An Environmentally Optimized Solidification/Stabilization for Disposal of Heavy Metal Sludge Wastes

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Abstract

This study reports on the testing carried out on solidification/stabilization for disposal of heavy metal sludge wastes. Pretests for solidification using different binding materials such as cement, rice husk ash, fly ash and sand are conducted at various weighed proportions, with a water/binder ratio of 0.4 - 0.8. Optimum compressive strengths are obtained for binders: 0.30 rice husk ash/binder ratio (73.2 kg/cm^2) and 0.15 fly ash/binder ratio (69.4 kg/cm^2). This level of compressive strength indicates durability of the specimen. Sludge-binder ratio studies reveal that sludge/binder of 0.5 is the optimum mixture ratio that minimizes toxic elements and provides sufficient compressive strength. Experiments indicate that optimum water/binder ratios are chosen as 0.55 for ordinary Portland cement (OPC), 0.6 for fly ash (FAC) and 0.65 rice husk ash (RHAC) mortars. The decreased leachate concentrations and increased compressive strength of solidified samples were found at higher curing time as the mortars underwent progressive hydration. In our experimental conditions, the sequence of metal contents in leachate concentration is zinc > copper > lead > chromium. OPC samples possess the highest compressive strength while those made from RHAC give the least compressive strength. Results from extraction batch tests on various cementitious binders show that leachate concentrations are highly pH-dependent for metals. The solubility of the metals is also increased by the decrease in pH. The maximum heavy metal desorption occurs in a pH range of 4 to 5 for all solidified samples studied. The finding also reveals that hardened cement paste fixed by cementitious binders can be assessed to some extent by comparing Freundlich's desorptive capacity (K_{des}) for the four metals.

Keywords: Compressive strength, fly ash, Freundlich's Isotherm, heavy metal sludge, leachate, ordinary Portland Cement, rice husk ash, solidification/stabilization.

1. Introduction

The public in Thailand has expressed concern about the pollution threat of 1.7 million tons/year of sludge generated from manufacturing industries operating in areas concerned with metal plating, photography, battery, paints and pesticide [1]. A great amount of the heavy metal sludge such as chromium, copper, lead and zinc are persistent in the aquatic system, with high toxicity to the flora and fauna. Their disposal by means of incineration is a costly process [2]. Due to their inherent hazardous nature, the indiscriminate release of wastes from these industries into the environment has in the past adversely affected the normal well-being of life and continue to be permanent danger to the hydrologic cycle and our food chain [3]. Prior to disposal, such wastes demand some stabilization or immobili-zation, but high treatment cost often limits viable options for safe disposal [4]. The great majority of these wastes are being illegally disposed of on land. A small percent is treated chemically, solidified or encapsu-lated prior to landfill disposal. By far, cement-based solidification/ stabilization is one of the most cost effective and widely used techniques to treat heavy metal sludge [5]. Solidification/ stabilization of heavy metals in cementitious matrices can transform the wastes in the form of their insoluble hydroxides, or may sometimes be absorbed in the cement matrix reducing their water leachability [6]. Cement paste is highly alkaline with high adsorption capacity for metals [7]. The factors responsible for the strength of cement is porosity, water/cement ratio, degree of hydration, pressure and moisture content [8]. Decomposition of cement paste is possible by the dissolution of lime and alumina. This reaction is negligently slow with most natural waters, but much faster with acidic solutions[9]. The mechanism is similar to the weathering of silica-rich minerals in the environment [10]. Under field conditions, leaching of hazardous constitu-ents from solidified test cubes is a function of the metallic valency, pH variation, surface area and curing period. Trussel [11] reported that inorganic wastes solidify and stabilize more easily than organic wastes. A wide variety of pozzolanic materials such as amorphous form of rice husk ash, fly ash, hydrated lime and silica fume can be applied to improve the stability of cement-waste mater-ial [12]. Active pozzolanic materials present in amorphous form of rice husk ash can chemically react with cement hydration product, calcium hydr-oxide, to form calcium silicate hydrate emulsion possessing good cementitious properties. Similarly, fly ash, waste-by products generated from pulver-ized coal power plants is utilized as cement additive in order to improve heavy metal binders [13]. In a previous paper [14], confirmed compressive strength and leaching tests carried out on lignite fly ash binders could also supply a product suitable for light aggregates. This has the potent-ial in large scale consumption of rice husk or fly ash, thereby solving the disposal problem, and also possibly provide an inexpensive building material for rural and urban areas [15].

