quad (2)$$

Where, A = Mass of oven-dry sample in air (g)
B = Mass of surface-dry sample in air after immersion (g)
C = Mass of surface-dry sample in air after immersion and boiling (g)
D = Apparent mass of sample in water after immersion and boiling (g)

2.6 Unit Weight

The unit weight was determined as described in ASTM C138 (2009). The unit weight was measured at the ages of 28 days using the compressive strength specimens. The reported results were the average of three samples.

2.7 Modulus of Elasticity

The 150 × 300 mm cylinder specimens were tested for the chord modulus at the age of 28 days in accordance with ASTM C469 (2002). The reported results were the average of two samples.

2.8 Thermal Conductivity

The 50 × 50 × 50 mm cube specimens were tested to determine the thermal conductivity at the age of 28 days in accordance with ASTM D5930 (2009). The reported results were the average of three samples.

3. Result and Discussions

3.1 Scanning Electron Microscopy

The results of SEM of DE are shown in Fig. 1. The DE consisted of cylindrical shape particles approximately 10 μm in diameter and 30 μm in length with square cellular structure as shown in Fig. 1(a). The surface consisting of micro-pores made DE very porous and low in density (Pimraksa and Chindaprasirt, 2009; Pimraksa *et al.*, 2011). The calcination at temperatures of 400, 600, and 800ºC for 4 hours did not appear to drastically change the morphology of particles. The cylindrical shape particles with cellular surface were still easily detected as shown in Figs. 1(b)-1(d).

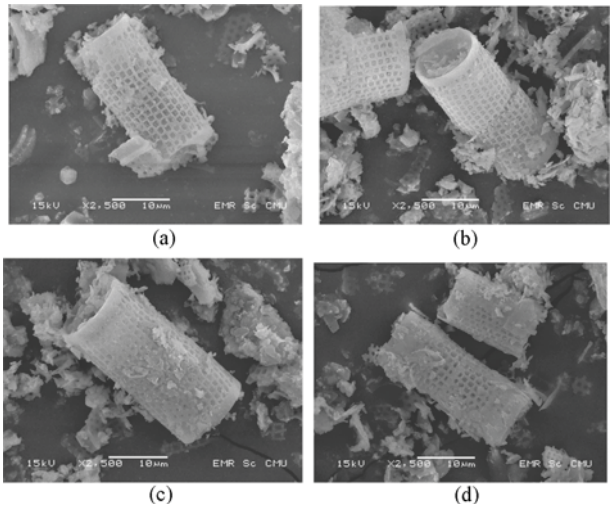


Fig. 1.SEM Photomicrographs of Diatomite: (a) Uncalcined DE (25DE), (b) 400DE, (c) 600DE, (d) 800DE

3.2 Differential Thermal Analysis (DTA) and Thermal Gravitation Analysis (TGA)

The results of DTA and TGA of diatomite are shown in Fig. 2. The endothermic peaks were observed at 71.6°C and 148.8ºC and were associated with loss of adsorbed water on particle surfaces of diatomite. The other peak at 482.2ºC ascribed to loss of dehydroxylation of clay minerals containing in DE (Pimraksa and Chindaprasirt, 2009). This, therefore, indicated that the optimum calcined temperature for reactive diatomite should not be less than 482ºC.

3.3 Mineralogical and Morphological Composition using XRD

The XRD results of DE are shown in Fig. 3. The DE contained

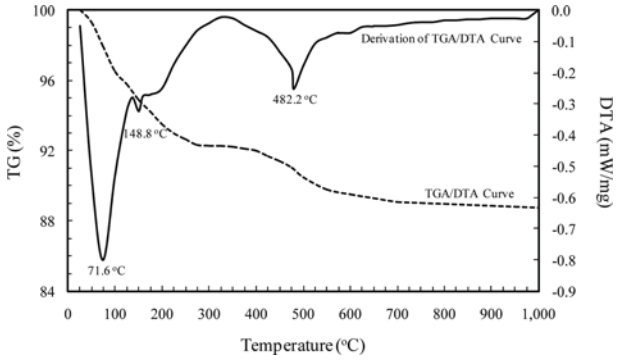


Fig. 2. DTA and TG Curves of Diatomite

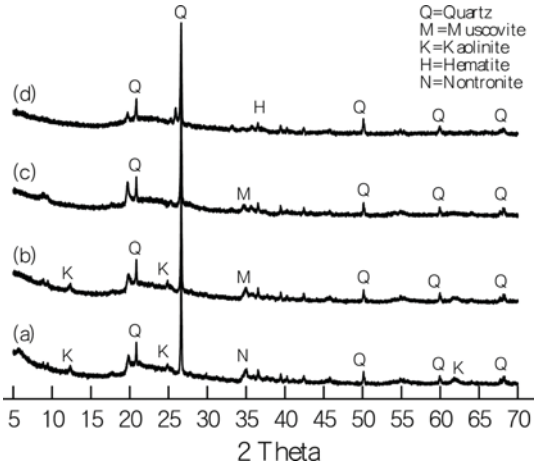


Fig. 3. XRD Patterns of Calcined DE: (a) Uncalcined DE, (b) 400ºC, (c) 600ºC, (d) 800ºC

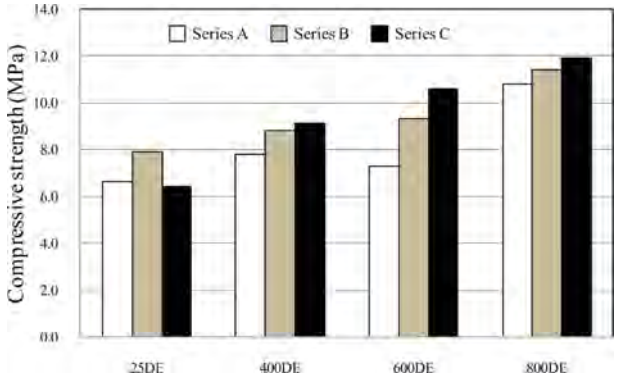


Fig. 4. Compressive Strength at 28 Days Lightweight Concrete

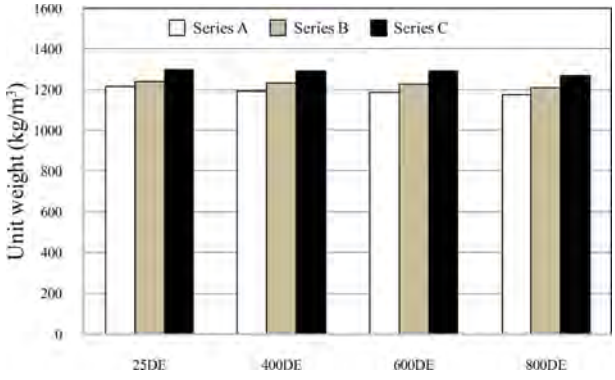


Fig. 5. Unit Weight at 28 Days of Lightweight Concrete

mainly quartz, kaolinite and some nontronite. Calcination at 400°C reduced the peaks of kaolinite and nontronite. At higher temperature of 600°C, the kaolinite and nontronite peak disappeared. This corresponded to the dehydroxylation of kaolinite when clay mineral (kaolinite) were calcined and thus became active (Baronio and Binda, 1997). This was confirmed by the disappearance of main peaks of kaolinite at 12.5, 24.8, and 61.8° 2θ. At 800°C, a small amount of hematite was observed. This mineral was stable and indicated that the calcinations temperature should be less than 800°C in order to obtain amorphous phase of DE and for the reduction of cost of calcination.

3.4 Compressive Strength

The results of compressive strength of lightweight concrete are shown in Fig. 4. The compressive strength slightly increased with the increasing calcined temperature of DE. For example, the 28-day compressive strengths of series B mixes for the 25DE, 400DE, 600DE, and 800DE were 7.9, 8.8, 9.3, and 11.4 MPa, respectively. The low compressive strength of the 25DE mix was due to the unstable and swelling of kaolinite (Charles *et al.*, 2007). The strength of 400DE mix was also low compared with those of 600DE and 800DE mixes. This conformed to the results of the DTA and TGA which indicated that the calcined temperature of DE should not be less than 482°C. A number of researches suggested the calcined temperature between 600-800°C as optimum temperature for DE (Pimraksa and Chindaprasirt, 2009; Pimraksa *et al*., 2011).

With regards to aggregate sizes, the mixes with a high amount of FA showed high compressive strength compared to those with the low amount of FA. For example, the 28-day compressive strengths of mixes with 600DE series A, B, and C were 7.3, 9.3, and 10.5 MPa, respectively. The small DE aggregate with high surface area resulted in the better bonding of matrix and aggregate than that of large DE leading to an increase in strength (Husem, 2003). Similar finding on the reduction of strength with the increase in coarse aggregate was reported (Unal *et al.*, 2007).

3.5 Unit Weight

The results of the unit weight of lightweight concretes are shown in Fig. 5. The unit weight slightly decreased with the increasing calcined temperature of DE and increased with the increasing amount of FA. For example, the unit weight of the concretes with 25DE, 400DE, 600DE, and 800DE of series A were 1216, 1193, 1185, and 1174 kg/m^3, respectively. The increased in calcined temperature resulted in a DE with a slightly reduced unit weight compared to the uncalcined DE, due to the calcination of burnable elements (Pimraksa and Chindaprasirt, 2009). The unit weight of series A, B, and C mixes with 800DE were 1174, 1211, and 1271 kg/m^3, respectively. The unit weights of FA, MA, and CA were 600, 425, and 417 k/m^3, respectively (Table 2). For series C mixes, the high amount of FA (small DE aggregate) filled the space in the matrices and made concrete more compact and stronger than those using low amount of FA.

3.6 Porosity and Water Absorption

The results of the porosity and water absorption are shown in Figs. 6 and 7. The porosities and water absorptions at the age of 28 days were obviously lowered with the increasing calcination temperature and amount of FA. The increase in calcined temperature reduced the burnable elements such as clay mineral kaolinite (Pimraksa and Chindaprasirt, 2009) as indicated by the result of mineralogical composition in Fig. 3. The burnable element was responsible for the high absorption of water. The increase in temperature thus slightly reduced the water absorption and porosity. For example, the porosities at 28 days of 25DE,

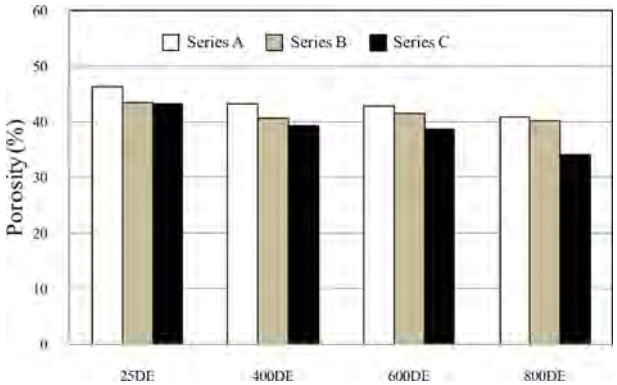


Fig. 6. Porosity at 28 Days of Lightweight Concrete

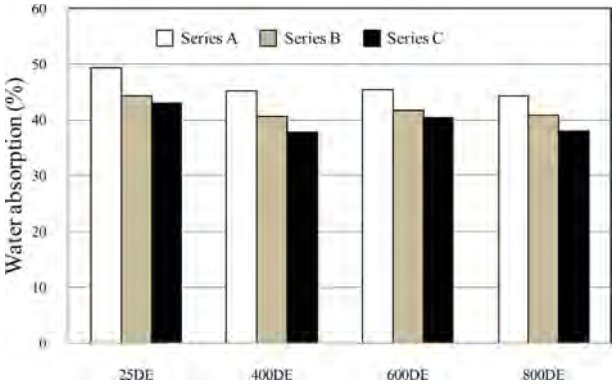


Fig. 7. Water Absorption at 28 Days of Lightweight Concrete

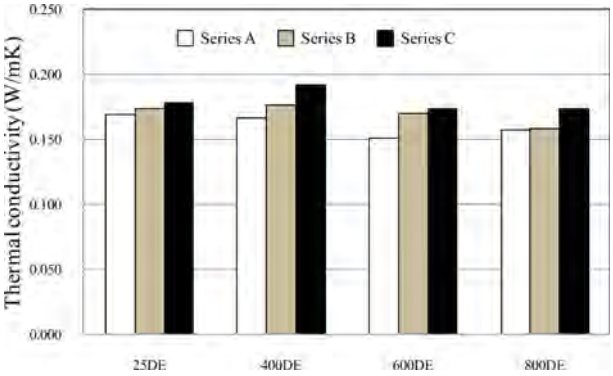


Fig. 9. Thermal Conductivity at 28 Days of Lightweight Concrete

400DE, 600DE, and 800DE of series C mixes were 43.2, 39.2, 38.7, and 34.0%, respectively and the porosities at 28 days of series A, B, and C of 800DE mixes were 40.9, 40.2, and 34.0%, respectively.

The water absorption slightly decreased with the increasing in calcination temperature and amount of FA in the same manner as the porosities. The water absorption at 28 days of 800DE mixes of series A, B, and C were 44.4, 40.9, and 37.9%, respectively. The water absorption increased with the increasing porosity as expected.

3.7 Modulus of Elasticity

The results of modulus of elasticity are shown in Fig. 8. The modulus of elasticity of LWC significantly increased with the increasing calcined temperature and amount of FA. The increase in calcined temperature to 600-800°C improved the properties of aggregate (Pimraksa and Chindaprasirt, 2009; Pimraksa *et al*., 2011; Yılmaz and Ediz, 2008; Zuhua *et al.*, 2009) and hence, its use resulted in the increased in modulus of elasticity. The increase in amount of FA also resulted in the increase in modulus of elasticity due to the small DE aggregates filled the space in matrices which made the concrete more compact and stronger than that with large DE. For example, the moduli of elasticity of 800DE mixes of series A, B, and C were 2.91, 3.56, and 4.33 GPa, respectively.

3.8 Thermal Conductivity

The results of the thermal conductivity of lightweight concretes are shown in Fig. 9. The thermal conductivity slightly decreased with the increasing calcined temperature of DE. For example, the thermal conductivity of the concretes with 25DE, 400DE, 600DE, and 800DE of series B were 0.174, 0.176, 0.170, and 0.158 W/mK, respectively. The reduction was due to the ridding of water molecule and other burnable minerals in aggregate with high calcination temperature (Pimraksa and Chindaprasirt, 2009). The reduction in the thermal conductivity is rather attractive thermal property of this LWC. The thermal conductivity increased with the increasing amount of FA.

The thermal conductivity values of series A, B, and C mixes with 600DE were 0.151, 0.170, and 0.174 W/mK, respectively. The thermal conductivity increased with the increasing of FA due to the increases in the filling of voids of small aggregate and the increase in the bonding of the small aggregate and the matrix and due to increased surface area and pozzolanic property of the aggregate.

3.9 Relationship of Compressive Strength, Modulus of Elasticity, Thermal Conductivity, Unit Weight, and Calcined Temperature

The relationship between modulus of elasticity and compressive strength of LWC is shown in Fig. 10. The modulus of elasticity tended to increase linearly to the square root of compressive

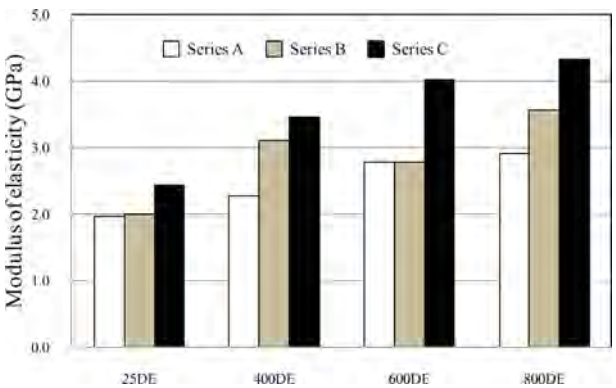


Fig. 8. Modulus of Elasticity at 28 Days of Light Weight Concrete

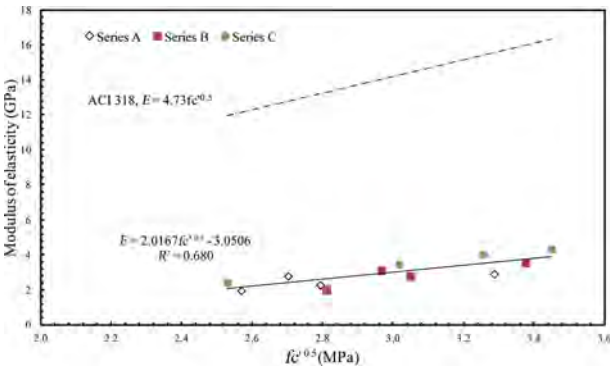


Fig. 10. Modulus of Elasticity of Lightweight Concrete

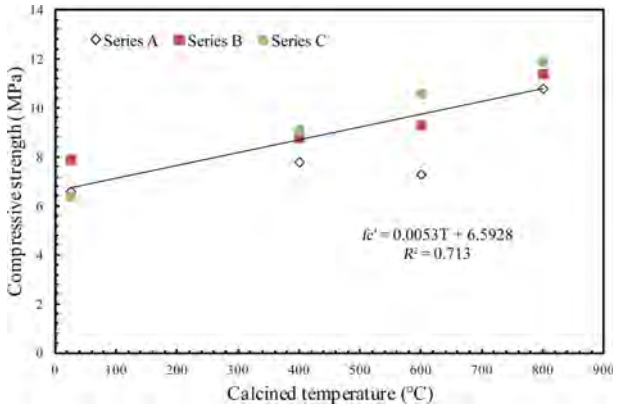


Fig. 11. Relationship between Compressive Strength and Calcined Temperature

strength. The relationship could be predicted in the form shown in Eq. (3). The resulted showed the same trend as that of other research (Chindaprasirt, 1980). The results indicated the modulus of elasticity between 2.0-4.3 GPa which is substantially lower than that of ACI 318 (2000) for normal concrete (Unal *et al.*, 2007). The trends of the relationship of the modulus of elasticity and the square root of compressive strength were similar.

$$E = 2.0167\sqrt{f_c'} - 3.0506 \quad (3)$$

Where E is modulus of elasticity (GPa) and f_c' is compressive strength (MPa).

Figure 11 shows the relationship of compressive strength and the calcined temperature of DE. The compressive strength increased with the increasing calcined temperature (Pimraksa *et al.*, 2011) and could be described by Eq. (4).

$$f_c' = 0.0053T + 6.5928 \quad (4)$$

Where f_c' is compressive strength (MPa) and T is temperature for calcined diatomite (C).

In addition, there appear to be a relationship between thermal conductivity and unit weight as shown in Fig. 12 and by Eq. (5). The unit weight increased with the increasing thermal conductivity

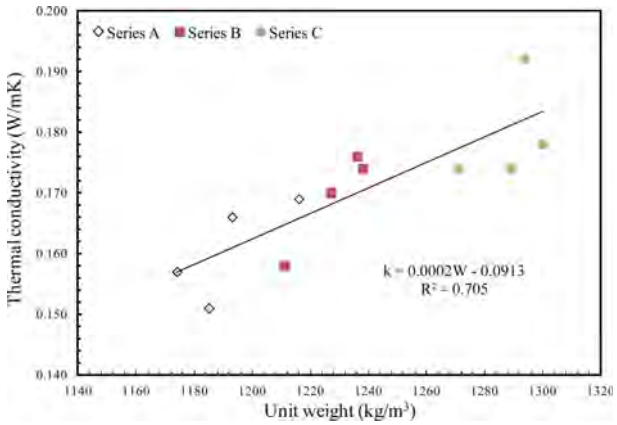


Fig. 12. Relationship between Thermal Conductivity and Unit Weight

(Uysal *et al.*, 2004). The thermal conductivity is, therefore, a function of density (Lu-Shu, 1980) as the unit weight increased, the void in the LWC reduced and the thermal conductivity increased.

$$k = 0.0002W - 0.0913 \quad (5)$$

Where k is thermal conductivity (W/mK) and W is unit weight (kg/m^3).

4. Conclusions

The calcined DE is a suitable material for making good lightweight concrete. The use of calcined DE aggregate increased compressive strength and modulus of elasticity, and reduced unit weight, porosity, water absorption, and thermal conductivity compared to those with uncalcined DE. The calcined temperatures of DE should be between 600-800°C. The aggregate sizes also had significant affect on the properties of LWC. The properties was improved with the increased amount of small aggregate due to the filling of space in the matrices which made concrete more compact and stronger than that with large aggregate. In addition, the lightweight concrete with compressive strength of 12.0 MPa and density of 1200 kg/m^3 could be classified as masonry concrete according to ASTM C331 (2010).

