

recent research has shown that the slow pozzolanic reactions could be accelerated using either chemical or thermal activation (Shi and Day, 1993a, 1993b, 2001; Roy, 1999).

Previous works have been done on thermal activation of blast furnace slag and fly ash cements (Shi *et al.*, 1991; Paya *et al.*, 2000; Asavapisit and Chotklang, 2004). Very few works were found on thermal activation of black husk ash (BHA) cement. The purpose of this work is to use BHA as solidification binder to solidify metal-containing waste. BHA is generated in large quantities from a boiler using rice husk to replace fossil fuel. In this work, BHA was used in combination with lime to solidify metal-containing waste and curing at room temperature (30°C - 32°C), 40°C and 50°C. Low temperatures curing 40°C and 50°C were selected to simulate the landfill conditions where the solidified wastes were placed and directly exposed to solar radiation. The metal-containing waste was added to the solidification binders (BHA and lime) at 0, 10, 30, and 50 wt% Strength development and heavy metals released from the solidified wastes were measured to evaluate their performances.

Materials and Methods

Materials

BHA used in this work was from Lad Bua Luang District, Phra Nakhon Si Ayutthaya. It is generated from the cyclone burner using rice husk as fuel to remove moisture from the paddies. The BHA was ground to a particle size of less than 45 mm using Los Angeles Abrasion

Machine. Chemical compositions of BHA were determined by X-ray fluorescence and are shown in Table 1. SiO₂ was present in BHA at 94.5% which was classified as pozzolan class C following ASTM C 618-97. In addition, the 28-day strength activity index of BHA was 95.4%.

The metal-containing sludge was brought from a central treatment plant in Bangkok, Thailand. The sludge was oven dried and ground to a particle size of less than 0.5 mm. The ground metal-containing waste was digested with 5 ml of concentrated nitric acid, 1 ml of hydrogenperoxide and 1 ml of hydrogenfluoride using microwave digestion. The concentration of heavy metals was analyzed using Atomic Absorption Spectroscopy (AAS) and the results are shown in Table 2.

Sample Preparation

Lime-BHA cements were prepared using lime and BHA at the ratios of 55 : 45, 50 : 50, 45 : 55, and 40 : 60, respectively. A water-to-solid ratio for each mix was obtained by conducting normal consistency test using the procedure described in the ASTM C 187-86 and results are shown in Table 3. The slurry was mixed following the ASTM C 305-94 standard test method to achieve a uniform distribution and later transferred to the cylindrical plastic mould. The optimum proportion between lime and BHA was selected from the strength development results during 56 days of curing under room temperature (30°C - 32°C).

The metal-containing waste was then loaded to the optimum proportion between lime and BHA at 0, 10, 30, and 50 wt% of binder.

Table 1. Chemical compositions of BHA (wt%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LOI
94.45	<0.01	0.14	0.80	0.26	0.04	2.45

Table 2. Concentration of heavy metals in the metal-containing waste (mg/kg dry waste)

Zn	Ni	Fe	Pb	Al	Cr	Cd	Cu
127.5	142.5	3,541.8	3.4	104.5	83.7	7.1	44.0

Water requirement for each mix is shown in Table 3. The sample specimens were wrapped with cling film and placed in the zip-locked plastic bag and sat in water bath. The sample specimens were cured under the controlled temperatures for 1 day and cured at room temperature thereafter (Table 4).

Unconfined Compressive Strength Test

Compressive strength of the samples was measured following ASTM D 1633-96 test method. The cylindrical moulds, 50 mm in diameter and 100 mm in height, were modified. Strength development of the solidified wastes was determined after curing for 1, 3, 7, 14, 28, 56, and 91 days. A set of three samples was used for the compression test to ensure the reproducibility of the results.

Leaching Test

Metal leaching from the solidified wastes was assessed using the test method defined by the Ministry of Industry on the samples cured for 28 days. A synthetic acid leachant composed of 80 wt% sulfuric acid and 20 wt% nitric acid and diluted with deionized water to a pH of 5 was used. This is designed to simulate waste exposure to acid rain.

The samples were crushed until the particle sizes were less than 9.5 mm. The crushed samples were then extracted with an amount of acid leachant equal to 20 times of the sample weight. The extraction vessels were rotated in an end-over-end manner at 30 rpm for 18 h. The leachates were filtered through a 0.45 μm membrane filter to remove suspended solids. The filtrates were measured for pH and heavy metals concentration by AAS. Each leachate was analysed in triplicate and the mean values were reported.