2. Materials and Methods

2.1 Sample Collection and Analysis

Sludge samples were collected from Ladkrabang Industrial Estate wastewater treatment plant, operated by the Industrial Estate Authority of Thailand (IEAT). Sludge samples were collected in 20 liters plastic containers and were then stored in 5 ^{0}C cold room. Fly ash samples were collected from the fly ash precipitator in Mae Moh lignite power plant, situated in northern part of Thailand. The Mae Moh lignite contains appr-oximately 30 percent ash which after burning, 80 percent of the total ash (10,000 tons per day) formed during lignite combust-ion is fly ash. The particle sizes of fly ash is >10 μm . Raw rice husk was collected from a local rice mill.

Prior to collection, all sample containers were thoroughly cleaned with metal free nonionic detergent solution, rinsed with distilled water, soaked in diluted acid and then rinsed with metal free water. All the sludge samples were dried, ground and passed through a 2 mm sieve. Sludge samples were digested by mixture of 1:2 (v/v) $HClO_4$: HNO_3. Heavy metal concentrat-ions were measured on an atomic absorption spectrophotometer (Hitachi Z-8230). All analytical measurements are performed in triplication to give mean values.

2.2 Description of Experiments

The following experiments were conducted in the laboratory to investigate the immobilization effect of cementitious binders affecting the compressive streng-th and leachability of hazardous wastes:

Pretests for Solidification

Pretests were conducted on stabilized sludge for evaluation of compressive strength and decided binder-sludge ratio of solidified waste. Binder-sludge mixtures were prepared using different binding materials such as cement, rice husk ash, fly ash and sand at various weighed proportions, with a water/binder ratio of 0.4 - 0.8. The ingredients were mixed together in a epicyclical concrete mixer for 1 minute in dry condition and then for 3 minutes after adding water. The mixtures were placed in the moulds of a 5x5x5 cm size as recommended by ASTM design-ation C 190-90 [16] and allowed to cure in a temperature and humidity cont-rolled chamber. The solidified mass released from the moulds was then used for compressive strength testing.

Sludge/Binder Ratio Studies

Experiments of varied sludge amounts were performed by different mass ratio of sludge-binder (0.2 to 1.0) to simulate the optimum sludge/binder ratio for ordinary Portland cement (OPC), rice husk ash (RHAC) and fly ash (FAC) mortars. The ingredients of binders with designed portions were mixed together by an electrically driven mixer. Adequate water was added to maintain the proper workability of cement mixture as recomm-ended by ASTM C230-90 [16]. For each sludge/ binder ratio, triplicate solidified samples were tested for both compressive strength and leach-ability. Control samples (samples without sludge) were prepared for parallel test. All samples were cured for 28 days to simulate the worst condition of actual field practice for disposal of solidified sludge.

Water/Binder Ratio Studies

Experiments were conducted for varied water amount in ordinary Portland cement (OPC), rice husk ash (RHAC) and fly ash (FAC) mortars using different water/ binder weight ratios (0.4 to 0.8). It was necessary to obtain an optimum water/binder ratio for the control and sludged binders because the strength of cement is dependent mainly upon two factors, the water/cement ratio and the degree of compaction. A good workability of a cement mix means the ability of having full compaction [17]. The effectiveness of the treat-ment was assessed by the mechanical tests. The compress-ive strength was measured using an electrically driven, hydraulic type Universal Testing Machine (UMH-200A, SHIMADZU).