Acknowledgements

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Synthesis and characterization of $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ ceramics by hydrothermal method

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Abstract

$Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZO) ceramics were prepared from nanopowders using a hydrothermal method. The phases and microstructures of samples were characterized by X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The XRD results indicate that the ceramic samples have a pseudo-cubic phase structure with a small $CaTiO_3$ phase observed at 1100 and 1200 °C. The samples were dense and the average grain sizes increase with increasing sintering temperature and were 0.89, 3.53 and 12.09 μm for sintering temperatures at 1100, 1200 and 1300 °C, respectively. The dielectric constants, ferroelectric hysteresis loops and piezoelectric strain factors of BCZTO ceramics were also investigated. The results show that their values increase with the increase in average grain size of ceramic samples.
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Keywords: $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$; Hydrothermal method; Dielectric constant; Ferroelectric hysteresis loop; Piezoelectric strain factor

1. Introduction

Ferroelectric materials with a perovskite structure have been extensively studied due to their wide applications in the fabrication of multilayer ceramic capacitors, actuators and electromechanical transducers [1]. Most of them belong to the family of lead-based perovskite oxides such as $PbTi_{1-x}Zr_xO_3$ (PZT) [2], $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) [3] and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) [4] and have attracted a lot of attention due to their excellent ferroelectric, dielectric and piezoelectric properties. However, these compositions have the obvious disadvantage of volatility and toxicity of lead. Therefore, the scientific community has been searching for new materials with appropriate chemical and physical properties in order to replace the Pb-based compounds for environmentally friendly applications. There are many lead-free materials with perovskite structure such as $BaTiO_3$ (BT) [5,6], $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ (BCZTO) [7–9] $(Bi,Na)TiO_3$ (BNT) [10], and $(Na,K)NbO_3$ (NKN) [11]. These materials have been investigated in terms of their diffuse phase transition, dielectric, ferroelectric and piezoelectric properties.

Among these compounds, the BCTZO compounds have been widely investigated because it is shown to possess a large piezoelectric coefficient (d_{33}) of 620 pC/N for $0.5Ba_{0.7}Ca_{0.3}TiO_3$–$0.5BaTi_{0.8}Zr_{0.2}O_3$ (BZT–BCT) composites [12]. This spurs the researcher's interest on the effects of the doping proportion, poling and sintering process of polymorphic phase transition temperatures, dielectric constant and piezoelectric properties. In particular, the high-performance BZT–BCT ceramics with various compositions were obtained [13–16]. The structure is close to a morphotropic phase boundary (MPB) showing excellent dielectric constant and piezoelectric properties. The dielectric constant and piezoelectric properties of $(Ba_{0.9}Ca_{0.1})(Ti_{0.85}Zr_{0.15})O_3$ ceramics can be improved by an increase in grain size [17]. However, the high sintering temperatures over 1300 °C are required for large grain size and dense ceramics. Therefore, it is necessary to use nano size

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powders in the synthesis. The hydrothermal method which is effective for the synthesis of BZT–BCT nanopowders at low sintering temperature may lead to a dense structure and excellent electrical properties of samples.

In this study, the $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZO) ceramics prepared from nanopowders synthesized using a hydrothermal method with low sintering temperature were reported. The phase and microstructure of samples were investigated by X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The dielectric constants, ferroelectric hysteresis loops and piezoelectric strain factors of the low sintering temperature BCZTO ceramics were also investigated.

2. Experimental

The BCZTO powders were prepared by hydrothermal method with $Ba(OH)_4$ (95%, Aldrich), $Ca(NO_3)_2.4H_2O$ (99.9%, Kanto chemical), $ZrCl_2O.8\ H_2O$ (99%, Kanto chemical), and TiO_2 (99%, Aldrich) as the starting materials. Initially, all materials were dissolved in de-ionized water under vigorous magnetic stirring for 10 h, and then NaOH solution with various concentrations (2 M, 6 M and 10 M) was added to the mixture. The solution was stirred using a magnetic stirrer at room temperature for another 10 h and transferred to the Teflon-lined stainless steel autoclave for hydrothermal treatment at 240 °C for 16 h. It was then left to cool down to room temperature. The product was washed with de-ionized water to remove sodium ions and dried in an oven at 80 °C for further characterization and fabrication of ceramic samples. The obtained powders were ground and mixed with 3wt% polyvinyl alcohol (PVA) binder. The mixed powders were pressed into discs with 13 mm in diameter and 1.5 mm in thickness. The disc samples were sintered at 1100, 1200, and 1300 °C for 3 h in air.

The obtained powders and sintered samples were characterized by XRD using PW3040 Philips X-ray diffractometer with CuK_α radiation ($\lambda = 0.15406$ nm), The Netherlands. For the structural analysis, the Rietveld refinement was performed on the XRD pattern to determine the phase contents using the X' Pert HighScore Plus software. The morphology and structure of these samples were characterized by a SEM (JEO VP1450, UK). The ceramic samples were polished to obtain the thickness of approximately 1 mm and were painted with silver paint and used as the electrode. The dielectric properties of the pasted ceramics were measured at different frequencies in the temperature range from −50 to 200 °C using Agilent 4294 A Precision impedance analyzer. The ferroelectric hysteresis loops of the pasted ceramics were measured using a modifier Sawyer-Tower circuit at room temperature with a frequency of 50 Hz. The piezoelectric properties of the pasted ceramics were polarized at room temperature in silicon oil for 20 min under an electric field of 1.5 kV/mm. After being held for 24 h at room temperature, the piezoelectric strain factor (d_{33}) of the pasted ceramics was measured using a d_{33} meter (Model 90-2030, APD International, Ltd.).

3. Results and discussion

The XRD patterns of the BCTZO powders synthesized at 240 °C for 16 h with 2 M, 6 M and 10 M solutions are shown in Fig. 1. All the BCTZO powders have a pseudo cubic-perovskite structure with $BaTiO_3$-like phase (JCPDS no. 31-0174). The impurity phases of $CaTiO_3$ (JCPDS no. 22-0153) and $BaZrO_3$ (JCPDS no. 06-0399) were also observed. The impurity phase of $BaZrO_3$ slightly increased when the NaOH concentration increased from 2 M to 6 M, and was not detected with 10 M NaOH sample. The $CaTiO_3$ phase slightly decreased with increasing NaOH concentration. This indicated that Zr^{4+} ions had entered the perovskite structure while only a small amount of Ca^{2+} ions had entered into $BaTiO_3$ lattices and formed $CaTiO_3$.

The peaks of $BaTiO_3$ were clearly observed and thus the particle size could be calculated with confidence. The average crystalline size (D) of BCTZO powders for 2 M, 6 M and 10 M NaOH were calculated from X-ray line broadening of the reflection planes (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0) and (2 1 1) using Scherrer's equation with $D = k\lambda/(\beta \cos\theta)$, where λ is the wavelength of the X-ray radiation, k is a constant taken as 0.98, θ is the diffraction angle and β is the full width at half maximum [18]. The D values from this calculation are 31.4 ± 6.5, 27.8 ± 5.3 and 25.3 ± 5.3 nm for 2 M, 6 M and 10 M NaOH solutions, respectively. The lattice parameters were also calculated as shown in Table 1. The SEM micrograph of BCTZO powders are shown in Fig. 2. The nanoparticles are uniform in size with average particle sizes of 304.2, 262.5 and 227.9 nm for 2 M, 6 M and 10 M NaOH solutions, respectively and the particles are agglomerated. The XRD and SEM results confirmed that the particles were nano-particle and the size slightly reduced with increasing NaOH concentration.

XRD patterns of BCTZO ceramics as shown in Fig. 3 indicated the presence of the pseudo cubic-perovskite structure with $BaTiO_3$-like phase. The impurity phase of $CaTiO_3$ was observed in the samples sintered at 1100 and 1200 °C. This indicates that the Zr^{4+} ions substituted Ti^{4+} ions at the B sites

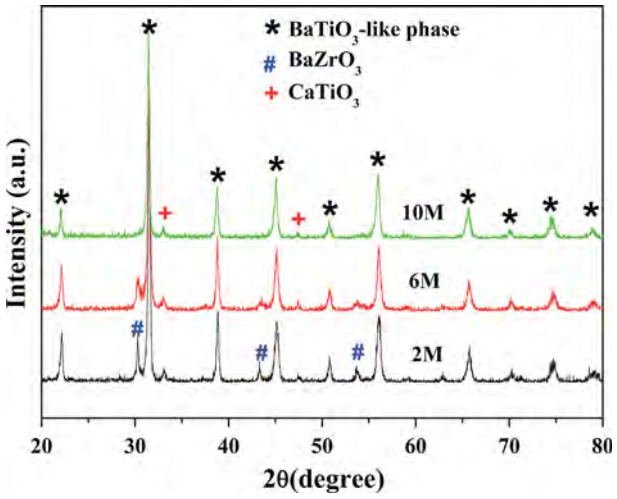


Fig. 1. XRD patterns of BCTZO nanopowders synthesized at 240 °C for 16 h with NaOH concentrations of 2 M, 6 M and 10 M.

Table 1
Various parameters of BCTZO powders synthesized at 240 °C for 16 h of NaOH content as 2, 6 and 10 M.

Various parameters	**Various NaOH content**		
	2 M	6 M	10 M
Phase (%Weight fraction)	(1) $BaTiO_3$-like phase (77.4%) (2) $BaZrO_3$ (9.6%) (3) $CaTiO_3$ (13.0%)	(1) $BaTiO_3$-like phase (76.3%) (2) $BaZrO_3$ (12.5%) (3) $CaTiO_3$ (11.2%)	(1) $BaTiO_3$-like phase (90.4%) (2) $BaZrO_3$ (0%) (3) $CaTiO_3$ (9.2%)
Good fit	1.152	1.050	1.121
Average crystalline size (nm) by XRD	31.4 ± 6.5	27.8 ± 5.3	25.3 ± 5.3
Lattice parameter (Å)	4.0207	4.0192	4.0235
Average particle size (nm) by SEM	304.2	262.5	227.9

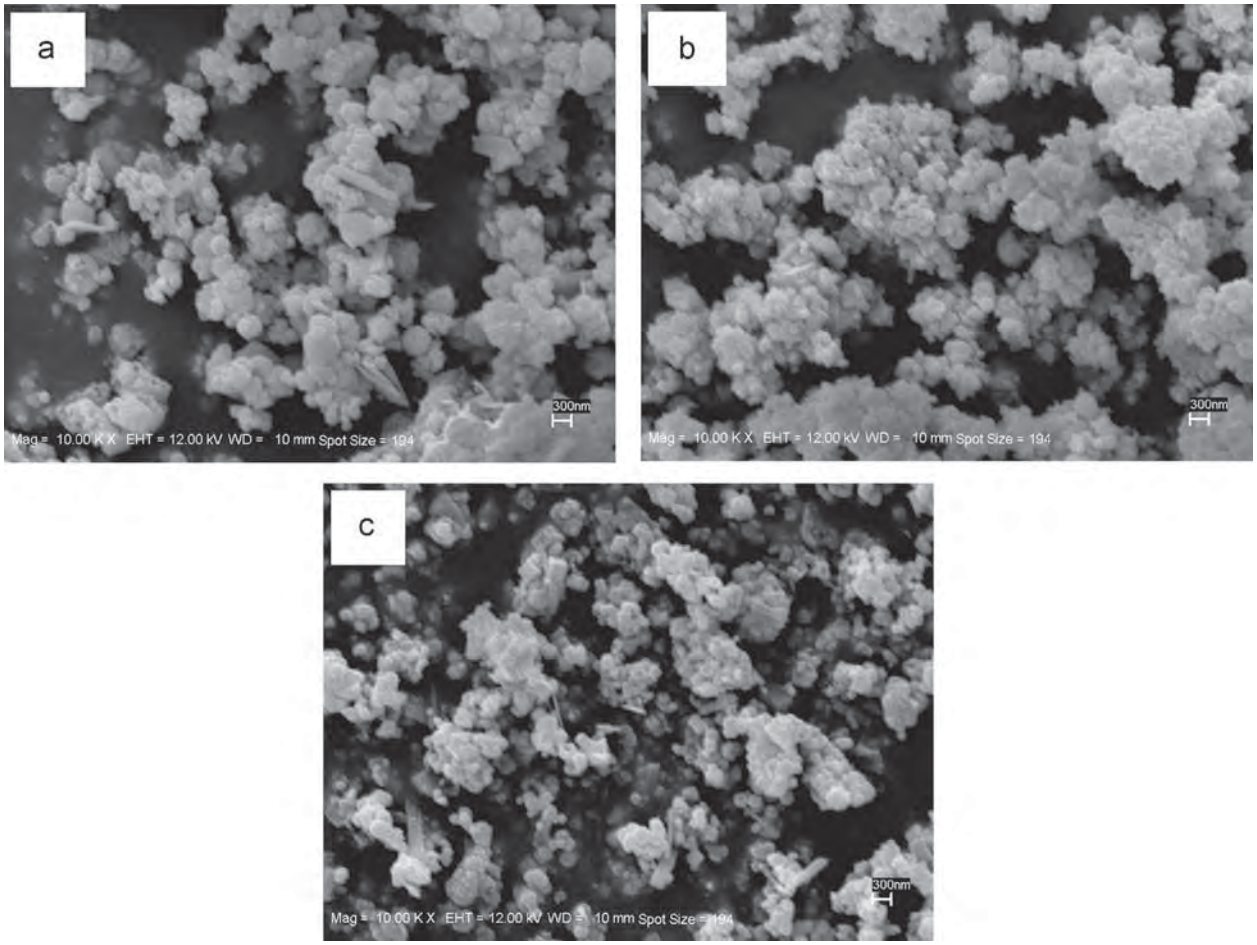


Fig. 2. SEM images of BCTZO nanopowders with NaOH concentrations of (a) 2 M, (b) 6 M and (c) 10 M.

of BTZO lattice because the ionic radius of Zr^{4+} (0.072 nm) is larger than that of Ti^{4+} (0.0608 nm). The samples sintered at 1300 °C have a pure phase and systematic shift of the XRD peaks at high angle (2θ). This indicates that the solubility of $CaTiO_3$ in BZT lattice increases with sintering temperature.

The SEM micrographs of BCTZO ceramics are shown in Fig. 4. All ceramic samples are dense and homogeneous at high sintering temperature. The average grain sizes of BCTZO ceramics are 0.85, 3.53 and 12.09 μm as temperature increases from 1100 to 1300 °C. This result confirmed that the BCTZO ceramics were prepared from nanopowders using a hydrothermal method. It can improve the homogeneity of grains and dense structure of the obtained BCTZO ceramics at low sintering temperature (1300 °C) when compare with those obtained from the conventional solid state reaction technique which require high temperature to form the dense ceramics [19].

The temperature dependence of dielectric constant (ε') and dissipation factor ($\tan\delta$) for the BCTZO samples at 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz are shown in Fig. 5(a–c). A single broad dielectric peak is observed for the sintered

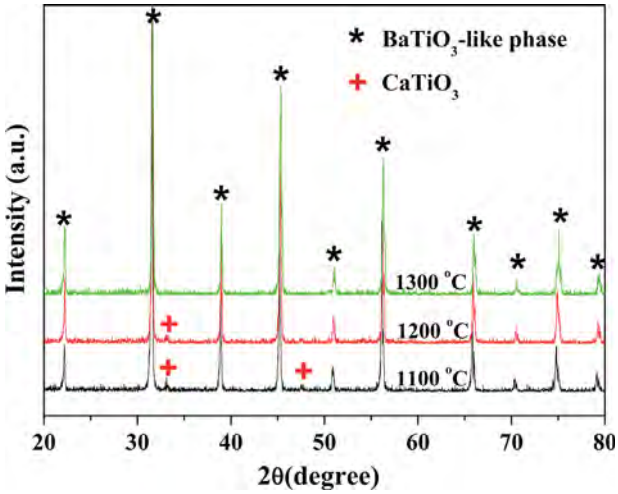


Fig. 3. XRD patterns of BCTZO ceramics sintered at 1100, 1200 and 1300 °C for 3 h.

ceramics at 1100 and 1200 °C. However, with high sintering temperature of 1300 °C, two dielectric peaks were observed. They corresponded to the phase transition temperatures of rhombohedral–tetragonal (~20 °C) and tetragonal–cubic (~70 °C) [12]. This indicates the coexistence of the two phase structures in this sintered sample which may lead to good electrical properties. The sintered samples at 1100 and 1200 °C exhibited the broadening diffuse phase transition behavior. This behavior could be induced by many reasons such as the microscopic composition fluctuation, the merging of micro-domains into macro-domains, the local disorder mode through local strain, and the relaxor behaviors of fine-grain size, grain boundary and paraelectric phase [7,20]. Therefore in this case, the effect of the paraelectric $CaTiO_3$ phase at low sintering temperature can be attributed to the lowering and broadening of dielectric constant arising from the inhibition of the grain growth in these samples [21]. In the previously published research, the modified Curie–Weiss law was successfully used to describe the diffuser ferroelectric behavior [22]. It is known that the classical ferroelectrics follow the Curie–Weiss law above Curie temperature and is expressed by the following relationship:

$$\frac{1}{\varepsilon'} = \frac{(T - T_0)}{C} \quad (1)$$

where T_0 is the Curie–Weiss temperature and C is the Curie–Weiss constant. The inverse dielectric constant as a function of temperature at constant frequency of 10 kHz is shown in Fig. 6. It is observed that T_0 changes from 78.3 °C to 85.8 and 97.9 °C as a result of the increase in sintering temperatures from 1100 °C to 1200 and 1300 °C. To explain the diffuser behavior, the parameter ΔT_m is used to show the degree of deviation. The dielectric constant of BCTZO ceramics follows the Curie–Weiss law at temperature higher than ΔT_m which is defined as

$$\Delta T_m = T_{dev} - T_m \quad (2)$$

here, T_{dev} is the temperature at which dielectric permittivity starts to deviate from Curie–Weiss law and T_m is the temperature at maximum dielectric permittivity. It can be found that ΔT_m values are 60, 70 and 60 °C for sintering temperatures of 1100, 1200 and 1300 °C, respectively. The differences in the ΔT_m values relatively small in this case and this method, therefore, cannot be used to explain the diffuser behavior. The modified Curie–Weiss law for the diffuseness phase transition is, therefore, used to explain

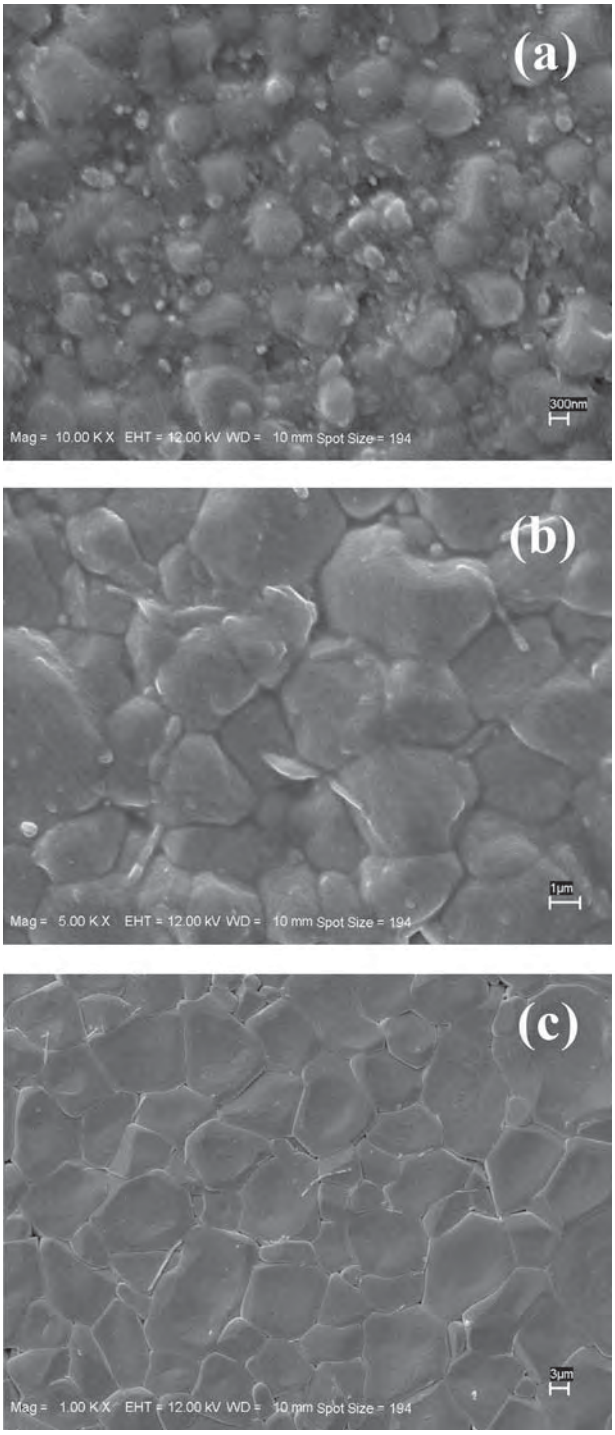


Fig. 4. SEM images of BCTZO ceramics sintered at (a) 1100, (b) 1200, and (c) 1300 °C.