Results and Discussion

Strength Development of Lime-BHA Cements

Figure 1 shows the strength development of lime-BHA cements containing lime and BHA at various proportions. BHA does not undergo self-cementing reactions like OPC to low lime

content (Table 1). In the presence of lime and water SiO_2 dissociates from the surface of BHA. The dissolved monosilicate ion $[\text{SiO}(\text{OH})_3]^-$ then reacts with Ca^{2+} ion dissociates from lime and as a result C-S-H gels are formed (Shi and Day, 2000). The experimental results showed that the highest rate of the strength development was obtained from the proportion of 45% lime and 55% BHA. This proportion was selected for further study throughout this work.

Effect of Curing Temperatures on Strength of Lime-BHA Cements

The strength development of lime-BHA cements containing 45% lime and 55% BHA and cured at room temperature, 40°C and 50°C is shown in Figure 2. At the age of 1 day, lime-BHA cements cured at room temperature could not be demoulded whereas those cured at 40°C and 50°C gained strength of 0.82 and 4.11 kg/cm^2 . A higher rate of the strength development from the samples cured at elevated temperatures was also observed at the age of

Table 3. Water requirement for each mix

Composition	W / S
BHA : Lime	
40 : 60	0.570
45 : 55	0.575
55 : 45	0.585
60 : 40	0.590
BHA : Lime : Waste	
55 : 45 : 10	0.585
55 : 45 : 30	0.595
55 : 45 : 50	0.600

W / S = water to solid ratio

Table 4. Curing conditions for lime-BHA cement and the solidified wastes

Identity	Curing condition
Curing regime 1	Room temperature
Curing regime 2	40°C for 1 day followed by room temperature
Curing regime 3	50°C for 1 day followed by room temperature

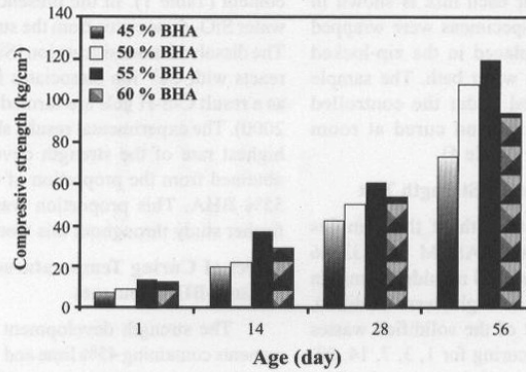


Figure 1. Strength development of lime-BHA cements

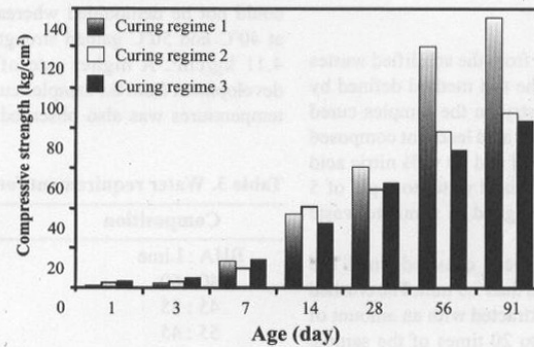


Figure 2. Strength development of lime-BHA cements containing 45% lime and 55% BHA cured at different temperatures

3 days. This is because the solubility of SiO_2 from the surface of BHA under alkali environment increases at the increasing curing temperatures. As a result, the soluble silicate reacts with lime and C-S-H gels are formed. This is responsible for the early strength development of lime-BHA cements.

At the later ages (after 7 days of curing), the strength of lime-BHA cements cured at 40°C and 50°C was lower than that cured at room temperature. The 28-day strengths of lime-BHA cements cured at 40°C and 50°C were 82%

and 87% that of the control (cured at room temperature). In addition, the strength of lime-BHA cements cured at 50°C was lower than that cured at 40°C at the age of 56 and 91 days. Similar observation was reported by Shi and Day (2001) that a rise in curing temperature from 23°C to 65°C affected the hydration rate at the later ages and the later ages strength. Possible explanation for this phenomenon is that under elevated temperature curing the dissolution of SiO_2 from the surface of BHA is accelerated. This leads to the