Curing Time Studies

This study was conducted to investigate the effect of variation of curing time on compressive strength and leachability of the solidified samples. Test samples were prepared according to various optimum sludge/binder ratios. Control samples (samples without sludge) were also performed as parallel tests. Curing time of 7, 14, 21 and 28 days were selected and main-tained for all mortars. Sub-samples were collected at intervals of the curing time for the specimen and performed for compressive strength and leach-ing tests in accordance with ASTM designation C 109-90 [16].

Heavy Metal Extraction

An appropriate way to evaluate the effectiveness of the immob-ilization of the contaminants after solidification is to perform extr-action tests. The solidified material is added to a leaching medium and shaken for a certain period of time. At the end of the leaching period, equilibrium reaches between the leachant and the stabilized sample. For leach-ing test, the heavy metal extra-ction was carried out three times to assess the reproducibility of the results. In the Toxicity Characteristic Leaching Proced-ure (TCLP) test, the solidified samples, after compressive stren-gth tests, were crushed to about 9.5 mm size by mortar and pestle. A mass ratio of 2.5:1 for leachant to solidified sample was used in order to avoid dilution of conta-minants to less than analytical detection limits (US EPA: SW-846; method 1311). About 100 grams of the crushed samples were mixed with 250 ml of de-ionized water in a 1000 ml plastic bottle. The de-ionized water was preadjusted to pH of 4.8 to 5.2 by the addition of 0.5 M acetic acid. Acetic acid was chosen to simulate the condition of sanitary landfill environment during the acidic stage of decomposition of municipal solid waste. The bottles were placed on an orbital shaker (Gallenkamp-SD-125) which was operated at a speed of 95 cycles per minute and at ambient conditions for 24 hours. After 24 hours of extr-action, all the extractants were filtered through 0.45 μm glass fibre filter paper. The filtrates were then acidified with nitric acid to pH <2 for metal analysis [18]. Heavy metals were measured using an atomic absorption spectrophotometer.

Influence of pH and Grain Size Studies

During the extraction, the pH was varied at 2 to 10 to study its effect on the leachability of waste constituents through the solidif-ied samples. This part of the experiment was a deviation from the USEPA Toxicity extraction pro-cedure, which specifies the pH of the extract solution to be in the range 4.8 to 5.2 [19]. Double distilled water was used as leaching medium. The pH adjustments were made by the addition of 1 M HCl or 1 M NaOH solutions. To study the effect of grain size on the leach-ability of heavy metals, the hardened mortars at an age of 28 days were ground at different grain sizes of 2 to 8 mm.

Desorption Isothermal Studies

The binding mechanism of heavy metals with the binder was suggested to be "adsorption" and the leaching of which could be explained by "desorption". Heavy metal desorption studies were conducted using a batch equilibration technique. 100 grams of crushed samples in 250 ml suspension at pH 4 were shaken in a controlled temper-ature shaker at 95 rpm for 24 hours to ensure equilibrium, at 30 ^{0}C. After equilibrium, each sample was filtered through GF/C filter paper and analyzed for heavy metals. A desorption isotherm developed by Freund-lich was applied to estimate the intensity of leachability. This simple mathematical relationship was also used to determine the coefficient of the leachability data. The linear form of the desorption model is given by the following equation:

Freundlich's Isotherm: $S = KC^{1/n}$

Where S is the amount of metal desorbed in the sample per unit weight of sample (mg/g). C is the equilibrium concentration of metal leaching out (mg/L). K is the empirical constant of the Freundlich isotherm, and repre-sents the desorptive capacity whereas the isothermal slope (1/n) provides an estimate of desorption rate.