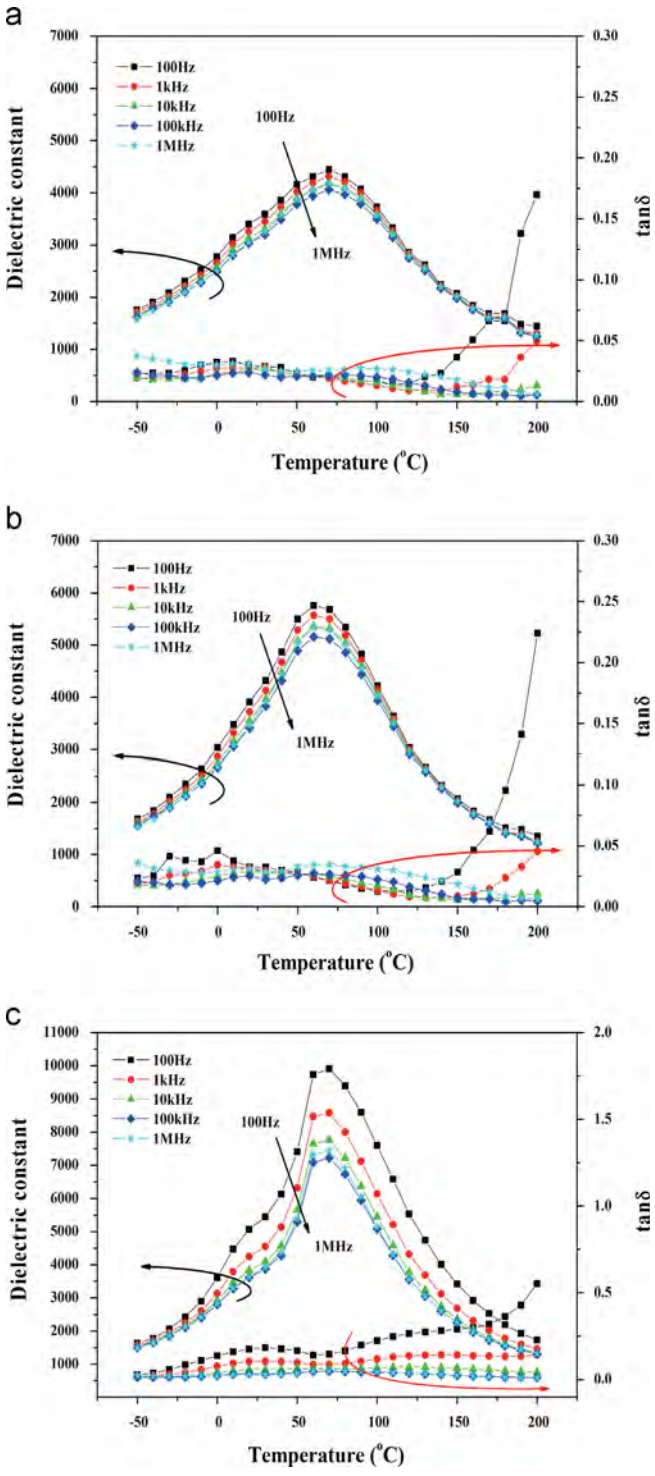


Fig. 5. The frequency and temperature dependence of dielectric constant and tan δ of BCTZO ceramics sintered at (a) 1100, (b) 1200, and (c) 1300 °C.

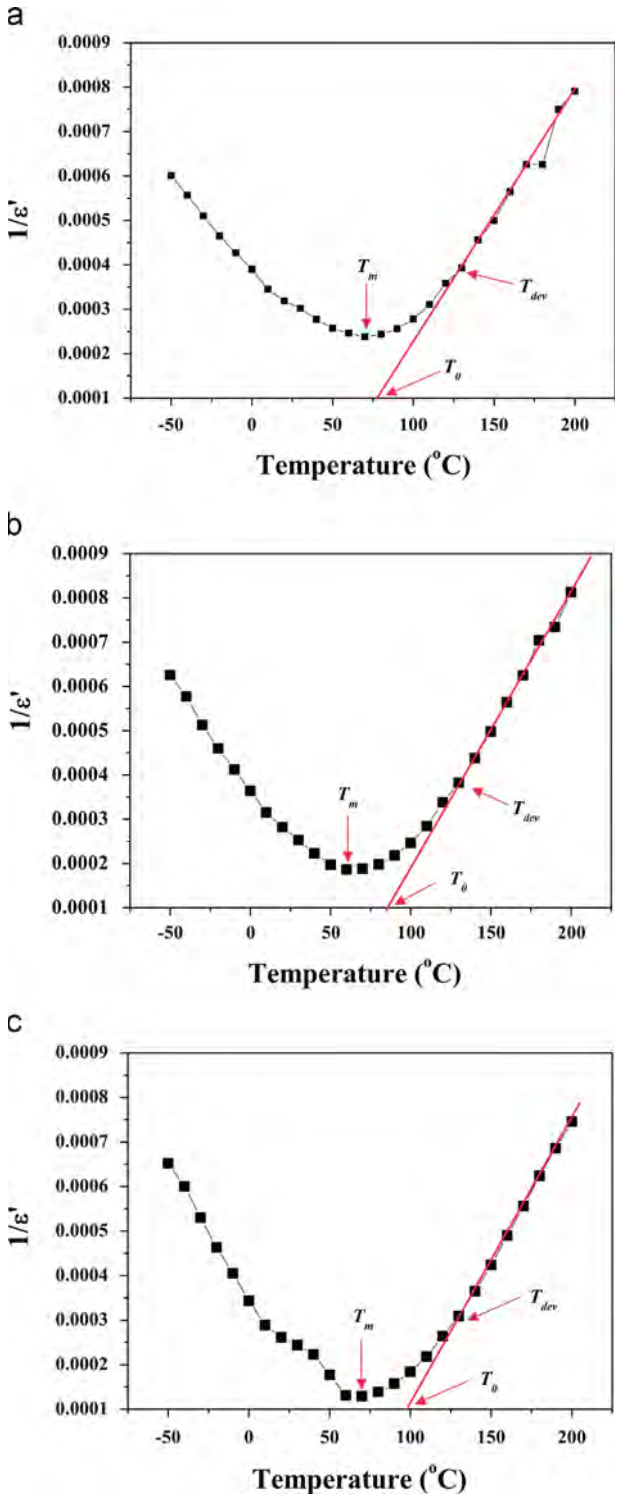


Fig. 6. The temperature dependence of the inverse dielectric constant of BCTZO ceramics sintered at (a) 1100, (b) 1200, and (c) 1300 °C.

this phenomenon as

$$\frac{1}{\varepsilon'} - \frac{1}{\varepsilon'_m} = \frac{(T - T_m)^\gamma}{C'} \tag{3}$$

where γ is modified constant with $1 < \gamma < 2$. The value of γ gives information about the character of phase transition. Its limiting values are $\gamma = 1$ and $\gamma = 2$. The value of γ is 1 for the case of a normal ferroelectric and $\gamma < 2$ (quadratic) is valid for an ideal ferroelectric relaxer or diffuser. A plot of ln $(1/\varepsilon' - 1/\varepsilon'_m)$ as a function of ln $(T–T_m)$ is shown in Fig. 7 for BCTZO samples. By curve fitting of Eq. (3), the γ values, determining the degree of diffuseness of phase transition, is obtained from the slope of ln $(1/\varepsilon' - 1/\varepsilon'_m)$ vs. ln $(T–T_m)$ plot which is shown

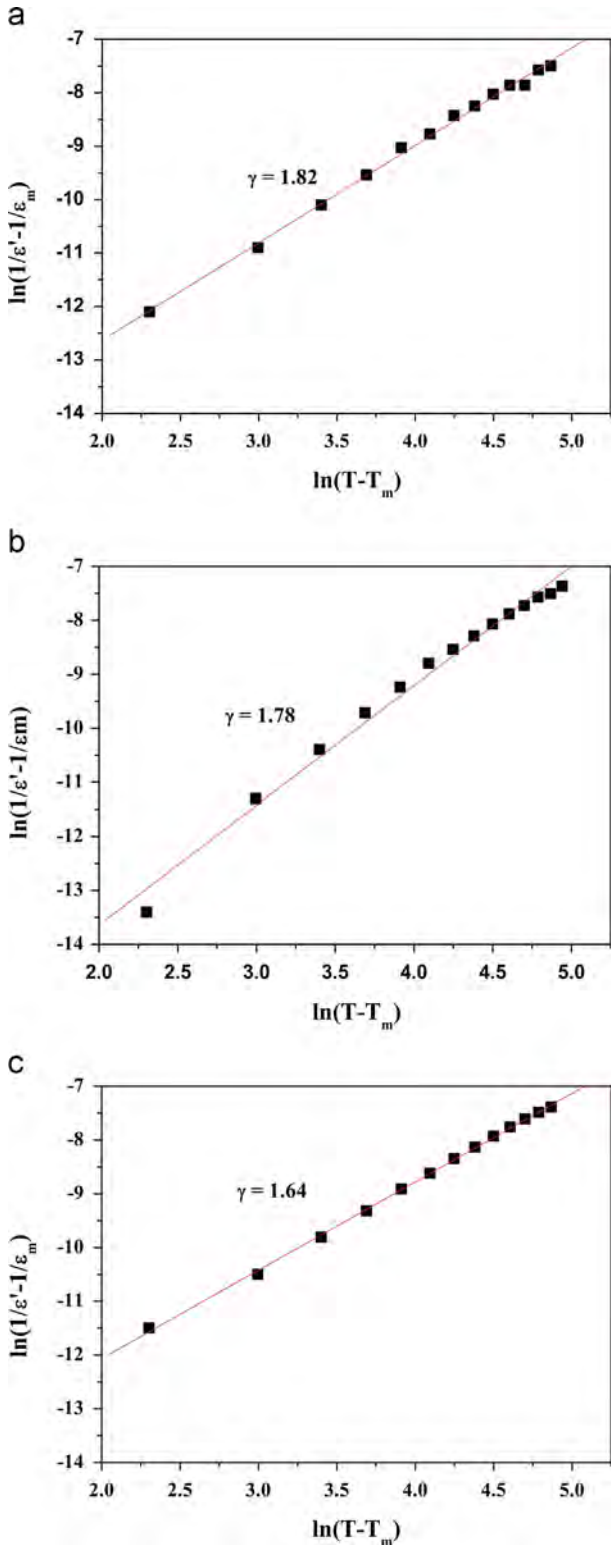


Fig. 7. Plot of $\ln(1/\varepsilon' - 1/\varepsilon'_m)$ as a function of $\ln(T-T_m)$ of BCTZO ceramics sintered at (a) 1100, (b) 1200, and (c) 1300 °C.

in Table 2. The γ values are 1.82, 1.78 and 1.64 for 1100, 1200 and 1300 °C. The high γ values of the sintered samples at 1200 and 1300 °C indicate the diffused phase transition which is supported by the small grain size and the mixing of para-electric $CaTiO_3$ at low sintering temperature [21].

Table 2
Various parameters of BCTZO ceramics sintered at 1100, 1200 and 1300 °C for 3 h for NaOH content of 10 M.

Various parameters	Sintering temperature		
	1100 °C	1200 °C	1300 °C
Phase	(1) $BaTiO_3$-like phase (2) $CaTiO_3$	(1) $BaTiO_3$-like phase (2) $CaTiO_3$	(1) $BaTiO_3$-like phase
Lattice parameter (Å)	4.0121	4.0066	4.0007
Average grain size (μm)	0.89	3.53	12.09
ε'_m	4,190	5,360	7,760
T_0 (°C)	78.3	85.8	97.9
T_m (°C)	70	60	70
ΔT_m (°C)	60	70	60
γ	1.82	1.78	1.64
$2P_r$ (μC/cm^2)	3.33	7.27	21.67
$2E_c$ (kV/cm)	2.52	3.04	4.53
d_{33} (pC/N)	52	123	164

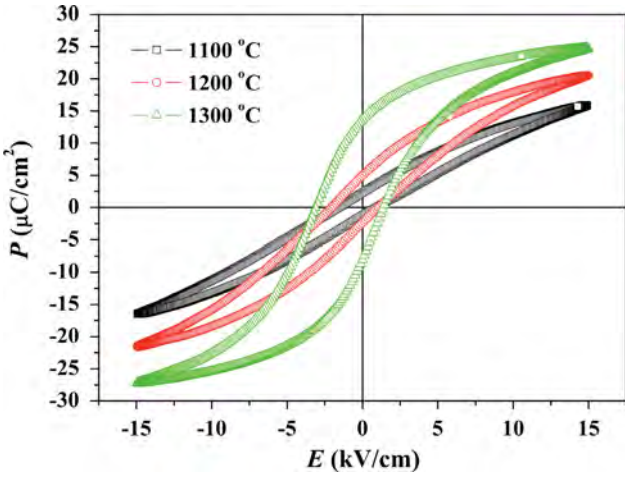


Fig. 8. The ferroelectric hysteresis loop of BCTZO ceramics sintered at different temperature measuring at frequency of 50 Hz.

Fig. 8 shows the ferroelectric hysteresis loops of BCTZO ceramics with different sintering temperature measured at 50 Hz at room temperature. The ceramic samples show the ferroelectric character. The remanent polarization ($2P_r$) and coercive electric field ($2E_C$) as a function of the sintered samples are shown in Table 2. The $2P_r$ values increase with increasing sintering temperature and are 3.33, 7.27 and 21.67 μC/cm^2 for 1100, 1200 and 1300 °C, respectively. The previous works indicated that the P_r value depends on the grain size, crystalline structure and Curie temperature of sample [23–26]. Tian et al. [23] reported that the decreasing P_r values of $(Ba_{1-x}Ca_x)(Zr_{0.1}Ti_{0.9})O_3$ ceramics depend on the change of crystalline structure. Li et al. [24] showed that the P_r values of $Ba_{0.7}Ca_{0.3}Ti_{0.9}O_3$ diphasic piezoelectric ceramics also reduce with the decrease of grain size of sample and the

variation of E_C values is not large. Therefore in this work, the P_r and E_C values increased because of the decrease of cubic paraelectric phase of $CaTiO_3$ and the increase in grain size with increasing sintering temperature. The piezoelectric strain factors (d_{33}) of BCZTO ceramics are shown in Table 2. The observed d_{33} values increase with increasing sintering temperature with maximum d_{33} value of 164 pC/N at 1300 °C. This is lower than that of ceramics prepared by conventional solid state method because of the smaller grain size.

The above result indicates that dense BCZTO ceramics with a high dielectric constant and a good remanent polarization can be fabricated at low sintering temperature of 1300 °C comparing with those prepared by the conventional solid state method. However, this method gives low d_{33} values similar to those by the sol–gel method [27].

4. Conclusion

The $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCTZO) ceramics were prepared from nanopowders using a hydrothermal method. The XRD results indicate that the ceramic samples have a pseudo-cubic phase structure with a small amount of $CaTiO_3$ at low sintering temperature. The average grain sizes increase with increasing sintering temperature and were 0.89, 3.53 and 12.09 μm for sintering temperatures at 1100, 1200 and 1300 °C, respectively. The optimum values of dielectric constants (ε'_m), remanent polarization ($2P_r$), coercive electric field ($2E_c$) and piezoelectric strain factors (d_{33}) of BCZTO ceramics for samples sintered at 1300 °C were 7,760, 21.67 μC/cm^2, 4.53 kV/cm and 164 pC/N, respectively.

Acknowledgments

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RESEARCH ARTICLE - CIVIL ENGINEERING

Effect of High-Speed Mixing on Properties of High Calcium Fly Ash Geopolymer Paste

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Abstract Geopolymers are produced by mixing aluminosilicate materials with alkaline activators, and the mixing process has a considerable impact on the dissolution of raw materials. This research studies the effects of mixing time, with a high-speed centrifuge mixer (1,000 rpm), on the setting and hardening properties of high calcium fly ash-based geopolymer paste. Setting time, strength, phase development, microstructure and porosity of the pastes were investigated. The results indicated that the increase in mixing time retarded the setting time which provided time for dissolution of starting materials. The optimum mixing time at high speed should be 1 min in order to obtain high strength and dense matrix in contrast to 10 min for the normal mixing. The mixing time also had an effect on the pore structure hence the total porosity of the paste.

Keywords Geopolymer · High calcium fly ash · Mixing parameter · Setting time · Compressive strength · Porosity

الخلاصة

يتم إنتاج المبلمرات الجيولوجية عن طريق خلط مواد ألومينا السيليكات بمنشطات قلوية، وعملية الخلط لديها تأثير كبير في حل المواد الخام. يدرس هذا البحث آثار وقت الخلط، مع خلاط جهاز للطرد المركزي بسرعة عالية (1000 دورة في الدقيقة)، على خصائص الإعداد والتصلب من رماد متطاير ذي كالسيوم مرتفع وأساسه معجون المبلمر الجيولوجي. وقد تم التحقيق في وقت الإعداد، والقوة، ونمو الحالة، والبنية المجهرية والمسامية للمعاجين. وأشارت النتائج إلى أن الزيادة في وقت الخلط تؤخر وقت الإعداد مما يوفر وقتا للبدء بحل المواد. إن زمن الخلط الأمثل عند سرعة عالية يجب أن تكون دقيقة واحدة من أجل الحصول على قوة عالية ومصفوفة كثيفة وعلى النقيض من عشر دقائق للخلط العادي. وأظهر وقت الخلط أيضا تأثيرا في هيكل المسام وبالتالي المسامية الكلية للمعجون.

1 Introduction

Fly ash is one of the important source materials for making geopolymer due to its high percentage of amorphous silica and alumina content [1,2]. The alkali activation of fly ash is a chemical process that transforms glassy phases (partially or totally amorphous and/or metastable) into compact well-cemented composites known as geopolymers [3]. When fly ash comes into contact with alkali solution, dissolution of silicate and aluminate species from the source materials starts [4]. Then, polymerization between dissolved silicate and aluminate species occurs leading to well-developed 3D structure of geopolymer. The extent of dissolution becomes an important step in the synthesis as the properties of the final product depend on the Si/Al ratio of the polymer. In addition, the presence of calcium in the system especially when high calcium fly ash is used as source material also plays an important role on the setting and strength development of geopolymer [5]. Phoo-ngernkham et al. [6] explained that the high calcium content leads to the formation of calcium silicate hydrate which coexisted with aluminosilicate geopolymer products.

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Thus, high calcium fly ash is suitable as source materials for making good geopolymer.

Proper mixing of initial raw materials is a very important step in any chemical synthesis process. It has been shown with Portland cement-based systems that mixing step plays a major role in initial dissolution of raw materials [7]. The movement of particles during mixing occurs by convective and dispersive transport mechanisms. The convective transport is a forced, directed movement of larger portions of the mix (coarse dispersion). Dispersive transport is the random movement of individual particles due to collisions between the particles which leads to a mixing in small area (fine dispersion), as well as a disintegration of agglomerates. Mixing parameters has to be chosen in a way that it provides adequate energy to achieve a homogeneous mixture via proper mixing of raw materials. It has been shown that for Portland cement-based systems, mixing time and speed/velocity of mixing can be optimized to achieve best outcomes [7].

Mixing time is one of the important parameters of mixing procedures, and it can be varied by the type of cement, mix proportion, amount of water or plasticizer added [8]. A study based on glass-ionomer cements [9] has shown that mixing time has an effect on the setting time and the strength of the product. The setting time of glass-ionomer cements was decreased as mixing time increased, with an increase in compressive strength to a maximum at 12 s of mixing time. The material essentially pre-gelled after few seconds of mixing and increasing mixing time resulted in breaking of the gel matrix and poor final properties. Moreover, most of published data discuss mainly the effect of dissolution of ions from starting materials. However, other parameters such as the type of starting material, speed and time of mixing, temperature, the media of dissolution or solvent and solid to liquid ratio [10–13] also play an important role on the efficiency of synthesis.

Normally, the mechanical mixing of hydraulic cement is prescribed by ASTM C305 [14]. The mixer shall be an electrically driven mechanical mixer of the epicyclic type, which imparts both a planetary and a revolving motion to the mixer paddle. Moreover, a few researches used the high-speed centrifuge mixer (Thinky mixer) to synthesis geopolymer [15–17]. In the thinky mixer, the principle is based on the simultaneous rotation and revolution (planetary) motions, where the mixer equipment rotates the container holding the material and at the same time revolves the container. Thinky mixer allows uniform and simultaneous mixing, degassing and dispersion of the materials. The previous research [18] study on setting time of fly ash geopolymer indicated that the mixing speed of Thinky mixer did not have significant effect on setting time, whereas the increased time of mixing tended to increase both initial and final sets.

This research studied the effect of mixing when used a high-speed mixer (1,000 rpm) at various mixing time on the setting time, compressive strength, mineral composition, microstructure and porosity of high calcium fly ash geopolymer pastes, and the results are compared with those prepared using a normal mixer (140 rpm).

2 Materials and Experimental Procedures

2.1 Materials

Lignite high calcium fly ash (FA) from Mae Moh power station in northern Thailand was used as a starting material. The chemical compositions were 35.21 % SiO_2, 16.57 % Al_2O_3, 13.66 % Fe_2O_3, 25.52 % CaO, 2.73 % Na_2O, 1.99 % K_2O, 3.28 % MgO and 1.04 % other by weight. The mineral compositions of fly ash are shown in Fig. 1. The FA consisted of a glassy matrix as shown by the hump at 25°–35° 2theta and crystalline phases of quartz (SiO_2), magnesioferrite ($MgFe_2O_4$), hematite (Fe_2O_3), anhydrite ($CaSO_4$) and lime (CaO). The sodium silicate solution with 28.70 % SiO_2, 8.90 % Na_2O, and 62.50 % H_2O by weight and ten molar NaOH solutions were used as alkali activated solutions.

2.2 Geopolymer Synthesis

The mix formulation of fly ash geopolymer used in this study is $Na_2O.1.17Al_2O_3.4.80SiO_2.11.45H_2O$ with the initial molar ratios of SiO_2/Al_2O_3, Na_2O/SiO_2, Na_2O/Al_2O_3, CaO/SiO_2 of 4.10, 0.21, 0.85 and 0.69, respectively. The constant ratio of liquid alkaline to fly ash (L/A) and the ratio of sodium silicate to sodium hydroxide solution were 0.40 and 0.67, respectively. The mixing procedure started with first mixing of FA and NaOH solution. Sodium silicate solution was then added to the mixture and mixed until a homogeneous paste was obtained.