Table 1. ExIstIng I;haracterIstIcs of The StudIed MaterIals

Parameter	Sludge	Portland Cement	Rice Husk Ash	Fly Ash	US EPA Clean Sludge Limits (mg/kg)
Heavy Metal (mg/kg)					
Cr	19.60				
Pb	28.24			7.69	300.00
Cu	83.23			30.21	1500.00
Zn	300.08			130.04	2800.00
Al				2849.00	
Nitrogen (mg/kg)	3.12				
Phosphorus (mg/kg)	2972.82				
Möisture Content	86.40			0.02	
pH	7.72			10.94	
Silicon Dioxide, SiO_2 (%)		20.81	91016	33.62	
Aluminum Oxide, Al_2O_3 (%)		5.57	0.51	15.08	
Ferric Oxide, Fe_2O_3 (%)		3.04	0.86	11.27	
Calcium Oxide, CaO (%)		65.60	0.57	23.96	
Magnesium Oxide, MgO (%)		0.77	0.24	3.52	
Sulphur Trioxide, SO_3 (%)		2.52	2.96	1.64	
InsolubleResidue (%)		0.40			
Loss on Ignition (%)		1.10	0.28	0.27	
Na_2O (%)			0.07	1.12	
K_2O (%)			2.88	1.93	
Carbon, C (%)			0.54		
Specific Gravity			2.13	2.41	
Specific Surface Area (cm^2~/g)		3315.00	12450.00	2739.00	
Porosity			0.65		

Note: All weights are on a dry weight basis.

3. Results and Discussions

3.1 Existing Characteristics Of The Studied Materials

Cementitious binders, sand and water were all solidifying agents used for stabilization of heavy metal hazardous waste. Three kinds of cementitious binders were used in the experiment: ordinary Portland cement (OPC), OPC with rice husk ash (RHAC) and OPC with fly ash (FAC). Table 1 presents the mean values for existing sludge, rice husk ash and fly ash characteristics.

Sludge

Analytical results of sludge samples show Cr: 19.60 mg/kg; Pb: 28.24 mg/kg; Cu: 83.23 mg/kg and Zn: 300 mg/kg, which are still lower than the guidelines for clean sludge limits as well as ceiling sludge limits as per US EPA regulation for the use of sludge on agricultural land. The total nitrogen and phosphorus in sludge samples are 3.21% and 2,973 mg/kg, respectively. It is observed as shown in Table 1 that zinc content in the sludge samples is rather high. This causes concern over severe damage to plant and stunted growth when the sludge is disposed to the environment [20]. Porter et al.[21] reported that nitrogen metabolism is disturbed in various ways by an excess of zinc. These values are quite high when compared with soil samp-les. Adriano, Adriano [22] reported that both high levels of phosphorus and zinc micronutrients might be reduced by P-Zn interaction that occurred in plant up take.

Rice Husk Ash

Raw rice husk was collected from a local rice mill. Rice husk ash was obtained by burning raw rice husk in a ferrocement drum, for 48 hours – the maximum temperature during this period was 760 ^{0}C and met the requirement of ASTM C618-90 [16]. The ash was sieved to pass through sieve size, ASTM no. 325 (45 μm) to reach 95%.

Fly Ash

It is noted in Table 1 that heavy metal contents in the ash are much lower than sludge samples. The result shows that concen-tration of zinc is higher than copper which are in turn higher than lead. Total and extractable of aluminum content (oxides) in fly ash were 2,849 mg/kg and 134.94 mg/kg, respectively. This can pose potential problem in aluminum toxicity to agricultural application. The mean pH value for fly ash is found to be 10.94 which is considered high for agricultural application.

Cement

Cement was manufactured by the Siam Cement, Thailand and confirmed to ASTM type-I Port-land cement. Portland cement contains by weight, 66% lime (CaO), 20% silica (SiO_2), 6% alumina (Al_2O_3) and 3% iron oxide (Fe_2O_3). There are also minor proportions of the oxides of magnesium, sodium, potas-sium, titanium, phosphorus and sulfur.

Sand

Natural silica sand having an effective size of 0.2 mm and was used for preparing the cement-sand mortar with ordinary tap water.

3.2 Selection of Optimum Ratio for Ash-Cement Mixtures

There was a need for selection of optimum cementitious material ratios with which further proper-ties of solidification process could be studied. In the pretest experiment, cement mixture was prepared by proportioning weight basis on amount of cement, sand and water with mass ratio of 1.0:2.0:0.5, as recommended by ASTM C-230-90 [16]. In this case, a fixed mass ratio of 0.30 for sludge was used throughout the experiment. Ade-quate mass ratio of water/binder (0.50 to 0.80) was used to maintain the proper workability of cement mixture. Figure 1 shows the pretest characteristics of ash-cement mixture at various ratios. The results indicate that 0.10 to 0.30RHAC mortars exhibited better compressive strengths than 0.40RHAC mortar, however for economic reasons, the 0.30RHA/cement ratio (0.70OPC + 0.30RHA) with compressive strength of 73.2 kg/cm^2 was chosen for optimum RHAC binder.

Similarly, optimum compressive strength of 69.4 kg/cm^2 was obtained among FAC binder with mixture ratio of 0.85OPC + 0.15FA. From the pretests, further experiments were conducted to study other solidification para-meters of solidified samples using ash/cement ratio of 0.30RHA and 0.15FA, respectively.

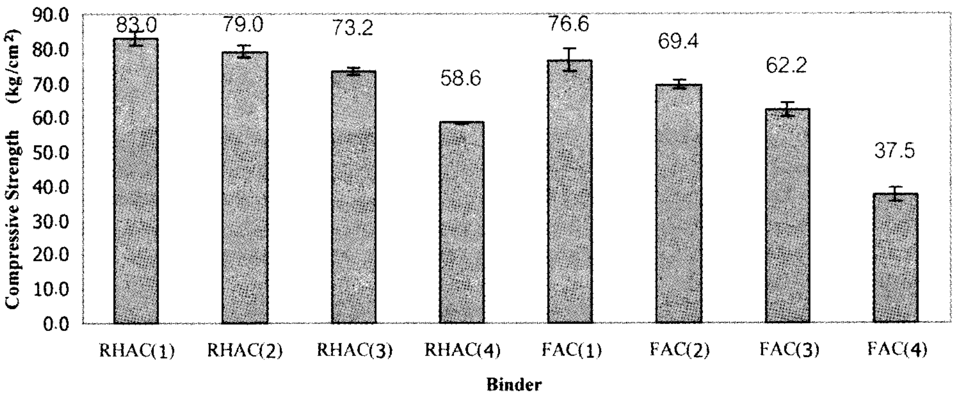


Figure 1. Pretest for Possible Binders

Note: RHAC (1) = 0.90 OPC + 0.10 RHA + 0.30 SL + 2.00 Sand + 0.50 Water/CMT;
RHAC (2) = 0.80 OPC + 0.20 RHA + 0.30 SL + 2.00 Sand + 0.60 Water/CMT;
RHAC (3) = 0.70 OPC + 0.30 RHA + 0.30 SL + 2.00 Sand + 0.70 Water/CMT;
RHAC (4) = 0.60 OPC + 0.40 RHA + 0.30 SL + 2.00 Sand + 0.80 Water/CMT;
FAC (1) = 0.90 OPC + 0.10 FA + 0.30 SL + 2.00 Sand + 0.50 Water/CMT;
FAC (2) = 0.85 OPC + 0.15 FA + 0.30 SL + 2.00 Sand + 0.60 Water/CMT;
FAC (3) = 0.80 OPC + 0.20 FA + 0.30 SL + 2.00 Sand + 0.70 Water/CMT;
FAC (4) = 0.70 OPC + 0.30 FA + 0.30 SL + 2.00 Sand + 0.80 Water/CMT;
Where: RHAC= Rice Husk Ash Cement, FAC = Fly Ash Cement, OPC = Ordinary Portland Cement, SL = Sludge,
RHA = Rice Husk Ash, FA = Fly Ash, CMT = Cementitious Materials (OPC + RHA or FA)