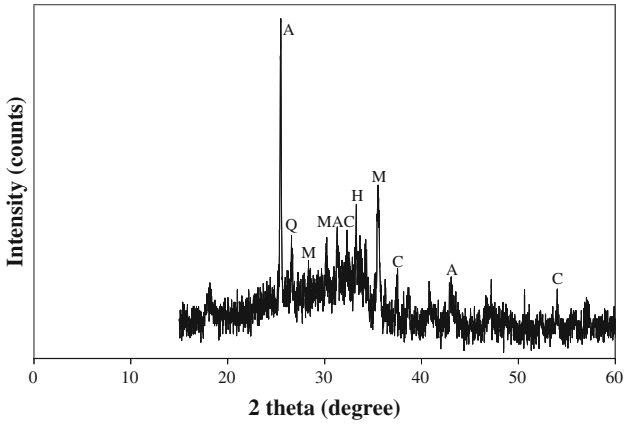


Fig. 1 XRD of fly ash (A = anhydrite, Q = quartz, M = magnesioferrite, C = lime, H = hematite)

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For the study of the effect of high-speed planetary centrifugal mixer (Thinky), the periods of mixing time of 1, 3 and 6 min were used at a constant speed (1,000 rpm). For the low-speed normal mixer (140 rpm) as described in ASTM C 305 [14], the mixing time of 10 min was used as suggested by pervious published researches [5,19].

After mixing, the setting time of fresh fly ash geopolymer pastes was tested at room temperature (22 °C) as described in ASTM C191 [20] using Vicat needle apparatus. The pastes were cast in 25×25×25 mm cubes mold. The molds were vibrated for 30 s to obtain good compaction and three layer wrapped with cling film to avoid moisture loss before curing at 60 °C for 24 h. They were then demolded and kept in a controlled room at 22 °C and 50 % RH. The compressive strengths were tested as described in ASTM C109 [21] at the age of 7 days. The reported compressive strength of geopolymer pastes was tested from five samples, and average compressive strength of all samples was considered within ±10 % of mean resulted. The phase development by X-ray diffraction (XRD), microstructure by scanning electron microscope (SEM) and porosity by mercury intrusion porosimetry (MIP) were studied on the hardened geopolymer pastes at age of 7 days.

3 Results

3.1 Setting Time

The initial and final setting times of geopolymer pastes with 1, 3 and 6 min high-speed mixing times and with 10 min mixing time using normal mixer are shown in Fig. 2. The results indicated that the setting time of high calcium fly ash geopolymer paste increased with mixing time. For high-speed mixer, the initial setting time of 1, 3 and 6 min pastes was 19, 33 and 33 min, respectively, while the final setting times were 47, 65 and 80 min, respectively. For normal mixer, the initial and final setting times of 10 min paste were 60 and 100 min, respectively, and were in line with the previously published data [6,22].

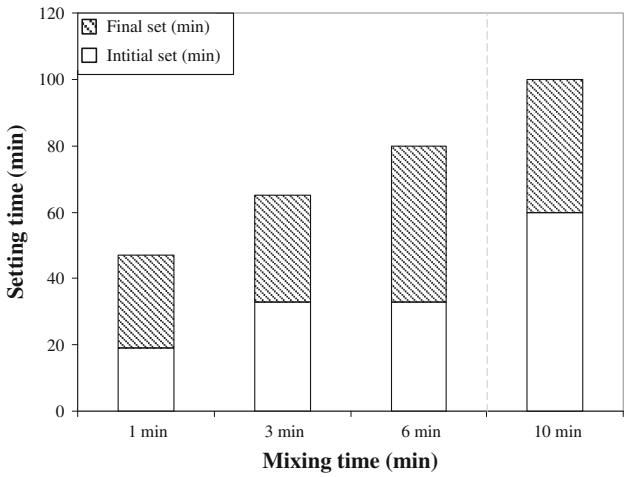


Fig. 2 Initial and final setting time of geopolymer pastes

Generally, the setting time of the normal geopolymer systems is mainly controlled by the dissolved silica and alumina ions content [23,24]. Pimraksa et al. [25] reported that the amorphous phase of Mae Moh high calcium fly ash was found to be approximately 52 %. Chindaprasirt et al. [26] explained that the amorphous phase of high calcium fly ash had high reaction degree and thus influenced the setting behavior. The increase in the time of mixing increased the time of dissolution of silica and alumina ions from raw materials to the geopolymer matrix [11,27]. Previous results indicated that the leaching of Si and Al ions in NaOH solution was dependent on mixing time [11]. Those results suggested that the initial and final set were related to many parameters such as liquid to ash ratio, sodium silicate to sodium hydroxide ratio, sodium hydroxide concentration and temperature of setting time testing [11,19,23,24]. The speed of mixing would also affect the leaching and the reaction of the silica, alumina and other ions. Accordingly, the initial molar ratio of SiO_2/Al_2O_3 (4.10) would change during leaching and geopolymerization. In a previous study, it was explained that the SiO_2/Al_2O_3 ratio, liquid to ash ratio, NaOH concentration and temperature also affected the rheology properties and setting behavior of fresh geopolymer pastes [28,30]. In addition, the results of this study showed that the mixing time (Thinky mixer - 1,000 rpm) also had an effect on the dissolution of silica and alumina ions from raw materials to the solution. Longer mixing times delayed the setting time of pastes.

3.2 Compressive Strength

The results of compressive strength of harden geopolymer pastes are shown in Table 1. For high-speed mixing, the strengths of pastes with 1, 3 and 6 min mixing were 75.1, 74.3 and 59.7 MPa, respectively, which were 120, 119 and 95 % of that of control paste (the paste made using the conventional mixer) of 62.6 MPa. The results indicated that high strength pastes could be obtained with high-speed mixing time of 1–3 min. The increase in mixing time to 6 min resulted in a

Table 1 Compressive strength result of geopolymer pastes

Mixing time	Compressive strength (MPa)
High-speed mixing	
1 min	75.1
3 min	74.3
6 min	59.7
Normal mixing 10 min (control)	62.6

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drop of the strength of paste. It generally that increased mixing time would facilitate the dissolution of Si^{4+} and Al^{3+} from the raw materials and hence product formation [27]. However, for the fly ash system investigated in this study, there seems to be an optimum mixing time of Thinky mixer favors maximum strength. This implies that rate of dissolution is not the only factor controlling strength. The rate of precipitation and other parameters play a role in controlling the strength development of these mixtures. The different mixing may also have played important role on the leaching of silica and alumina ions, porosity and denseness of the pastes.

3.3 Mineralogy of Geopolymer Paste

The XRD patterns of geopolymer pastes with high-speed mixing and normal mixing are shown in Fig. 3a–d. The XRD patterns of the geopolymer pastes (Fig. 3a–d) are similar with that of FA (Fig. 1). The amorphous phases were easily detected as broad hump around 25°–38° 2theta representing a small shift of this hump compared with that of fly ash [5,11]. For high-speed mixing for 1 min, quartz, calcium carbonate, calcium silicate hydrate (CSH) and magnesioferrite were detected as shown in Fig. 3a. The presence of CSH phase can be confirmed by the presence of peaks at 29.5 degree and 32.05 degree [31]. Quartz and magnesioferrite were the remnant of the phases found in fly ash. Calcium carbonate possibly came from the reaction between calcium oxide and carbon dioxide. For 1 min high-speed mixing, the peak of CSH was very prominent indicating a substantial amount of hydration reaction occurred and CSH formed. The CSH coexisted with the geopolymer products and enhanced the strength of the geopolymer [32].

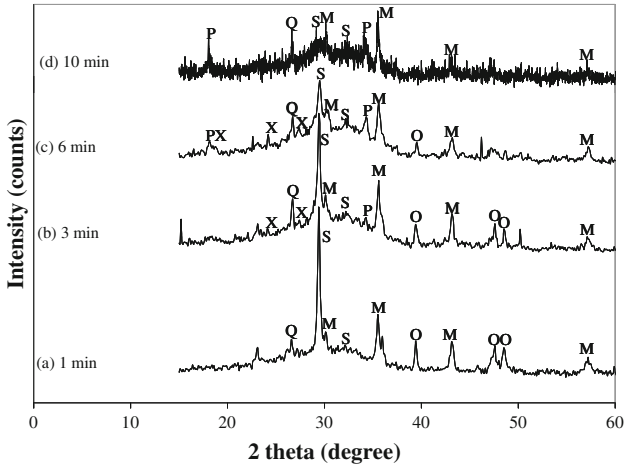


Fig. 3 Mineral compositions of geopolymer pastes with various mixing times at 1,000 rpm and normal mixing at 10 min (Q = quartz, M = magnesioferrite, O = calcium carbonate, X = phase x, S = calcium silicate hydrate, P = calcium hydroxide)

For 3 min paste, the peak of CSH reduced compared with that of 1 min paste. In addition, phase X ($Na_{14}Al_{12}Si_{13}O_{51}.6H_2O$) and calcium hydroxide were detected. The reduction in CSH resulted in an excess in calcium and this reflected in the appearance of calcium hydroxide. For 6 min paste, the peak of CSH reduced further compared with those of 1 and 3 min pastes. From the XRD results, the increase in mixing time (1, 3 and 6 min) resulted in increased phase X and calcium hydroxide with reduction in CSH and the decrease in compressive strength.

The setting time of paste was related to formation of CSH. At 1 min high-speed mixing, the setting time was relatively short and associated with the formation of large amount of CSH. The mixing at high speed for 3 and 6 min reduced the amount of CSH formed, and the setting time of pastes were increased. The amount of sodium-aluminosilicate hydrate (NASH) also increased with the increase in the high-speed mixing time as indicated by the large hump at 25°–38° 2theta [5,11,31]. The increase in the amount of NASH gel compensated the reduction in the formation of CSH.

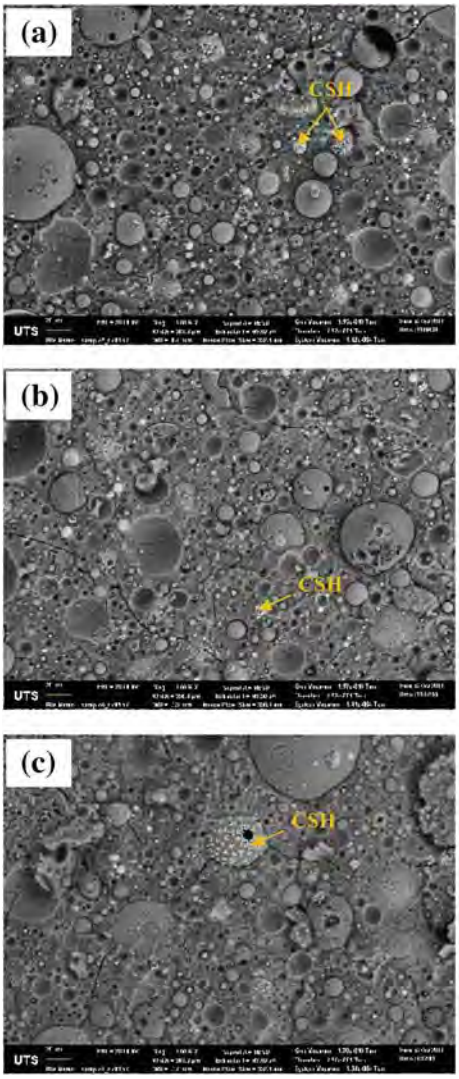
For 10 min normal mixing (Fig. 3d), the CSH and calcium hydroxide were found and phase X and calcium carbonate disappeared. The amount of CSH was, however, less than those of high-speed mixing pastes. This resulted in the longer setting time than those of the high-speed mixing and also resulted in the normal strength level of paste.

3.4 Morphology of Geopolymer Paste

The morphology of hardened geopolymer pastes with high-speed mixing times of 1 and 6 min and normal mixing for 10 min (control) are shown in Fig. 4a–c, respectively. The SEM showed that the structure of paste was dense with unreacted fly ash particles embedded in a continuous matrix. The 1 min high-speed mixing paste (Fig. 4a) was slightly denser than the 6 min paste (Fig. 4b) and normal mixing paste (Fig. 4c). The SEM of pastes confirmed to strength and XRD results. It also contained white globules of CSH or CASH in the matrix. The CSH was easily detected in the 1 min high-speed mixing paste, and this is conformed to the result of X-ray diffraction. However, for the 6 min high-speed mixing paste, the matrix contained less CSH and increased number of cracks which led to low strengths observed with this sample. For 10 min normal mixing paste (Fig. 4c), the structure looked very similar to the 6 min high-speed mixing paste and this reflected in similar compressive strengths of the two mixes.

The EDXA analyses on the dense matrix area of control, 1 and 6 min pastes show composition oxides of SiO_2, Al_2O_3 and CaO as shown in Fig. 4a–c. In all three mix compositions investigated, the percentage of CaO was rather high at around 20 % in the matrix. Therefore, this percentage of CaO confirmed the presence of Ca^{2+} as CSH or CASH phase.

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Formulas	Intensity (%)
SiO_2	27.02
Al_2O_3	9.55
CaO	26.19

Formulas	Intensity (%)
SiO_2	28.50
Al_2O_3	10.54
CaO	21.62

Formulas	Intensity (%)
SiO_2	22.71
Al_2O_3	9.17
CaO	26.04

Fig. 4 SEM of geopolymer pastes **a** high-speed mixing for 1 min **b** high-speed mixing for 6 min **c** normal mixing for 10 min

Moreover, for the 1 min high-speed mixing paste, the SiO_2/ Al_2O_3 ratio was 2.82 and confirmed to previous study [5] which reported the SiO_2/ Al_2O_3 ratio range between 2.80-3.50 with significant influence on strength development. On the other hand, the SiO_2/ Al_2O_3 ratio of 1 and 3 min high-speed mixing pastes were 2.70 and 2.47, respectively.

3.5 Porosity and Average Pore Diameter of Geopolymer Paste

The results for percentage of pore volume of geopolymer pastes are shown in Fig. 5. The total porosities of 1, 3 and 6 min of pastes were 20.19, 22.20 and 23.28 %, respectively. The total porosity increased slightly with increased mixing time. The increase in mixing time increased air void and large capillary pores and thus adversely affected the compressive strength. For the high-speed mixing, the time of mixing of 1 min was sufficient to produce dense paste with low pore volume. Prolong mixing resulted in the increase in porosity mainly in the air void and large capillary pore. In particular, the large capillary pores increased from 1.68 % for 1 min paste to 6.8 and 8.6 % for 3 and 6 min pastes, respectively. For 6 min mixing time, the pastes were coherent and deterred the formation of CSH with increase in pore volume due to the condensation of water and formation of additional large capillary pores. For the 10 min paste, the total porosity was 21.89 % and was in the same order as those of 3 and 6 min pastes. However, the pore consisted mainly of air void and large capillary pore of 6.5 and 14.8 %, respectively. This indicated that the short duration high-speed mixing could be used to produce homogeneous and degassed geopolymer pastes.

The graphs of pore diameter and incremental pore volumes of geopolymer pastes are shown in Fig. 6. The high-speed mixing and the normal mixing produced different patterns of pore distributions. The high-speed mixing produced pastes with three main categories of pore. A small portion of air void, a large portion of medium and large capillary pores and a sizable portion of gel pores. The normal mixing

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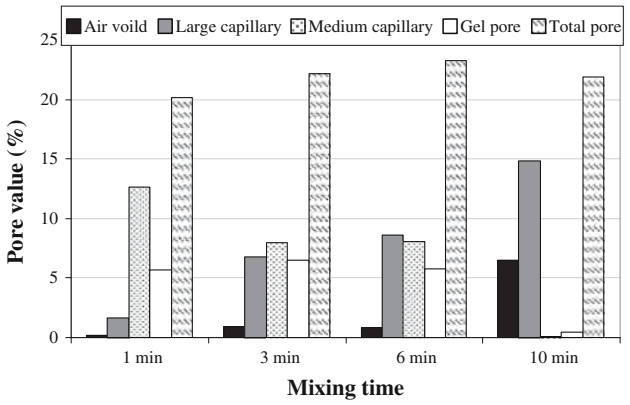


Fig. 5 Percentage of pore volume of geopolymer pastes

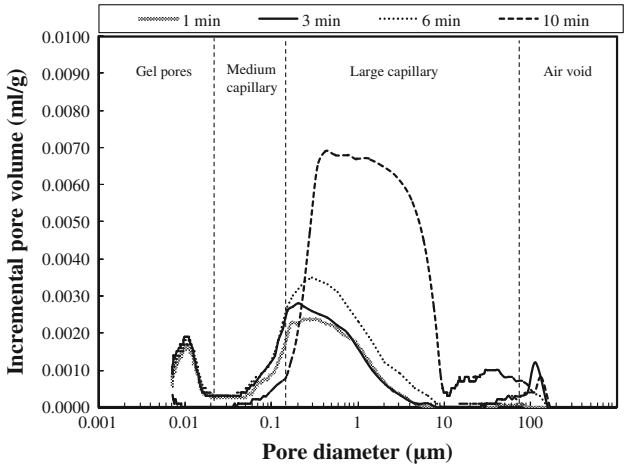


Fig. 6 The relationships between the differential pore volume and pore diameter of geopolymer pastes

produce pastes with predominantly large capillary and air voids. The amount of gel pores in the high-speed mixing pastes seemed to be associated with the formation of CSH and/or CASH. Although not large amount, the air voids of the 3 and 6 min pastes indicated the possible trapping of some air in homogenous paste during high-speed mixing. As demonstrated here also, the high-speed mixing of only 1 min was sufficient to produce geopolymer paste with high strength and low porosity.

4 Conclusions

From this study, it can be concluded that the properties of the high calcium fly ash geopolymer pastes are dependent on the mixing speed and time. High-speed mixing for 1 min was sufficient to produce homogenous and dense paste with high compressive strength of 75.1 MPa due to the formation of CSH and/or CASH. Additional mixing time delayed the setting time and produced pastes with slightly lower strength due to the reduced formation of CSH. The normal mixing required more mixing time in the order of 10 min to have good strength and this further delayed the setting time with less formation of CSH. High-speed mixing produced geopolymer paste with high strength and low porosity compared to normal mixing which produced a lower strength paste with substantial amount of large capillary and air voids.

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Properties of Wood Flour/Expanded Polystyrene Waste Composites Modified With Diammonium Phosphate Flame Retardant

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The objective of the study was to evaluate properties of waste plastic composite samples manufactured from expanded polystyrene waste (EPS) and sawdust containing diammonium phosphate (DAP) as flame retardant. Thermal degradation along with dimension stability and mechanical characteristics of the specimens as a function of DAP content were determined. The wood fiber/EPS composite modified with DAP content up to 20 wt% resulted in the best linear burning rate. The rate of thermal degradation of samples also substantially decreased while limiting oxygen index and char residual increased. Overall dimension stability in the form of water absorption and thickness swelling along with flexural characteristics of the samples were found comparable to those of commercial wood plastic composites. The wood fiber/EPS containing DAP showed high potential for use as wood composite products with adequate fire resistance. POLYM. COMPOS., 00:000–000, 2014. © 2014 Society of Plastics Engineers

INTRODUCTION

Wood plastic composite (WPC) is material that consists of wood and thermoplastics or thermosets [1]. WPCs are relatively new products as compared to the long history of natural lumber or traditional wood composites such as particleboard or fiberboard. Nowadays, the industrial scope of WPCs has expanded rapidly into various applications such a building, interior decoration, door, window, flooring and automotive interior sectors [2, 3]. WPC products have been produced from different types of natural fiber resources and virgin thermoplastics including polyethylene (HDPE) [4], polypropylene (PP) [5], polyvinyl chloride (PVC) [6], polystyrene (PS) [7], poly(lactic acid) (PLA) [8]. However, effort on investigation of recycled thermoplastic matrix with natural fiber composite is still very limited. Generally, polyolefins-based plastics are widely used for many applications, including packaging, which can potentially be recovered for recycling. Plastic is significant source as raw material for the development of thermoplastic composites with natural fibers, due to its large volume and low cost [9, 10]. These composites provide several advantages, including low cost, low density, low manufacturing energy, low CO_2 emission, and renewability [11]. Recently, the physical and mechanical properties of wood composite based on plastic waste and palm leaves were investigated and indicated that the obtained properties of wood composites proved an acceptable final and promising WPC product. It can be efficiently used in outdoor structure and construction industry [12]. In addition, Poletto et al. [13] observed that using of recycle expanded PS as matrix for WPC had a potential in manufacturing of low density composites with high mechanical properties. However, the application of WPCs is still limitation due to the problem of fire performance. The main components of WPC such a wood and plastic are thermally degradable and combustible materials [14]. Therefore, improvement

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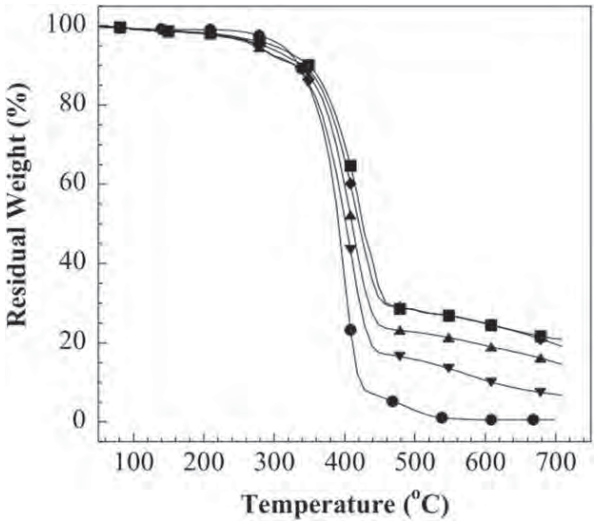


FIG. 1. TGA thermograms of wood flour/EPS composites modified with DAP: (●) 0 wt% DAP, (▼) 10 wt% DAP, (▲) 20 wt% DAP, (◆) 30 wt% DAP, and (■) 40 wt% DAP.

of flame retardancy of the composite materials plays a very important role to comply with the safety requirements of the wood composite products.