3.3 Effect of Sludge/Binder Ratio

Tests on compressive strength and leachability were performed for different sludge/cement ratios. Figure 2 depicts a comparison of compressive strengths for OPC, RHAC and FAC mortars, while Figure 3 shows an account of their leachate concentration for different sludge/binder ratios. From the result, it is observed that there was a decreasing trend of compressive strength and an increasing trend of leachate concentration, with the increase of sludge/binder ratio. The average compressive strength for each sludge/binder ratio was greater for OPC mortar than that for FAC and RHAC mortars. The compressive strengths of three mortars reduced to smaller values as the sludge/binder ratio appro-ached to 1.0. A review of data in Figure 2 revealed that the compressive strength of all three types of mortars were not much affected with the increase of sludge/binder ratio up to 0.5. When the ratio increased beyond 0.5, the decrease in compressive strength was quite significant, especially for the OPC mortars.Likewise, Figure 3 reveals that the increasing trend of leachate concentrations in three mortars was observed until sludge/ binder ratio of 0.5. At higher sludge/ binder ratio of 0.5 to 1.0, the leachability curve approached to an almost horizontal line implying that the leachate conc-entration increased in constant rate with addition of sludge amount in the mortar. The total horizontal line could not be achieved up to the sludge/binder ratio of 1.0. This implies that cement matrix was not effective in immobilizing the further amount of sludge to be added.Rinaldi [23] commented that the heavy metals either get precipitated by the cement hydration product $Ca(OH)_2$ or get enmeshed and / or adsorbed in the cement matrix in the calcium silicates present in the binder. The leachate concentration of RHAC mortar was observed to be higher than that of FAC and OPC mortars and the difference between the three continued to widen as sludge/binder ratio was varied from 0.0 to 1.0. Maximum leachate concentrat-ions were detected in the samples having a sludge/binder ratio of 1.0. Samples made from OPC and FAC showed a better stabilizing effect than RHAC binders for Cr, Cu and Zn. Although slightly higher amounts of lead, as compared to chromium were present in the sample, the result showed that chromium was better adsorbed and / or precipitated in all the three binders. The samples formed with RHAC were found to be most effective amongst the three binders to immobilize lead. The sequence of leachable metal contents in three solidified samples is zinc > copper > lead > chromium. In this study, an optimum sludge/binder of 0.5 was employed for all other experiments.

3.4 Effect of Water/Binder Ratio

Experimental studies were conducted to determine the optimum water/cement ratios for OPC, RHAC and FAC mortars. Graphs were plotted to show the variation in compressive strength with the water/binder ratio (Figure 2.b). The patterns of compressive strengths were almost similar in all three mortars and followed a decreasing trend at higher water/binder ratio. In the case of control and OPC samples, a water/binder ratio of 0.50 and 0.55, respectively were found to exhibit the optimum compressive strength (Control: 497.18 kg/cm^2 and OPC: 373.48 kg/cm^2) and very good workability. Very good workability and optimum compressive strength (158.70 kg/cm^2) were recorded at a water/binder ratio of 0.60 for FAC samples. It is observed that a water/binder ratio of 0.55, which was considered optimum for OPC mortar, was not suitable for RHAC mortar. It was found that RHAC mortar prepared with the water/ (cement + RHA) ratio of 0.55 were not be able to maintain as a consistent mixture and two out of three cubes were broken after 24 hours curing. In this case, it is due to high water absorption of RHAC. This is in accordance with Conner [4], who reported that the water/ binder ratio affects the porosity of the hardened cementitious binder samples. Hamernik et al. [14] noted that the degree of porosity reflects an increase in volume of hydration substance, which is regarded as an important strength parameter. In this case, higher water/binder ratio of 0.65 demonstrated good workability as well as optimum compressive strength (58.30 kg/cm^2) for RHAC mortar. All samples showed a decrease in their compressive strength as compared to their respective control samples. The samples made from OPC had a higher strength than the other binder samples. The samples made from RHAC were lowest in strength. The criteria of minimum compr-essive strength of 50 kg/cm^2 were required for controlled landfill [13]. With respect to the effect of water/ binder ratio on criteria of minimum compressive strength, it is concluded that optimum water/binder ratios are chosen as 0.55 for OPC, 0.6 for FAC and 0.65 RHAC mortars.

3.5 Effect of Curing Period

Effect of curing period was studied by the compressive stren-gth and leachability. In this test, optimum sludge/binder and water /binder ratios obtained in previ-ous experiments were employed for all the samples. Stabilized waste-binder samples were cured for 7, 14, 21 and 28 days in moisture controlled chamber.