A number of flame retardants for polymers and composites have been developed, and many of these are suitable for use in fiber-based composites [15]. Especially, nonhalogenated-based flame retardant, phosphorus containing compounds are frequently used as flame retardants owing to their low generation of smoke and toxic gases. They work very effectively in condensed phase by formation of char which is difficult to ignite. Char inhibits gaseous products from diffusing to the pyrolysis zone and protects the polymer surface from heat and air [16]. From previous works, Chen [17] and Gaan and Sun [18] investigated using diammonium phosphate (DAP) as fire retardant in natural fiber. It was found that such product was safe, inexpensive, and more efficient at improving the limiting oxygen index (LOI) of natural fiber than other phosphorus compounds such as tributyl phosphate, tri-allyl phosphate, or triallyl phosphoric triamide. Suardana et al. [15] also observed that jute and coconut fiber treated with 5% DAP provide the best linear burning rate, i.e., the burning time of wood composite increased up to 69% for jute reinforced PP and 36% for coconut reinforced PP. Furthermore, the effect of boron and phosphate compounds on fire properties of wood–PP composites was studied by Ayrilmis et al. [19]. The heat release rates from the cone calorimeter tests indicated that the phosphate treatments provided better improvements in the fire performance than the boron treatments. Consequently, it appears that DAP was a good candidate for improvement of fire resistance of WPCs.

Currently, there is no information about flammability, thermal degradation, as well as physical and mechanical properties of the wood fiber/EPS composites modified with flame retardant. Therefore, the objectives of this work are to produce the wood composites from expanded PS waste and sawdust including evaluate the effects of flame retardant (DAP) content in the composites on properties of the wood flour/EPS composites.

EXPERIMENTAL

Materials

The EPS was acquired from the packaging of food, electronic goods and home appliances. Wood sawdust particles obtained from carpentry and wood-working processes and supplied by a wood manufacture from Khon Kaen in the northeast of Thailand was used as wood flour. The average size of wood flour used in this work was in the range of 100–300 μm. DAP (≥98% purity) was purchased from Ajax Finerchem. The specimens were produced by a conical co-rotating twin screw extruder (Labtech LTE 20-40) and injection molded (Manumold).

Preparation of Wood Flour/EPS Composites Modified with DAP

The EPS was preheated in oven at temperature of 110°C for 15 min. In the next step, EPS samples were ground in a rotary knife mill into flakes, with a particle size range from 5 to 15 mm. Wood flour was dried at a temperature of 105°C for 24 h in a laboratory oven until they reached a constant weight. Samples were prepared with EPS flakes and 0, 10, 20, 30, and 40 wt% of DAP with addition of 20 wt% wood flour. The mixtures were then processed in a co-rotating twin-screw extruder at 200 rpm at 170°C. The specimens were produced by employing injection molder at a barrel temperature in range of 160 and 190°C and mold temperature of 40 ± 2°C.

Characterization of the Composite Samples

The thermal degradation of the wood flour/EPS composites was studied using a TGA-50, Shimadzu. The testing temperature program was ramped at a heating rate of 20°C/min from room temperature to 700°C under nitrogen atmosphere. The purge nitrogen gas flow rate was maintained at 20 ml/min. The sample mass used was 10–20 mg. Degradation temperature of each specimen was determined from the temperature at 5% weight loss whereas char yield was obtained the weight residue at 600°C.

LOI values of samples were measured using an instrument from Stanton Redcroft on bar ($70 \times 7 \times 3$ mm^3) in accordance with the standard oxygen index test as per ASTM D2863-10. The test was based on the determination of the lowest volume concentration of oxygen in a gas mixture of nitrogen and oxygen (O_2 and N_2) required

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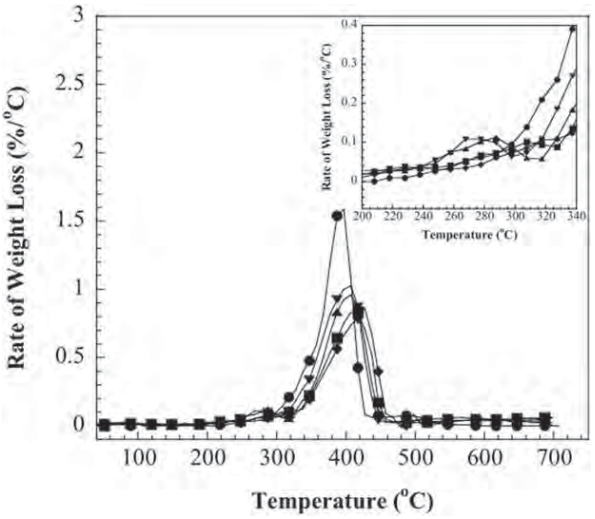


FIG. 2. TGA derivative curves of wood flour/EPS composites modified with DAP: (●) 0 wt% DAP, (▼) 10 wt% DAP, (▲) 20 wt% DAP, (◆) 30 wt% DAP, and (■) 40 wt% DAP.

for ignition and the onset of burning. LOI values were calculated according to the following equation:

$$\mathrm{LOI}\,(\%) = \frac{O_2}{O_2 + N_2} \times 100. \quad (1)$$

The flame retardant properties of the wood flour/EPS composites were measured in accordance with ASTM D 635-10. Specimens with dimensions of 125 × 13 × 3 mm^3 were held horizontally in the burning test. They were ignited by fuel gas at one of the ends of the sample. The flame time from the first mark (25 mm from the ignition end) until the second mark (100 mm from the ignition end) was measured to determine the linear burning rate (V) of the sample.

Attenuated total reflection infrared (FTIR-ATR) spectra of all samples after LOI testing were acquired by Bruker Tensor 27 spectrometer. All spectra were taken as a function of time with 64 scans at a resolution of 4 cm^{-1} and a spectral range of 4000–650 cm^{-1}.

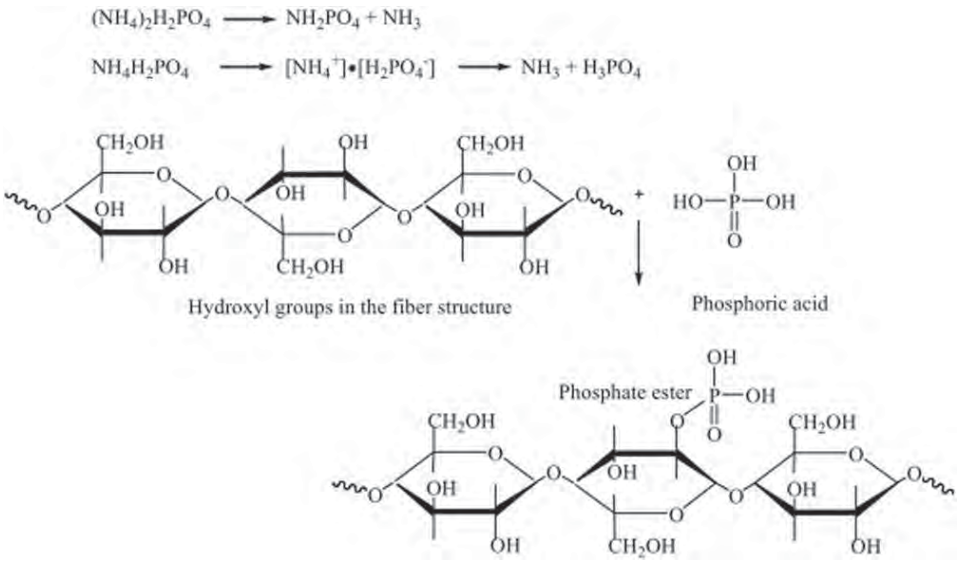
Water absorption and thickness swelling characteristics of the samples were conducted following ASTM D 570-98. Before testing, the thickness and weight of each sample were measured. All samples were submerged in distilled water and the weight measurements were performed at 2, 6, 24 h up, and 1 week. The samples were removed, wiped, weighed, and immediately returned to water bath at each test period. The amount of water adsorbed was calculated based on the initial conditioned mass of each sample. The samples were removed, wiped, weighed and immediately returned to water bath at each test period. The amount of water adsorbed was calculated based on the initial conditioned mass of each sample.

Flexural modulus and flexural strength of the wood polymer composite specimens were determined according to ASTM D 790-10 employing a Universal Testing Machine, Instron, Model 5567 equipped with a 10 kN load cell. The measurement was performed in a 3-point bending mode with a support span of 48 mm at the crosshead speed of 1.2 mm/min. The dimension of the each specimen was 12.7 × 60 × 3.2 mm^3.

RESULTS AND DISCUSSION

Thermal Degradation

Thermal degradation of wood flour-EPS composites was investigated by thermogravimetric analysis (TGA) as illustrated in Figs. 1 and 2. The degradation temperature (T_d) of the wood flour/EPS composites was 328°C



SCH. 1. The possible reaction between phosphoric acid (H_3PO_4) and primary hydroxyl groups during thermal decomposition.

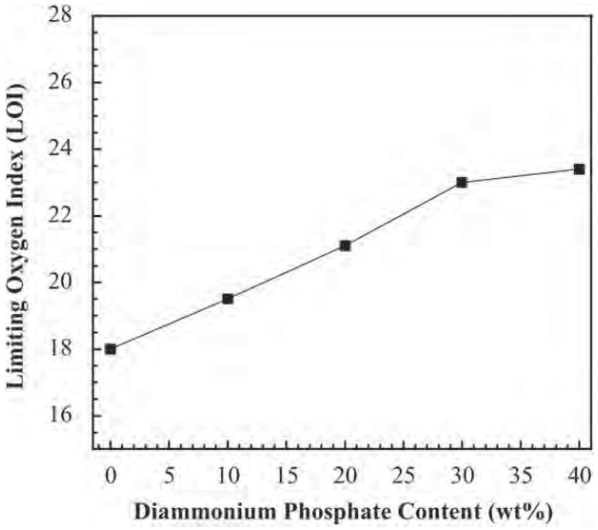


FIG. 3. Limiting oxygen index (LOI) of wood flour-EPS composites at various DAP contents.

whereas wood flour/EPS composites modified with DAP at 10–40 wt% showed the T_d values within range of 267–269°C. As shown in Fig. 1, the T_d's of wood flour/EPS composites modified DAP were found to be slightly lower than that of the unmodified wood flour/EPS composites. Due to flame retardant decomposition under temperature scan, DAP tended to be released from the specimens before degradation of EPS matrix and wood flour. Meanwhile, the char yields of wood flour/EPS composites in the presence of DAP were observed to be higher than that of the unmodified wood flour/EPS composites as illustrated in Fig. 1. The char yields of wood flour/EPS composites modified with DAP tended to increase with increasing DAP contents, i.e., 0.54 (0 wt% DAP), 10.61 (10 wt% DAP), 19.40 (20 wt% DAP), 24.80 (30 wt% DAP), and 25.01 (40 wt% DAP). The improved char yield was probably caused by the esterification of phosphoric acid (H_3PO_4) and primary hydroxyl groups in the fiber during thermal decomposition of DAP. This interaction leads to the thick and compact char [20, 21]. It has been observed that DAP was easily converted to H_3PO_4 because the ammonia cations (NH_4^+) were driven off at low temperature [22]. The possible reaction between phosphoric acid (H_3PO_4) and primary hydroxyl groups during thermal decomposition was depicted in Scheme 1. Similar results were also observed in the wood composites manufactured using natural fiber treated with DAP and PP/PLA as matrix [15]. Char yield of material has been correlated with its flame retardancy. Increasing char yield implied greater fire resistance of the sample as it was proposed that char formation would limit production of combustion gases, inhibit combustion gases from diffusing to the pyrolysis zone and protect the polymer surface from heat and air [16]. Therefore, the fire-resistant property of wood flour/EPS composites improved with the DAP addition.

Furthermore, the thermal decomposition of wood flour/EPS composites was also examined by the derivatives of TGA thermograms. Generally, pyrolysis of hemicellulose, cellulose and lignin occurred at temperatures around 220–315, 315–400, and 160–500°C, respectively [23–25]. Figure 2 depicts two main decomposition steps of all samples. The temperatures for the maximum mass loss at first

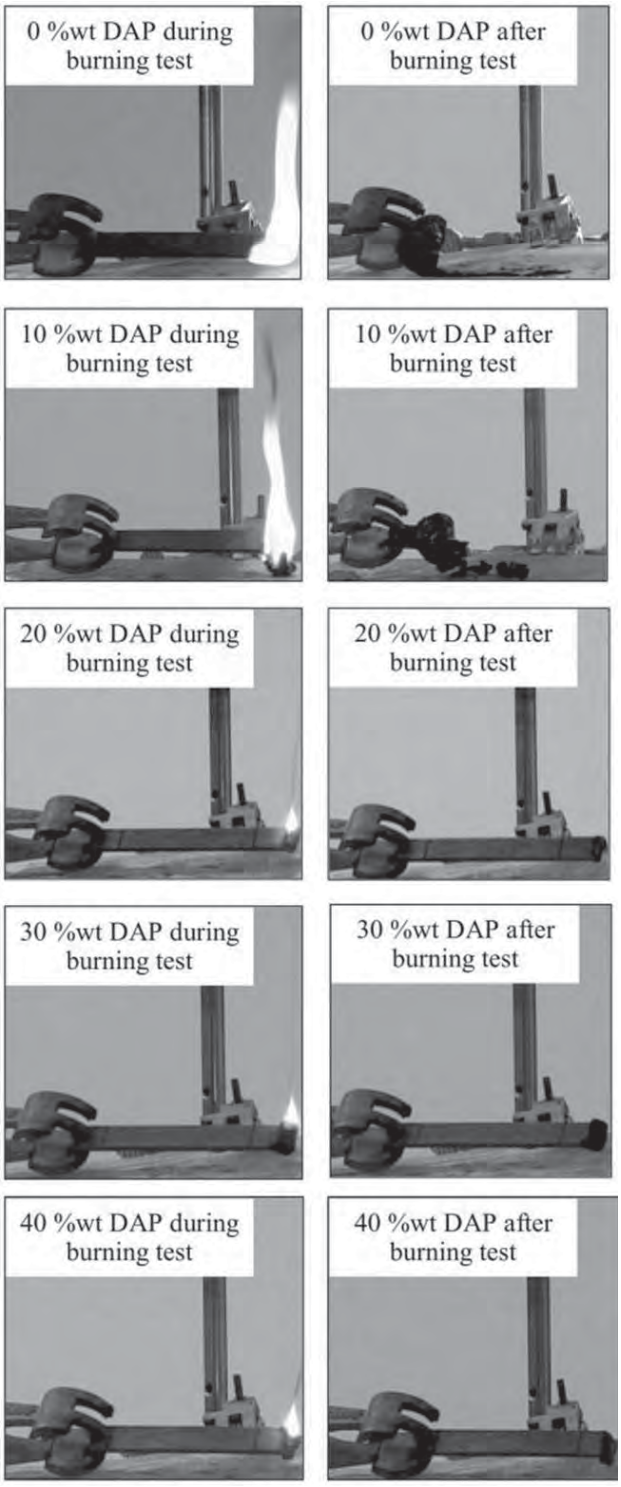


FIG. 4. Pictures of horizontal burning test.

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TABLE 1. The horizontal burning test of the wood flour/EPS composites.

Wood flour-EPS composites at various DAP contents (wt%)	Linear burning rate (mm/min)
0	44.6 ± 3.1
10	26.1 ± 0.9
20	Flame front did not pass 25-mm reference mark
30	Flame front did not pass 25-mm reference mark
40	Flame front did not pass 25-mm reference mark

step were observed around 282 and 298°C for the unmodified and DAP-modified wood flour/EPS composites, respectively. The presence of DAP in wood flour/EPS composites reduced the first decomposition temperature. This behavior could be attributed to the first decomposition step corresponded to the decomposition of hemicellulose, lignin, and release of DAP's component such as NH_3 and H_2O [26]. The char residual from this step might act as heat insulator to protect and improve thermal stability for other components at the second step. Figure 2, the second decomposition temperature of wood flour/EPS composite was determined as 393°C whereas those of DAP-modified wood flour/EPS composites at 10–40 wt% were observed within the range of 404–426°C. The second decomposition temperature substantially increased with increasing DAP contents. Moreover, the rate of weight loss also revealed that wood flour/EPS composites modified with DAP reduced the degradation rate from 1.57 to 0.86%/°C when they were modified with DAP having a range of 0–40 wt%. The results confirmed the observed

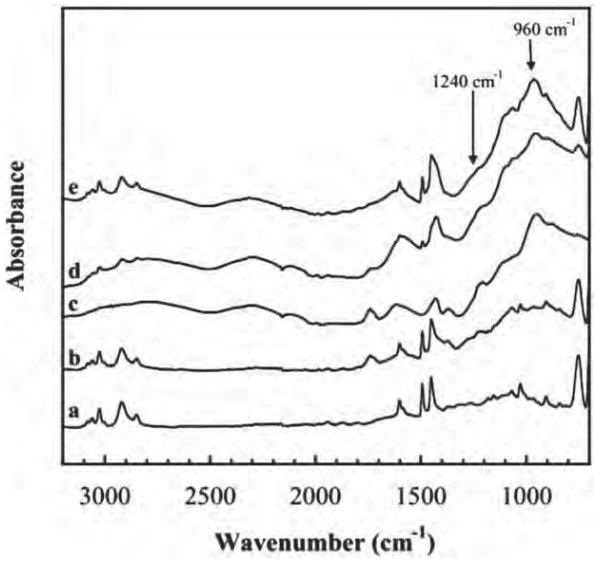


FIG. 5. ATR spectra of char residues of wood flour/EPS composites modified with DAP: 0 wt% DAP (a), 10 wt% DAP (b), 20 wt% DAP (c), 30 wt% DAP (d), and 40 wt% DAP (e).

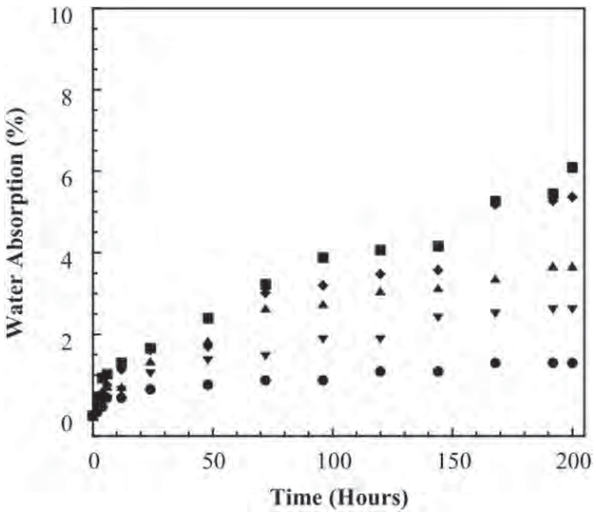


FIG. 6. Percentage water absorption of wood flour/EPS composites modified with DAP: (●) 0 wt% DAP, (▼) 10 wt% DAP, (▲) 20 wt% DAP, (◆) 30 wt% DAP content, and (■) 40 wt% DAP content.

enhancement in thermal stability of these wood composites at second step.

Flame Retardancy

LOI is widely used as a simple and precise method for evaluation of fire self-extinguishment and to determine the flame retardant properties of polymeric material [26]. The lager the LOI value of the material, the less susceptible it is to burn. In general, air is composed of approximately 21 vol% oxygen, any material with an LOI of less than 21 will easily burn in air. Materials with LOI between 21 and 27.9 vol% are well known as slow burning. Above this range, materials are considered to be self-extinguishing [27]. Figure 3 shows LOI data of all wood flour/EPS composites modified with DAP at various

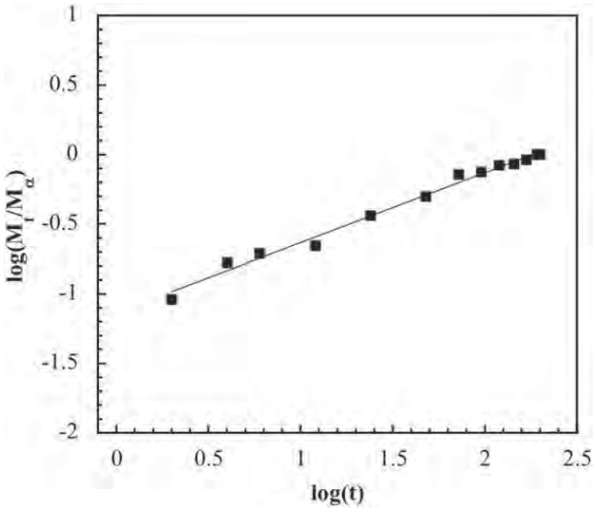


FIG. 7. Diffusion curve fitting plots of wood flour/EPS composite modified with 20 %wt DAP to determine *n* parameter.

TABLE 2. Diffusion case selection parameters and diffusion coefficients of the wood flour/EPS composites.

Wood flour-EPS composites at various DAP contents (% wt)	N	Diffusion coefficient $\times$ 10^{-9} (m^2/s)
0	0.46	1.18
10	0.48	1.60
20	0.52	4.26
30	0.56	4.39
40	0.50	4.96

contents. The unmodified-DAP wood flour/EPS composites was founded to be easy flammable and its LOI was only 18 because both EPS and wood flour were easily flammable materials. The LOI of wood flour/EPS composites tended to increase from 19.5 to 24.3 when these specimens were modified with DAP within a range of 10–40 wt%. The higher LOI values confirmed that DAP was an effective flame retardant for wood flour/EPS composites. These results were also consistent with those char yield values found from the TGA characteristics of samples. The char yields also increased with increasing DAP content, as shown in Fig. 1. The char of samples formed during combustion and acted as a protective layer so that oxygen diffusion to the surface of the specimen was prevented resulting in more oxygen needed for combustion process. Such results are in good agreement with the findings of the PP- and PE-based wood composite modified with ammonium phosphate [15].

Burning rates of wood flour/EPS composites containing different DAP contents are depicted in Fig. 4 and displayed in Table 1. The unmodified-DAP wood flour/EPS composites showed the highest linear burning rate at 44.6 $\pm$ 3.1 mm/min whereas the addition of 10 wt% DAP reduced the burning rate to 26.1 $\pm$ 0.9 mm/min. In case of modification with 20–40 wt% DAP, the flame front did not pass 25-mm reference mark as illustrated in Fig. 4. These results implied that the additions of 20 wt% DAP in wood flour/EPS composites was a sufficient and its burning rate was significantly lower than that of commercial WPCs of about 7.1–18.1 mm/min [28]. Based on the flame retardancy results, it is clearly seen that during fire disaster with high temperature, building decoration materials made of flame retardant modified WPCs would show better performance in gaining time for rescuing.

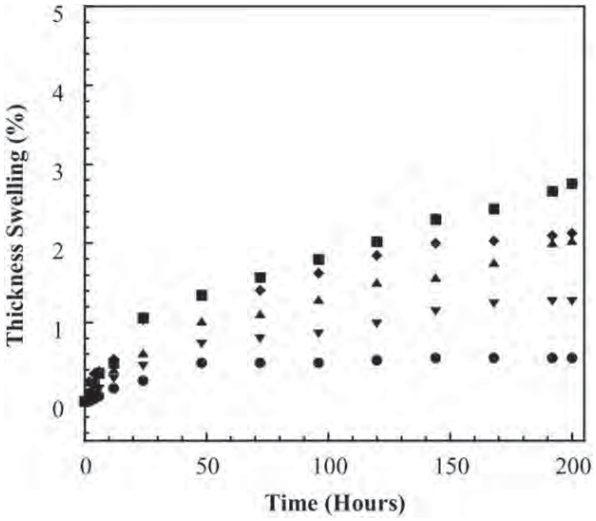


FIG. 9. Percentage thickness swelling of wood flour/EPS composites modified with DAP: (●) 0 wt% DAP, (▼) 10 wt% DAP, (▲) 20 wt% DAP, (◆) 30 wt% DAP, and (■) 40 wt% DAP.

Attenuated Total Reflection Infrared Analysis of Char Residues

To better understand the action of the flame retardant, further study of the structures of char residues after the LOI test were observed by FTIR-ATR. Figure 5 shows

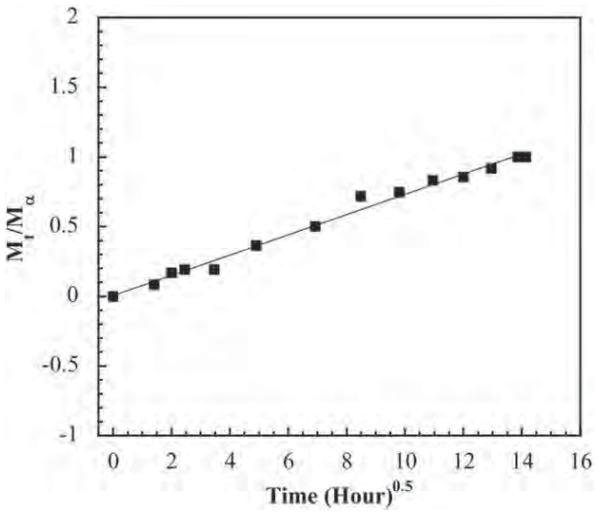


FIG. 8. Diffusion curve fitting plots of wood flour/EPS composite modified with 20 %wt DAP to determine diffusion coefficient.

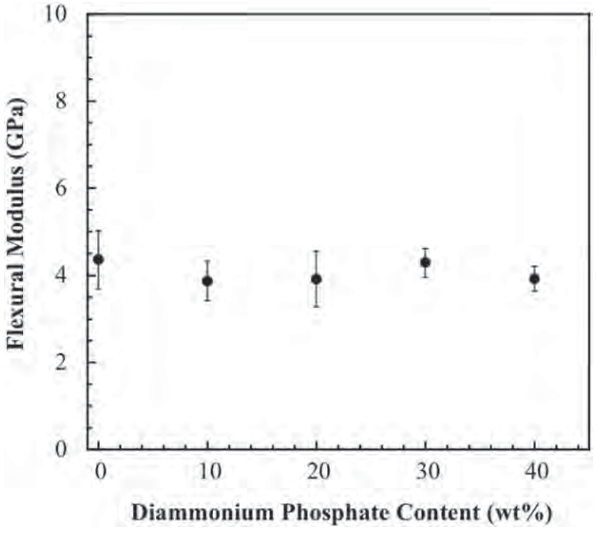


FIG. 10. Flexural modulus of wood flour/EPS composites modified with DAP.

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TABLE 3. Flexural modulus and flexural strength of various wood plastic composites.

Composite type	Mass fraction of fiber (wt%)	Mass fraction of flame retardant (wt%)	Flexural modulus (GPa)	Flexural strength (MPa)
Commercial wood flake reinforced HDPE [33]	50–70	–	2.7–3.1	18–31
Recycled-HDPE bio-composite from rice husk and sawdust as filler and flame retardants (sodium meta-silicate and zinc borate) [34]	41.6	0–40	2.0–2.5	16–18
Wood flour–PE composite modified with various types of flame retardants [35]	50	2.5–10	3.6–5.2	30–36
Wood flour–PP composite modified with various types of flame retardants [36]	25	5–25	2.9–3.3	53–56

the strong absorption of phosphorus ester at 960 cm^{-1} (P-O-C, aromatic streching) and 1240 cm^{-1} (P=O) for the char residues of wood flour/EPS composites modified with DAP [15, 29]. It implied that the interaction between phosphoric acid and the primary hydroxyl group provided phosphate ester as mentioned in Scheme 1. These results were also consistent with the increasing of char yield from the TGA results.

Water Absorption of the Wood Flour/EPS Composites

The values of water absorption and thickness swelling for the wood flour/EPS composites at varied DAP loadings are shown in Fig. 6. The percentage of water absorbed plotted against time for all samples showed a similar behavior, i.e., the samples absorbed water more rapidly during first stages (0–24 h). The water adsorption values of samples were in range of 0.64–1.66% after 24 h and 1.26–6.05% after 200 h of immersion. The water absorption values were significantly lower than the reported commercial WPC of 4.59% after 24 h of immersion [28]. Moreover, the water absorption of all samples increased with increasing DAP content. This is likely caused by the hydrogen bonding of the water molecules to free OH groups presented in the DAP structure, and possible diffusion of water molecules into the composite. The similar tends of water absorption were also observed in the wood–PP composites modified with phosphate compounds as flame retardant [19].

Kinetic of Water Sorption

It is necessary to study the kinetic water sorption to have better understanding of the water sorption mechanism and to minimize water uptake of materials. Generally, the analysis of diffusion mechanism and kinetics was performed based on Fick's theory. The generalized equation can be expressed as:

$$\frac{M_t}{M_\alpha} = kt^n \tag{2}$$

where M_t is the moisture content at time t; and M_α is the moisture content at equilibrium; k and n are constants.

The diffusion behaviors can be classified as: super case II ($n > 1$), case II ($n = 1$), anomalous ($1/2 < n < 1$), classical/Fickian ($n = 1/2$), or pseudo-Fickian ($n < 1/2$). From the plots of log M_t/M_α versus log t, a good linear correlation was observed and slope value of wood flour/EPS composite modified with 20 %wt DAP was also calculated from the fitted curve, as illustrated in Fig. 7. The obtained slope values of all samples were summarized in Table 2. The absorption of water in the wood flour/EPS composites approached toward the Fickian diffusion case, as the value of n were determined to be in the range of 0.46–0.56. Generally, the water adsorption in natural fiber reinforced plastics usually follows Fickian behavior [30].

Transport Coefficients

The diffusion coefficient (D) is the most important parameter of the Fick's model. This parameter presents the ability of solvent molecules to penetrate inside the composite structure and can be calculated using the following equation:

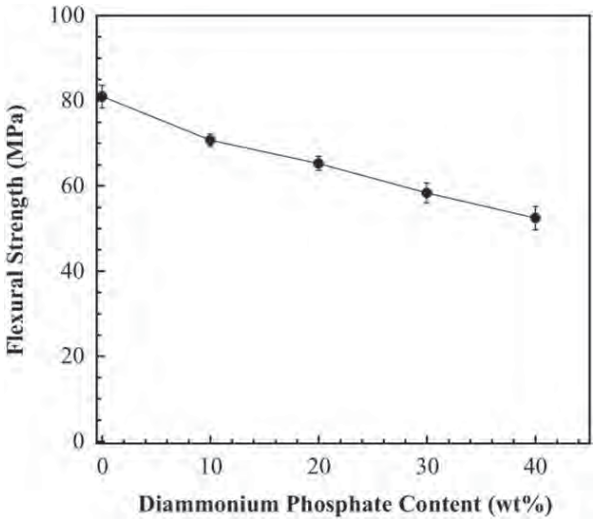


FIG. 11. Flexural strength of wood flour/EPS composites modified with DAP.

$$\frac{M_t}{M_\alpha} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{0.5} t^{0.5} \quad (3)$$

where L is the thickness of sample.

From *Eq. 3*, the diffusion coefficient was obtained from the slope of the plot of M_t/M_α versus $(\text{time})^{0.5}$, as depicted in Fig. 8. The obtained values from curves fitting were shown in Table 2. The diffusion coefficient values of wood flour/EPS composites expectedly showed an increasing trend with increasing DAP contents. This was due to the hydrophilic characteristics of DAP incorporated.

Thickness Swelling of the Samples

The thickness swelling (TS) of sawdust filled EPS is illustrated in Fig. 9. The thickness swelling of specimens increased with increasing DAP content similar to water absorption results. The TS values of 0–40 wt% DAP samples after 24 h and 7 days water immersion varied from 0.26 to 1.06%. Overall TS values of the samples were within the same range of that of commercial wood-based composite products such as fiberboards (1.6–5.45%) [31]. As shown in Fig. 8, the thickness swelling increased only in the initial stage and thereafter remained almost constant. After 7 days, the thickness swelling leveled off and the percentages of the TS values were observed to be within the range of 0.55–2.43% which was lower than the low-density polyethylene wood composite modified with carbon nanotube (4–7.8%) [32].

Flexural Properties of Wood Flour/EPS Composites

Flexural properties of wood flour/EPS composites modified with DAP at different contents are illustrated in Fig. 10. The average flexural modulus of our wood composites ranged from 3.9 to 4.4 GPa. From Table 3, the flexural modulus of wood flour/EPS composites was significantly higher than those of reported wood plastic composites, e.g., commercial wood particles reinforced HDPE (2.7–3.1 GPa) [33], recycled-HDPE biocomposite from rice husk and saw dust as filler and flame retardants (sodium metasilicate and zinc borate: 2.0–2.5 GPa) [34] as well as wood flour–PE composite and –PP composite modified with various types of flame retardants (3.6–5.2 and 2.9–3.3 GPa, respectively) [35, 36]. Figure 11 exhibits the flexural strength of wood flour/EPS composites ranging from 52 to 81 MPa. The flexural strength of composites slightly decreased when the amount of DAP increased. Similar trend of result was also observed in the wood flour–PP composite modified with DAP due possibly to, the poor compatibility between DAP on the fiber surface and polymer matrix [15]. However, all wood flour/EPS composites still showed higher flexural strength than the major wood plastic composite products listed in Table 3.

CONCLUSIONS

The effect of DAP on thermal degradation, flammability, dimension stability, and mechanical properties of wood flour/EPS composites was investigated. The fire resistant properties of the wood flour/EPS composites tended to increase with the increasing DAP contents. The rate of thermal degradation substantially reduced from 1.57 to 0.86%/°C. Especially, wood fiber/EPS composite modified with DAP up to 20 wt% provided the best linear burning rate. Both water absorption and thickness swelling values were within same range of commercial wood plastic composite. Flexural modulus and flexural strength characteristics were higher than those of commercial wood plastic composite and other wood composite modified with flame retardant. Based on results, wood flour/EPS modified with DAP has a potential to use in furniture, floor, and decoration panels which can increase security of interior building with increasing time for rescuing during fire disaster.

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Role of Filler Effect and Pozzolanic Reaction of Biomass Ashes on Hydrated Phase and Pore Size Distribution of Blended Cement Paste

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Abstract: The role of filler effect and pozzolanic reaction of biomass ash on hydrated phase and pore size distribution of blended cement paste was studied. Rice husk ash (RHA), palm oil fuel ash (POFA), and river sand (RS) were ground to two fineness values, and used to replace Type I portland cement (OPC) at 0, 20, and 40% by weight of binder. A water to binder ratio of 0.35 was used. The compressive strength, pore size distribution, and thermogravimetric analyses of the blended cement pastes were investigated. Partial replacement of OPC with fine RHA and POFA at a dosage of 20% by weight of binder resulted in pastes with higher compressive strengths than that of OPC paste. The compressive strengths of RHA paste were slightly higher than those of POFA pastes at the same age. The differences between mass losses (at 30–450°C) of RS and RHA (or POFA) blended pastes at the same fineness, curing time, and replacement rate were due to the pozzolanic reaction, which increased in accordance with particle fineness and cement replacement rate. In addition, the weight losses (at 30–450°C) due to the pozzolanic reaction were higher than those due to the filler effect. The use of fine RHA and POFA enhanced the pozzolanic reaction, and reduced the average pore diameters of pastes. **DOI: 10.1061/(ASCE)MT.1943-5533.0000921.** © *2013 American Society of Civil Engineers.*

Author keywords: Biomass ash; Filler effect; Pozzolanic reaction; Thermogravimetric analysis; Porosity; Hydrated phase.

Introduction

Currently, there are many types of pozzolans such as fly ash and silica fume used as supplementary cementations materials in the concrete industry. In Thailand, rice husk ash (RHA) is a byproduct of electricity generation biomass power plants. It has been estimated that more than 1.6 million tons of RHA are produced every year (Wansom et al. 2010). Palm oil fuel ash (POFA) is a byproduct of the burning of palm shells, empty fruit bunches, and palm fiber in palm oil factories. The annual production of POFA is greater than 100,000 tons. Ground RHA and POFA are good pozzolanic materials, and can be used to replace portland cement up to 30% by binder weight (Ganesan et al. 2008; Rukzon et al. 2009; Sata et al. 2004). Use of ground RHA and POFA to partially replace Type I ordinary portland cement (OPC) improves its resistance to chloride penetration (Chindaprasirt et al. 2008; Ganesan et al. 2008) and sulfate resistance (Chatveera and Lertwattanaruk 2011; Tangchirapat et al. 2009).

The compressive strength of OPC mortar or concrete with pozzolanic material is contributed by three major causes, as follows: (1) a hydration reaction between cement and water, (2) the filler effect of small particles that leads to a more homogeneous paste, and (3) a pozzolanic reaction occurs when silicon dioxide (SiO_2) and aluminum trioxide (Al_2O_3) in a pozzolanic material react with calcium hydroxide [$Ca(OH)_2$]. Thermal analysis has been used successfully to analyze the hydration products (Chaipanich and Nochaiya 2010; Chaipanich et al. 2010; Wongkeo and Chaipanich 2010). These studies show that there are three main temperature intervals associated with dehydration of hydration products, decomposition of $Ca(OH)_2$, and mass loss of calcium carbonate ($CaCO_3$).

The pozzolanic reaction has two effects, as follows: (1) there is a decrease in the amount of $Ca(OH)_2$ in accordance with the increases in curing time, replacement level, and fineness of pozzolan [the $Ca(OH)_2$ has an adverse effect on strength and durability of concrete]; and (2) calcium-silicon-hydrogen (C-S-H), calcium-aluminum-hydrogen (C-A-H), and calcium-aluminum-silicon-hydrogen (C-A-S-H) phases increase in accordance with increasing curing time. C-S-H possesses greater mechanical strength than C-A-H and C-A-S-H, whereas $Ca(OH)_2$ has low strength because it has a lamellar structure (Askarinejad et al. 2012; El-Bouny 1994).

Use of pozzolanic materials to partially replace cement in concrete gives the filler effect and pozzolanic reaction. However, it could delay the early strength development due mainly to the insufficient fineness of pozzolan. A number of studies have reported the results of both the filler effect and pozzolanic reaction. Goldman and Bentur (1993) found that the microfiller effect (from carbon black) led to a greater strength than the pozzolanic reaction of silica fume. Tangpagasit et al. (2005) studied the packing effect and the pozzolanic reaction of fly ash on the compressive strength of mortar. They reported that the strength due to the pozzolanic reaction of 20% fly ash at 3 days was 3% of the control, and at 28 and 90 days increased to 20 and 27%, respectively. Jaturapitakkul et al.

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(2011) reported that the pozzolanic reaction of ground palm oil fuel ash increased in accordance with increasing particle fineness, cement replacement rate, and age of mortar. In addition, the compressive strength due to the pozzolanic reaction had a greater effect than the filler effect.

Researchers have reported use of river sand (RS) as an inert material to replace Type I portland cement to evaluate influences the hydration reaction, filler effect, and pozzolanic reaction on the compressive strength, sulfate resistance, and chloride resistance (Jaturapitakkul et al. 2007; Chindaprasirt et al. 2008; Sinsiri et al. 2012). However, the separation of the hydration reaction, filler effect, and pozzolanic reaction on the hydrated phase and total porosity of blended cement pastes has not been well established. Thus, the objective of the research reported in this paper is to study the role of filler and pozzolanic reaction of biomass ash on the hydrated phase and pore size distribution of blended cement paste. The results should help lay the foundation for the use of biomass ash in concrete and help reduce the volume of waste disposed in landfills.

Experimental Details

Materials

The materials used in the research reported in this paper are portland cement Type I (i.e., OPC) in accordance with ASTM C150-09 (ASTM 2009). Rice husk ash and palm oil fuel ash from a thermal power plant in Thailand were used as a pozzolan, and the inert material used was ground river sand (RS). The RHA, POFA, and RS were ground to two fineness values, i.e., a coarse material with similar median particle size to OPC, with a grinding machine. The fine rice husk ash (FRHA), fine palm oil fuel ash (FPOFA), and fine river sand (FRS) were obtained from the sieving and milling. They were first sieved through a sieve No. 200. After sieving, they were intense ground using attrition milling for 60 min. Attrition milling was selected based on the work of Kumar et al. (2008) and Kumar and Kumar (2011), who reported efficient milling of slag to median particle sizes of 3.9 μm after 60 min of milling. The finenesses of the milled materials were measured after milling to ensure the required fineness. Table 1 shows the physical properties and chemical compositions of materials. The sums of SiO_2, Al_2O_3, and Fe_2O_3 in course rice husk ash (CRHA) and FRHA were 91.1 and 89.2%, respectively, which are higher than 70% for Class N pozzolan specified in ASTM C618-01 (ASTM 2001). For coarse palm oil fuel ash (CPOFA) and FPOFA, the sums were 56.9 and 58.6%, respectively. The results are similar to those obtained by Awal and Hussin (1997), who reported that POFA might be grouped between Class C and F pozzolan in accordance with ASTM C618-01 (2001), and the sum of SiO_2, Al_2O_3, and Fe_2O_3 content of palm oil fuel ash used in their study was 59.7%, which was close to the findings in the research reported in this paper. The major chemical compositions of coarse river sand (CRS) and FRS were 92.0 and 91.2% SiO_2, respectively. For quantitative X-ray diffraction (XRD), an analysis based on the Rietveld method was performed and calculated using Bruker's TOPAS. The percentages of amorphous CRHA, FRHA, CPOFA, and FPOFA were 70.1, 69.6, 70.2, and 67.2% (by mass), respectively. The CRS and FRS, however, contains 100% (by mass) crystalline phase. Thus, ground RS is inert material. The results agree with those of Idir et al. (2011) and Kiattikomol et al. (2000). The median particle sizes of OPC, CRHA, CPOFA, and CRS were 14.6, 14.8, 15.6, and 15.9 μm in accordance with a laser particle size analyzer and Blaine fineness values of 3,600, 7,600, 6,700, and 3,900 cm^2/g, respectively (Rukzon et al. 2009; Jaturapitakkul et al. 2011). For the fine particle size group, the median particle sizes and Blaine finenesses of FRHA, FPOFA, and FRS were 1.9, 2.1, and 2.2 μm, and 18,000, 14,900, and 6,300 cm^2/g, respectively. Fig. 1 shows a comparison of the particle size distributions of Type I portland cement RS, RHA, and POFA. The two group of materials particle size are similar to the particle size of the cement and smaller, respectively.

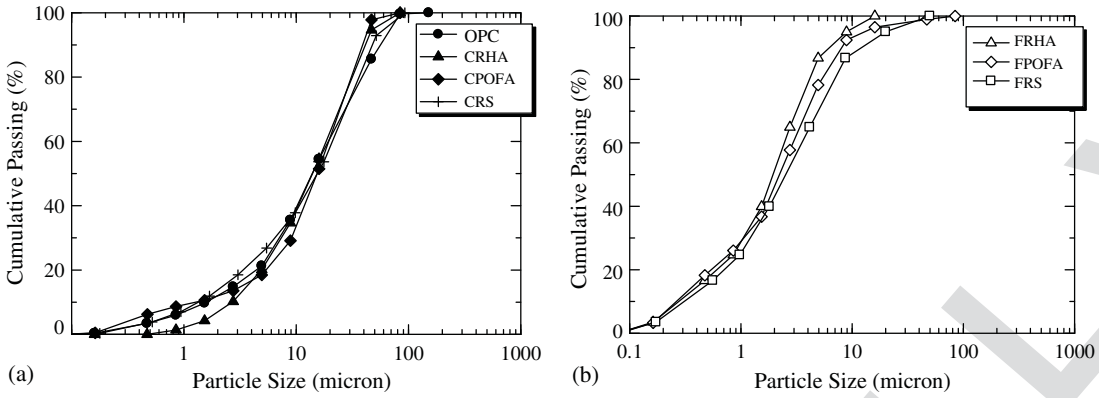
Mix Proportion of Cement Paste

The OPC was replaced with ground RHA, POFA, and RS at 0, 20, and 40% by weight of binder. A water to binder (WB) ratio of 0.35 was used for all blended cement pastes to separate the hydration reaction, filler effect, and pozzolanic reaction. Keeping the same water to cement ratio for comparison is convenient especially for the strength at same WB ratio, but this method gives different workability of mixes. After mixing, the cement pastes were immediately cast into cube specimens of $50 \times 50 \times 50$ mm. The cast specimens were covered with plastic to prevent water loss. After casting for 24 h, the specimens were removed from the molds and cured in saturated lime water at a temperature of 23 ± 2°C. The compressive strength was tested using $50 \times 50 \times 50$-mm cube specimens in accordance with ASTM C109-02 (ASTM 2002) at ages of 7, 28, and 90 days. Five samples were tested for each age group.

Table 1. Chemical and Physical Compositions of Materials

Chemical composition (%)	OPC	CRHA	CPOFA	CRS	FRHA	FPOFA	FRS
Silicon dioxide (SiO_2)	20.8	88.8	54.0	92.0	87.8	55.7	91.2
Aluminum oxide (Al_2O_3)	4.7	0.6	0.9	1.6	0.5	0.9	1.8
Iron oxide (Fe_2O_3)	3.4	1.7	2.0	0.6	0.9	2.0	0.2
Calcium oxide (CaO)	65.3	1.1	12.9	0.9	1.2	12.5	0.7
Magnesium oxide (MgO)	—	0.6	4.9	0.1	0.6	5.1	0.1
Sodium oxide (Na_2O)	0.1	0.2	1.0	0.1	0.2	1.0	0.1
Potassium oxide (K_2O)	0.4	2.0	13.5	2.2	2.2	11.9	2.3
Sulfur trioxide (SO_3)	2.7	0.1	4.0	—	0.1	2.9	—
Loss on ignition (LOI)	0.9	3.6	3.7	2.1	5.2	4.7	1.8
Quantitative X-ray diffraction, Rietveld method							
Amorphous (%)	—	70.1	70.2	—	69.6	67.2	—
Crystalline (%)	—	29.9	29.8	100.0	30.4	32.8	100.0
Physical properties of materials							
Specific gravity	3.14	2.29	2.36	2.59	2.31	2.48	2.61
Median particle size, d_{50} (μm)	14.6	14.8	15.6	15.9	1.9	2.1	2.2
Blaine fineness (cm^2/g)	3,600	7,600	6,700	3,900	18,100	14,900	6,300

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F1:1 **Fig. 1.** Particle size distributions of the materials: (a) coarse material; (b) fine material

Thermal Analysis

The samples were submerged directly into liquid nitrogen for 5 min and were then evacuated at a pressure of 0.5 Pa at 40°C for 48 h. This method has been used previously to stop the hydration reaction of cement paste (Galle 2001; Konecny and Naqvi 1993). The samples were subjected to thermogravimetric analysis using Netzsch STA 409 C/CD equipment. The samples were heated from room temperature to 1,000°C at a heating rate of 10°C/ min under a nitrogen atmosphere. The weight loss of sample in the range of 30–450°C was determined to semiquantitatively calculate the gel products of the blended cement pastes. The amount of $Ca(OH)_2$ was calculated from the weight loss between 450 and 580°C (El-Jazairi and Illston 1977).

Determination of the Porosity of the Pastes

The pore size distribution in hardened cement pastes was determined using a mercury intrusion porosimeter (MIP) with a pressure range from 0–228 MPa (0–33,000 lb · in^{-2}). The samples were obtained by carefully breaking the cube specimens with a chisel. Representative samples thickness of 3–6 mm weighing between 1 and 1.5 g were taken from the middle part of specimen. Before testing, the hydration reaction was stopped with liquid nitrogen (Galle 2001; Konecny and Naqvi 1993). The pressure was expressed with the Washburn (1921) equation. A constant contact angle of 140° and a constant surface tension of mercury 480 dynes/ cm were used for the pore size calculation.

Results and Discussion

Compressive Strength

Table 2 shows the compressive and normalized compressive strength of pastes. The compressive strengths of ground RS blended paste especially at the high replacement were significantly less than that of OPC paste at the same age. This effect is due to the inert material and the reduced amount of OPC, which causes low hydration reaction (Tangpagasit et al. 2005). The compressive strength of paste with FRS was higher than that of CRS because the small particles of FRS filled the voids and increased the compressive strength of the paste. These results confirmed that the small particles exerted a filler effect and contributed to the compressive strength of the pastes (Goldman and Bentur 1993; Tangpagasit et al. 2005).

The compressive strengths at 28 days of all pastes containing coarse ashes were less than that of OPC paste. After 90 days, the compressive strengths of 20CRHA and 20CPOFA pastes were higher than that of OPC paste, whereas those of 40CRHA and 40CPOFA were still lower. For the 20% replacement of fine ashes, the compressive strengths at 28 days of 20FRHA and 20FPOFA pastes were higher than that of OPC paste. The higher strengths indicated that the FRHA and FPOFA were better dispersed in the blended cement paste and gave a faster pozzolanic reaction, leading to an increased C-S-H compared with the coarser pastes.

The increased compressive strengths of blended cement paste were due to filler effect and pozzolanic reaction. The small particles

Table 2. Compressive Strengths of Pastes

Symbol	Compressive strength (MPa)				Normalized compressive strength (%)			
	7 days	28 days	60 days	90 days	7 days	28 days	60 days	90 days
OPC	53.0	75.0	84.6	99.1	100.0	100.0	100.0	100.0
20CRS	42.9	60.8	67.9	78.6	80.9	81.1	80.3	79.3
40CRS	31.5	45.6	51.5	59.6	59.4	60.8	60.9	60.1
20FRS	45.0	63.4	70.8	82.1	84.9	84.5	83.7	82.8
40FRS	34.2	49.2	55.4	63.9	64.5	65.6	65.5	64.5
20CRHA	49.8	74.2	88.3	106.0	94.0	98.9	104.4	107.0
40CRHA	42.4	64.7	77.4	92.1	80.0	86.3	91.5	92.9
20FRHA	52.9	78.7	93.1	113.2	99.8	104.9	110.0	114.2
40FRHA	44.5	66.9	79.5	96.1	84.0	89.2	94.0	97.0
20CPOFA	48.3	72.0	84.6	102.0	91.1	96.0	99.6	102.9
40CPOFA	41.0	61.5	72.8	88.1	77.4	82.0	85.7	88.9
20FPOFA	51.9	77.3	92.2	109.6	97.9	103.1	108.6	110.6
40FPOFA	44.0	66.5	78.6	94.1	83.0	88.7	92.6	95.0

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filled the voids of paste, allowing for denser packing within the matrix phase. The pozzolanic reaction also increased as the fine pozzolanic materials was able to react better with $Ca(OH)_2$ to form extra hydration products than that of coarser pozzolans. Incorporation of ashes refined the porosity of paste and resulted in high compressive strength (Chindaprasirt et al. 2005, 2007). These results suggested that both RHA and POFA with high fineness are good pozzolanic materials and can be used to replace portland cement. The use of 20% replacement produced pastes with higher compressive strength. However, 40% replacement led to a slight reduction in compressive strengths of 40FRHA and 40FPOFA pastes to 96.1 and 94.1 MPa, or 97.0 and 95.0% of that of the OPC paste at 90 days, respectively. The reduction was due to the large reduction in OPC and the associated reduced hydration.

Thermal Analysis of the Blended Cement Pastes: Influence of Ground River Sand on Hydrated Phase

Fig. 2 shows the thermogravimetric analysis (TGA) curves of OPC paste and RS blended pastes. The mass loss transitions occurred in three steps, as follows: (1) mass loss from dehydration of ettringite, C-S-H, C_2ASH_8 , and C_4AH_{13} at 30–450°C (Bai et al. 2003); (2) mass loss of $Ca(OH)_2$ occurred at 450–580°C (El-Jazairi and Illston 1977); and (3) 580–1000°C represented the mass loss of calcium carbonate ($CaCO_3$; El-Jazairi and Illston 1977). The mass loss at 30–450°C of RS blended pastes increased in accordance with fineness and decreased in accordance with replacement level. It was likely that the addition of fine RS, the particles of which were finer than those of portland cement, caused segmentation of large pores and increased nucleation sites for precipitation of hydration products in cement paste similarly to the addition of fine fly ash (Mehta 1987). This mass loss increased in accordance with curing time as a result of the increase in hydration reaction, which caused an increase in compressive strength (Kroehong et al. 2011).

Fig. 3 shows the $Ca(OH)_2$ content of OPC paste and RS blended pastes. The $Ca(OH)_2$ content of all pastes increased in accordance with curing time as a result of hydration of cement. The $Ca(OH)_2$ content of RS blended pastes was less than that of OPC paste especially at high replacement level due to the reduced reaction from the reduced OPC content and the nonreactive RS. The $Ca(OH)_2$ content of FRS blended pastes was less than those of pastes with the CRS due to the higher nucleation effect of fine particles (Askarinejad et al. 2012; El-Bouny 1994; Metha 2007).

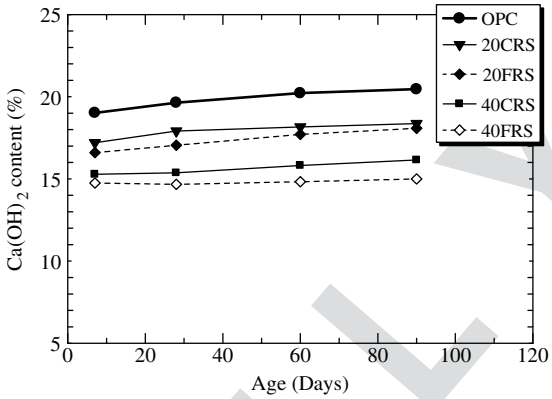


Fig. 3. $Ca(OH)_2$ content of OPC and RS blended cement pastes

Table 3. $Ca(OH)_2$ Content of Pastes

Symbol	$Ca(OH)_2$ (%) 7 days	28 days	60 days	90 days
OPC	19.02	19.64	20.22	20.46
20CRS	17.20	17.91	18.16	18.37
20CRHA	15.57	15.45	15.37	14.34
20CPOFA	15.82	15.74	15.44	15.10
40CRS	15.28	15.37	15.82	16.15
40CRHA	12.12	11.01	9.45	8.83
40CPOFA	12.28	11.30	9.65	9.24
20FRS	16.60	17.05	17.71	18.08
20FRHA	14.80	14.13	13.64	13.33
20FPOFA	15.24	14.87	14.42	13.93
40FRS	14.75	14.67	14.83	15.00
40FRHA	11.46	9.09	7.68	6.43
40FPOFA	11.75	10.06	7.85	7.19

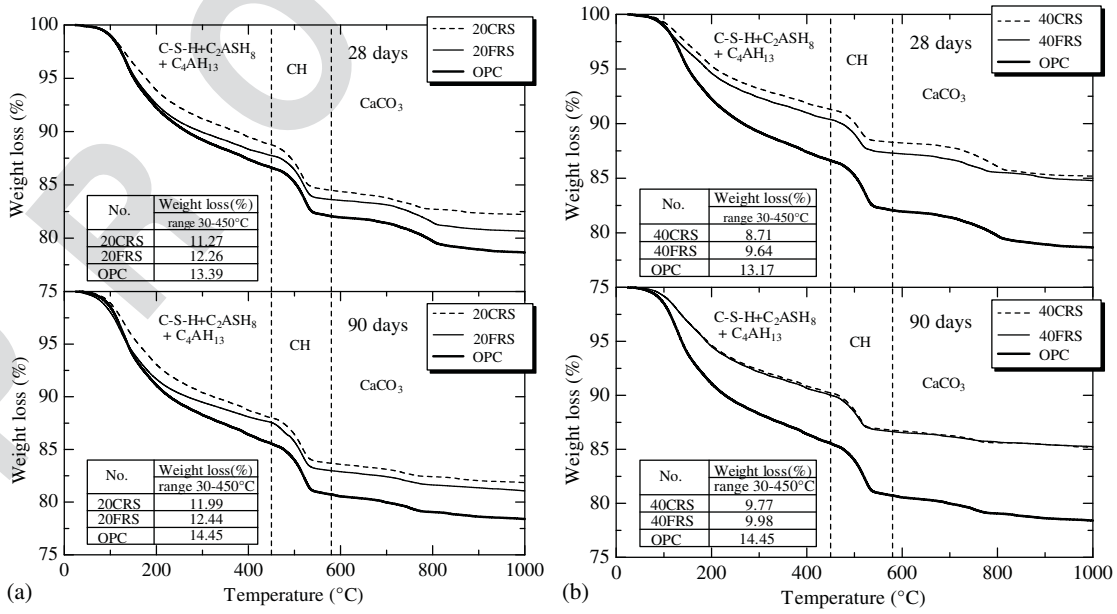
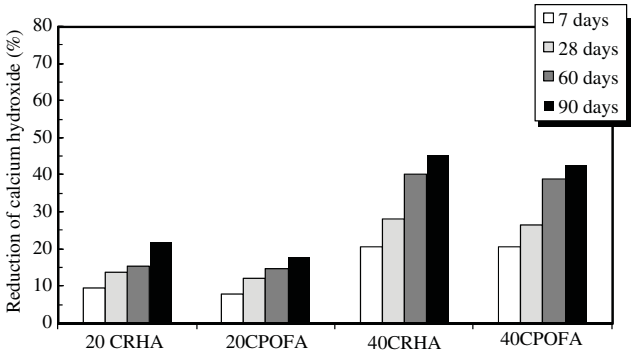
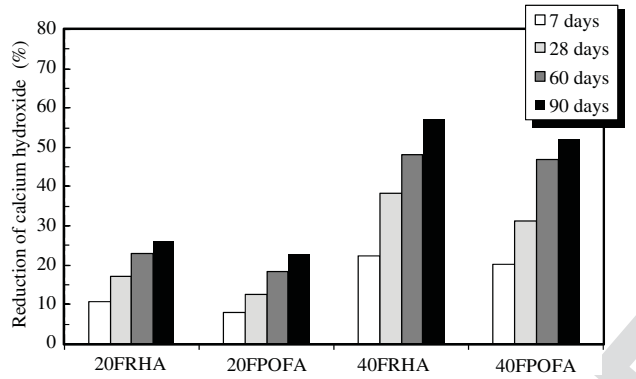


Fig. 2. Thermogravimetric analysis curves of OPC and RS blended cement pastes: (a) 20% replacement; (b) 40% replacement

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F4:1 **Fig. 4.** Reduction of $Ca(OH)_2$ content of CRHA and CPOFA pastes

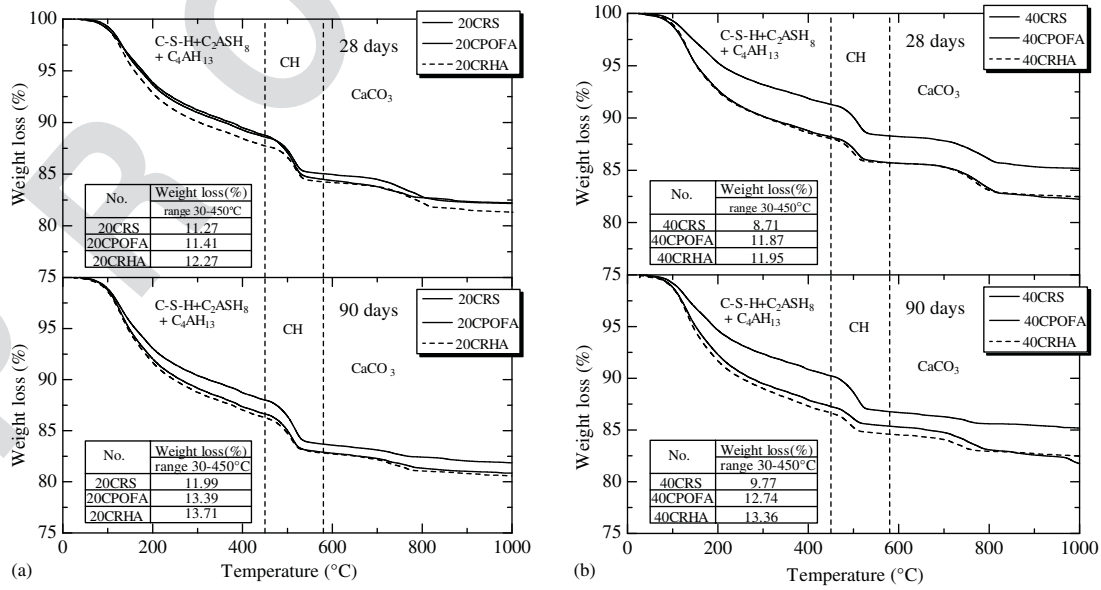


F5:1 **Fig. 5.** Reduction of $Ca(OH)_2$ content of FRHA and FPOFA pastes

Thermal Analysis of the Blended Cement Pastes: Influence of Pozzolanic Reaction on Hydrated Phase

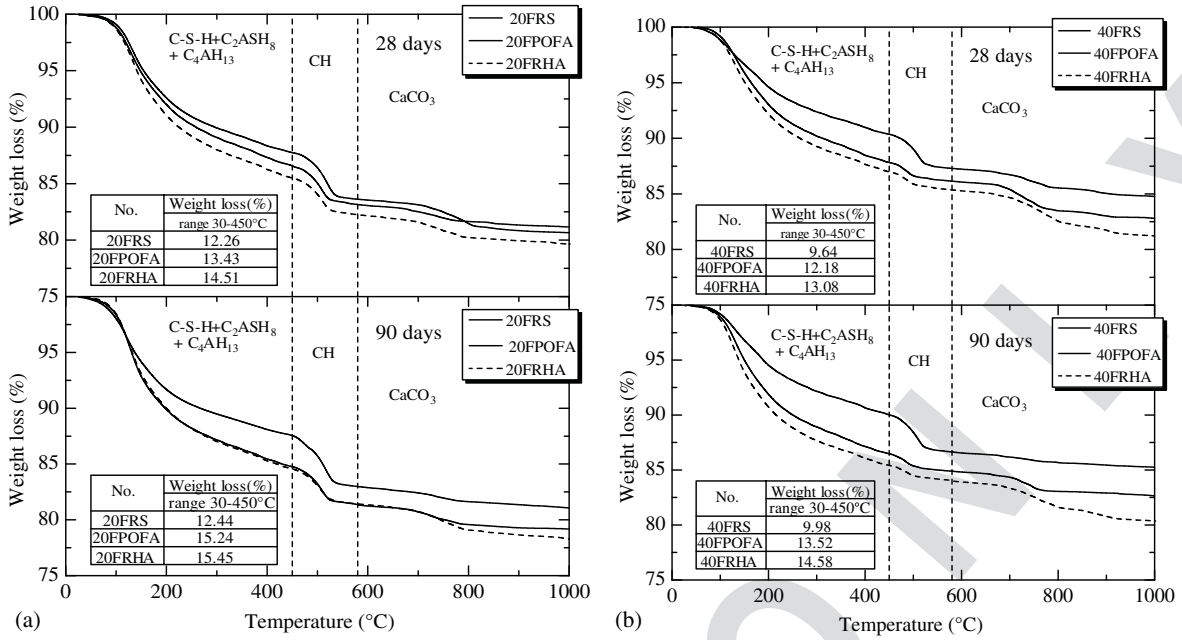
Table 3 shows the results of $Ca(OH)_2$ contents of pastes at 7, 28, 60, and 90 days. Figs. 4 and 5 show the reductions of $Ca(OH)_2$ content of RHA and POFA pastes, which were determined from the difference in $Ca(OH)_2$ content between RS blended pastes and RHA (or POFA) pastes with the same particle size, replacement level, and age. The $Ca(OH)_2$ contents of RS blended pastes were higher than those of RHA and POFA pastes because the SiO_2 in RS was nonreactive. For the coarse pozzolans, the $Ca(OH)_2$ content of 20CRHA, 20CPOFA, 40CRHA, and 40CPOFA pastes were reduced from the ages of 28 to 90 days from 15.57 to 14.34%, 15.82 to 15.10%, 12.12 to 8.83%, and 12.28 to 9.24% (or approximately 22, 18, 45, and 43%) compared with RS blended pastes, respectively. The reductions of $Ca(OH)_2$ content in the RHA and POFA pastes indicated its consumption by the pozzolanic reaction. In addition, the reduction of $Ca(OH)_2$ content for high replacement level was higher than that of low replacement level. For fine pozzolans, the $Ca(OH)_2$ contents of 20FRHA, 20FPOFA, 40FRHA, and 40FPOFA pastes were also reduced from the ages of 28 to 90 days from 14.80 to 13.33%, 15.24 to 13.93%, 11.46 to 6.43%, and 11.75 to 7.19% (or approximately 26, 23, 57, and 52%) compared with RS blended pastes, respectively. The $Ca(OH)_2$ contents of RHA and POFA pastes decreased in accordance with the increases in curing time, fineness, and replacement level (Barbhuiya et al. 2009; Chindaprasirt et al. 2007; Poon et al. 2001).

Figs. 6 and 7 show the TGA results for RS, RHA, and POFA blended pastes. The first mass losses (at 30–450°C) of RHA and POFA pastes were higher than those of RS blended pastes. For example, the mass losses of 20CRHA, 20CPOFA, 40CRHA, and 40CPOFA pastes at 28 days were 12.27, 11.41, 11.95, and 11.87%, respectively, whereas those of 20CRS and 40CRS blended pastes at 28 days were less at 11.27 and 8.71%, respectively. At 90 days, they increased to 13.71, 13.39, 13.36, and 12.74%, whereas those of 20CRS and 40CRS blended pastes were still less at 11.99 and 9.77%, respectively. The first mass losses of CRHA and CPOFA pastes were higher than those of RS blended pastes, especially at a higher replacement level, due to the pozzolanic reaction of RHA and POFA compared with no pozzolanic reaction of RS. For pastes with fine ashes, the first mass loss of FRHA and FPOFA pastes were similar to those of CRHA and CPOFA pastes, but the first mass losses for the FRHA and FPOFA pastes were higher than those of the CRHA and CPOFA pastes because FRHA and FPOFA had large surface areas, which produced increased



F6:1 **Fig. 6.** Thermogravimetric analysis curves of CRS, CRHA, and CPOFA pastes: (a) 20% replacement; (b) 40% replacement

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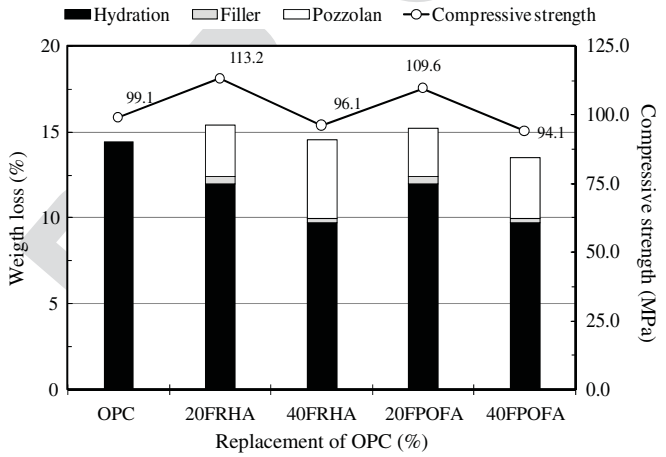


F7:1 **Fig. 7.** Thermogravimetric analysis curves of FRS, FRHA, and FPOFA pastes: (a) 20% replacement; (b) 40% replacement

C-S-H, C_2A-S-H_8, and C_4A-H_{13}. These first mass loss (at 30–450° C) increased in accordance with curing time, particle fineness, and cement replacement rate.

Thermal Analysis of the Blended Cement Pastes: Relationships between Mass Losses of C-S-H $+C_2ASH_8 + C_4AH_{13}$ and Compressive Strength

Fig. 8 shows the relationships between mass losses of C-S-H + C_2-A-S-H_8 + C_4-A-H_{13}, and compressive strengths of FRHA and FPOFA pastes, at 90 days. The mass losses of C-S-H + C_2-A-S-H_8 + C_4-A-H_{13} were divided into three portions, as follows: (1) cement hydration, (2) filler effect, and (3) pozzolanic reaction. The mass losses of C-S-H, C_2-A-S-H_8, and C_4-A-H_{13} of CRS blended cement paste is cement hydration. The difference in the mass losses of C-S-H, C_2-A-S-H_8, and C_4-A-H_{13} between the blended cement paste with inert material with high fineness and the blended cement paste with inert material with the same particle size as the cement is the filler effect. The mass losses of C-S-H, C_2-A-S-H_8, and C_4-A-H_{13} due to the pozzolanic reaction is the difference in the C-S-H, C_2-A-S-H_8, and C_4-A-H_{13} between the RHA or POFA paste, and the inert material paste. The use of 20% RHA and POFA increased the mass losses of C-S-H + C_2-A-S-H_8 + C_4-A-H_{13} and increased the compressive strength compared with those of OPC paste at 90 days due to the filler effect, and the pozzolanic reaction of both RHA and POFA. However, the mass losses of C-S-H + C_2-A-S-H_8 + C_4-A-H_{13} of 40% RHA and POFA were slightly less than that of OPC paste. The mass losses of C-S-H + C_2-A-S-H_8 + C_4-A-H_{13} due to the pozzolanic reaction increased in accordance with increasing replacement of RHA and POFA, but the losses from cement hydration were reduced. The weight losses of C-S-H + C_2-A-S-H_8 + C_4-A-H_{13} due to the pozzolanic reaction were higher than those due to the filler effect, which were similar to the findings of Jaturapitakkul et al. (2011). At this range of displacement level of 0–40%, the cement hydration was the major contributor to strength development of the blended cement and to a lesser extent the pozzolanic reaction. The filler effect also contributed but to a much lesser extent.

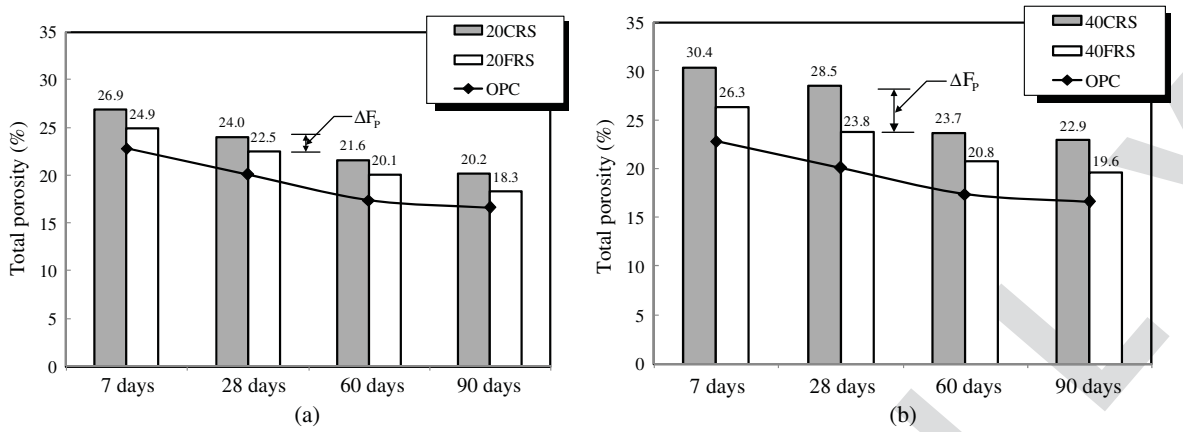


F8:1 **Fig. 8.** Mass losses of C-S-H + C_2-A-S-H_8 + C_4-A-H_{13} and compressive strength of pastes at 90 days
F8:2

Pore Size Distribution of Blended Cement Paste: Influence of Filler Effect on Total Porosity

Fig. 9 shows the results of total porosity of OPC and RS blended pastes. The total porosities of pastes reduced in accordance with curing. For example, the total porosities of OPC pastes were 22.8, 20.1, 17.4, and 16.6% at ages of 3, 7, 28, and 90 days, respectively. Total porosities of RS blended pastes were higher than that of OPC paste. The total porosities increased in accordance with the incorporation of RS and increased in accordance with the replacement level. For example, the total porosity of 20CRS blended pastes at 28 days was 24.0%, whereas that of 40CRS blended paste was higher at 28.5% because of the reduction in cement content and the associated reduced C-S-H. The differences between total porosities of fine RS and coarse RS blended pastes at the same replacement level and age was the filler effect, designated as ΔF_P. The total porosity of paste containing fine RS was less than that of paste containing coarse RS because the small particle size led to good dispersion and filler effect, and reduced the

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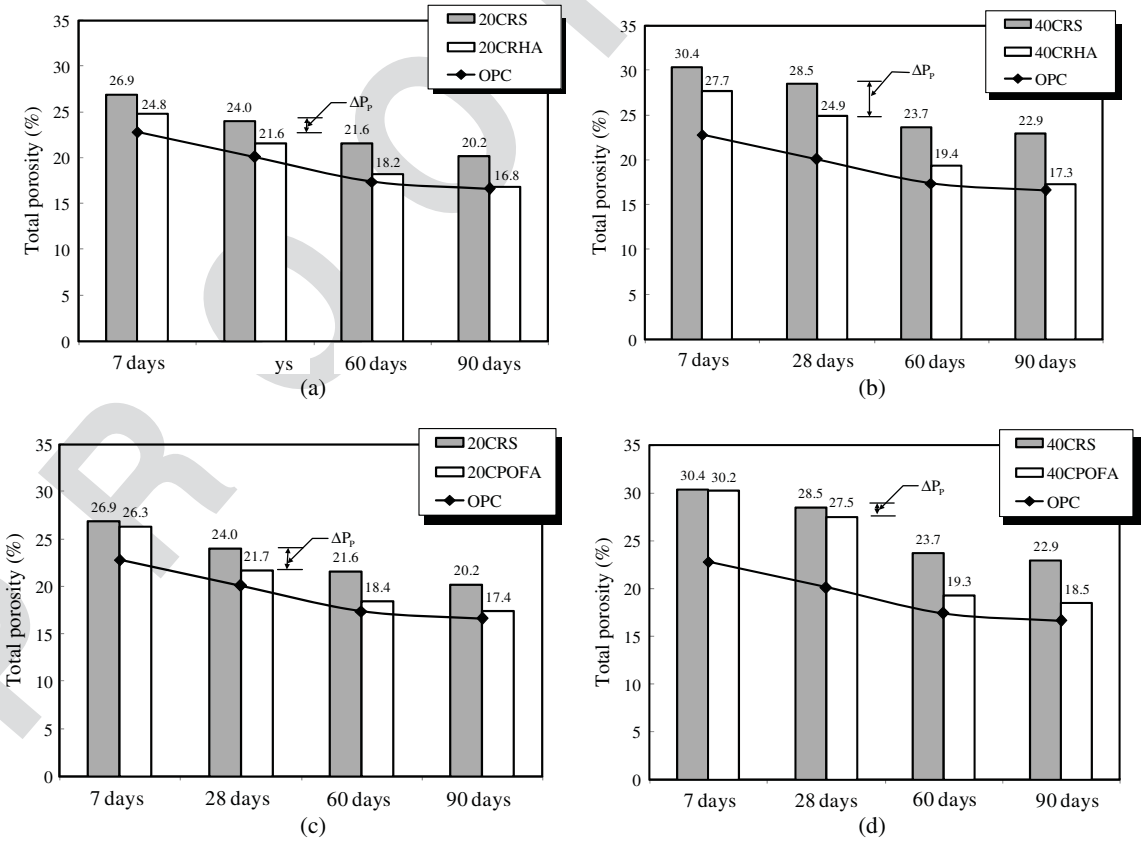


F9:1 **Fig. 9.** Total porosity of OPC and RS blended cement pastes: (a) 20% replacement; (b) 40% replacement

voids (Goldman and Bentur 1993; Isaia et al. 2003; Tangpagasit et al. 2005). The total porosity of the paste due to the filler effect increased in accordance with an increase in the replacement of inert material.

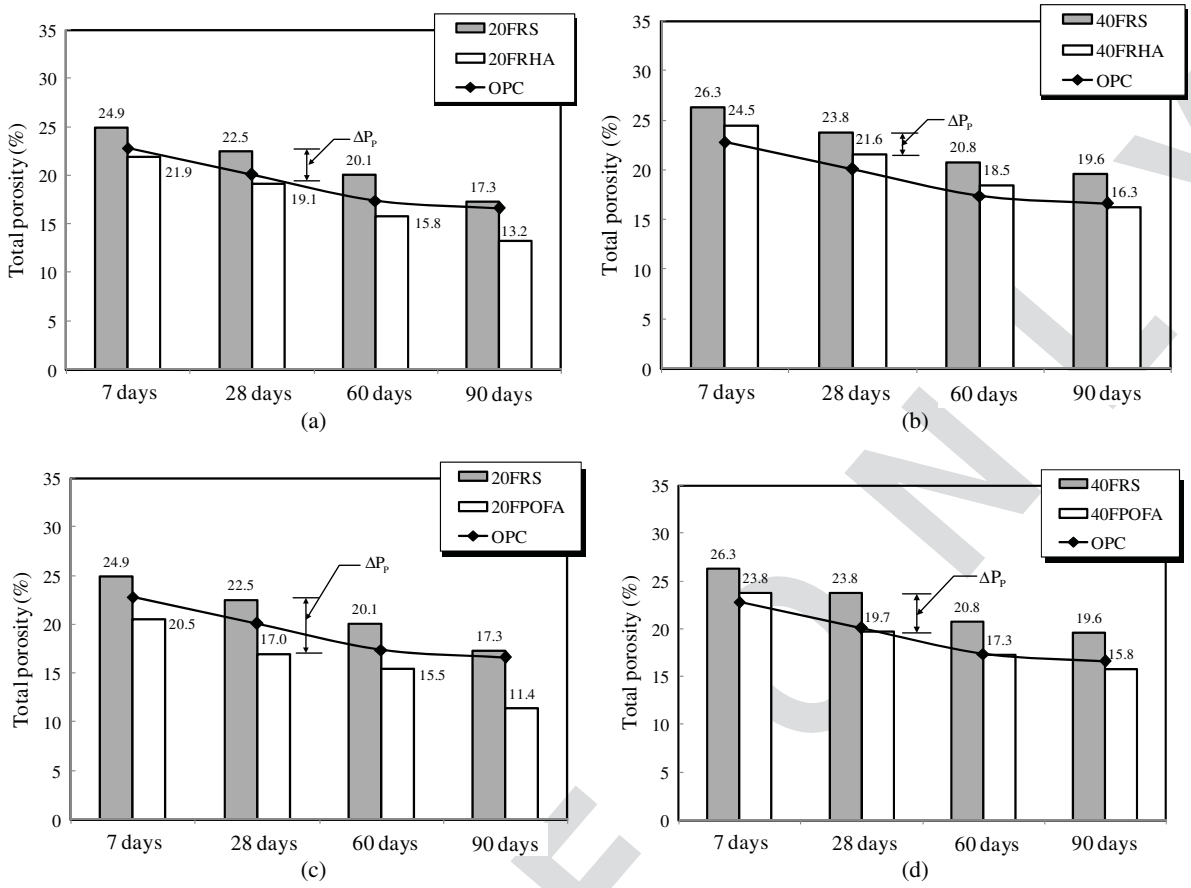
Pore Size Distribution of Blended Cement Paste: Influence of Pozzolanic Reaction on Total Porosity

Figs. 10 and 11 show the results of total porosity of pastes. For pastes with CRHA and CPOFA with the same particle as that indicated in Fig. 10, the total porosities of CRHA and CPOFA pastes were higher than those of OPC paste at all ages, but less than those of RS pastes at the same replacement and curing time. However, at 90 days, the total porosities of 20CRHA, 20CPOFA, and 40CRHA pastes were 16.8, 17.3, and 17.4, which were slightly more than 16.6% of OPC paste because of the pozzolanic reaction of RHA and POFA. The results are in agreement with Li and Ding (2003). For the case of pastes with a small particle as that indicated in Fig. 11, the total porosities of 20% FRHA and 20FPOFA pastes were less than those of OPC paste and RS pastes at all ages. Total porosities of 40FRHA and 40FPOFA paste at 90 days were less than that OPC paste, because the high fineness RHA and POFA had a faster pozzolanic reaction. The differences between total

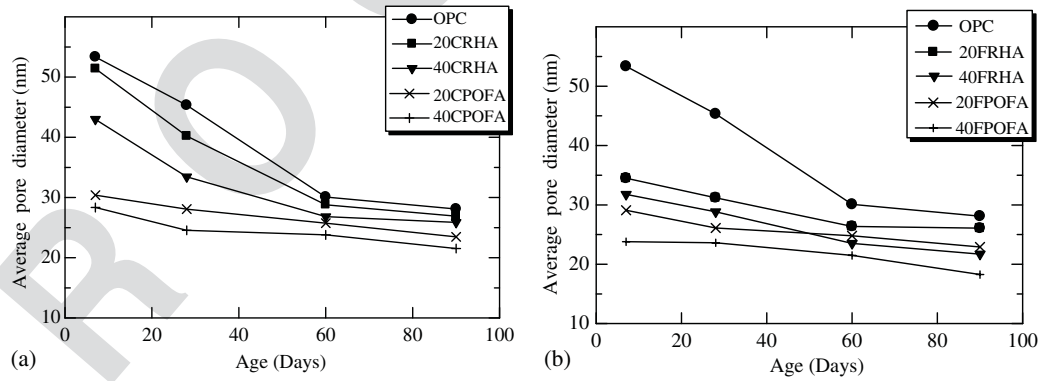


F10:1 **Fig. 10.** Total porosity of the OPC, CRS, CRHA, and CPOFA blended cement pastes: (a) 20% replacement of OPC, CRS, and CRHA; (b) 40%
F10:2 replacement of OPC, CRS, and CRHA; (c) 20% replacement of OPC, CRS, and CPOFA; (d) 40% replacement of OPC, CRS, and CPOFA

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F11:1 F11:2 **Fig. 11.** Total porosity of the OPC, FRS, FRHA, and FPOFA blended cement pastes: (a) 20% replacement of OPC, FRS, and FRHA; (b) 40% replacement of OPC, FRS, and FRHA; (c) 20% replacement of OPC, FRS, and FPOFA; (d) 40% replacement of OPC, FRS, and FPOFA



F12:1 **Fig. 12.** Average pore diameters in accordance with curing time: (a) CRHA and CPOFA pastes; (b) FRHA and FPOFA pastes

porosities of RS blended pastes and RHA (or POFA) pastes at the same replacement level and age were the pozzolanic reaction, designated as ΔP_P. The small particles showed a good filler effect in reducing the voids of cement paste. This again confirmed that the pozzolanic reaction of fine ashes was higher than that of the coarse ashes, with also increased filler effect of fine ashes. The results confirmed that partial replacement of OPC with fine RHA and POFA at rate of 20% by weight of binder had lower total porosity than that of OPC paste at all ages.

Pore Size Distribution of Blended Cement Paste: Effect of the Pozzolanic Reaction on the Pore Size Distribution

Fig. 12 shows the average pore diameters of all pastes. The average pore diameters of the OPC paste at 7, 28, 60, and 90 days were 53.4, 45.3, 30.1, and 28.1 nm, respectively. For pastes with CRHA and CPOFA with the same particle sizes as the cement, the 20 and 40% CRHA (or CPOFA) pastes had average pore diameters that were less than those of OPC paste at all ages, whereas the total porosity was higher than that of the OPC paste. For pastes

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containing high fineness RHA and POFA, the average pore diameters of the 20 and 40% of FRHA (or FPOFA) pastes were less than that of the OPC paste, and the total porosity of 20FRHA and 20FPOFA paste was less than that of the OPC paste at all ages. The average pore diameter decreased in accordance with the use of RHA and POFA, and in accordance with an increase in the replacement level. In addition, the fine particles of RHA and POFA were more effective in reducing the average pore diameter due to dispersion, the filler effect, and increased pozzolanic reactions (Chindaprasirt et al. 2005; Frías and Cabrera 2000).

Conclusions

Based on the results of the research reported in this paper, the following conclusions can be drawn:

- Use of ground RHA and POFA with particle sizes smaller than that of OPC to replace portland cement Type I at 20% by weight of binder lead to a high compressive strength. In addition, the compressive strengths of the RHA pastes were slightly higher than those of the POFA pastes.
- The mass loss (at 30–450°C) of RS blended pastes increased in accordance with curing time, particle fineness, and cement replacement rate. The increase in compressive strength was due to the filler effect. In contrast, the $Ca(OH)_2$ content in the fine RS pastes was less than that in the coarse RS blended pastes.
- The differences between mass loss (at 30–450°C) of RS and RHA (or POFA) blended pastes at the same fineness, curing time, and replacement rate was due to the pozzolanic reaction, which increased in accordance with particle fineness and cement replacement rate. In addition, the weight losses (at 30–450°C) due to the pozzolanic reaction were higher than those due to the filler effect. Reduction of the $Ca(OH)_2$ content in the RHA and POFA pastes decreased in accordance with increases in the curing time and cement replacement rate of the blended cement.
- Use of both RHA and POFA with high fineness reduced the total porosity of the RHA and POFA pastes. The average pore diameters of the RHA and POFA pastes were smaller than those of the OPC paste. The effect due to the pozzolanic reaction was greater than that due to the filler effect.

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