The leaching test was performed to determine the effectiveness of the cementitious binders to entrap the waste constituents within their matrix. Figure 4. shows the variation of leachate concentration and compressive strength for OPC, FAC and RHAC mortars at different curing periods. The leachate concentrations of solidified sam-ples were found to decrease at higher curing time as the cemen-titious binders undergo progr-essive hydration. The sequence of metal contents in leachate concentration is zinc > copper > lead > chromium. Similarly, the compressive strengths of all samples were found to increase with time, which is an inherent property of cementitious binders during hydration. The hydration of cement during curing is a complex dissolution – precipitation process in which the various hydration reactions proceed simultaneously at different influenced rates,

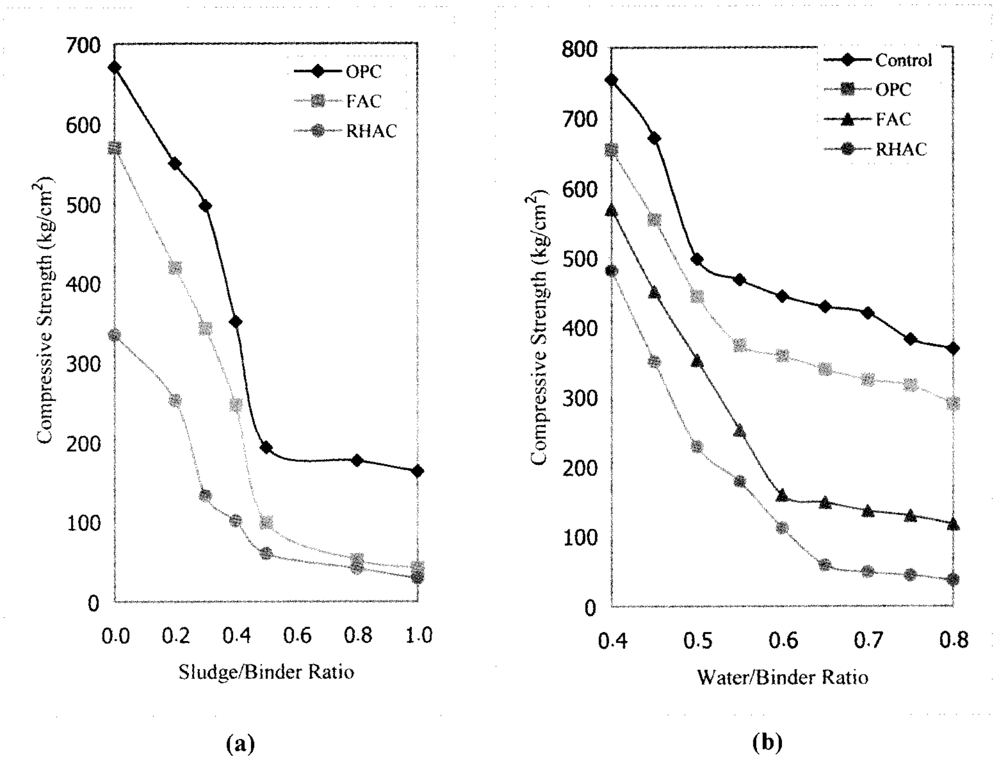


Figure 2. Effect of (a) Sludge/Binder and (b) Water/Binder Ratios on Compressive Strength for OPC, FAC and RHAC Binders.

Note:RHAC = 0.70 OPC + 0.30 RHA + Varied SL + 2.00 Sand + Varied Water/CMT; Control = 1.00 OPC + 2.00 Sand + Varied Water/CMT;
FAC = 0.85 OPC + 0.15 FA + Varied SL + 2.00 Sand + Varied Water/CMT; OPC Binder = 1.00 OPC + Varied SL + 2.00 Sand + Varied Water/CMT
Where:RHAC= Rice Husk Ash Cement, FAC = Fly Ash Cement, OPC = Ordinary Portland Cement, SL = Sludge,
RHA = Rice Husk Ash, FA = Fly Ash, CMT = Cementitious Materials (OPC + RHA or FA)

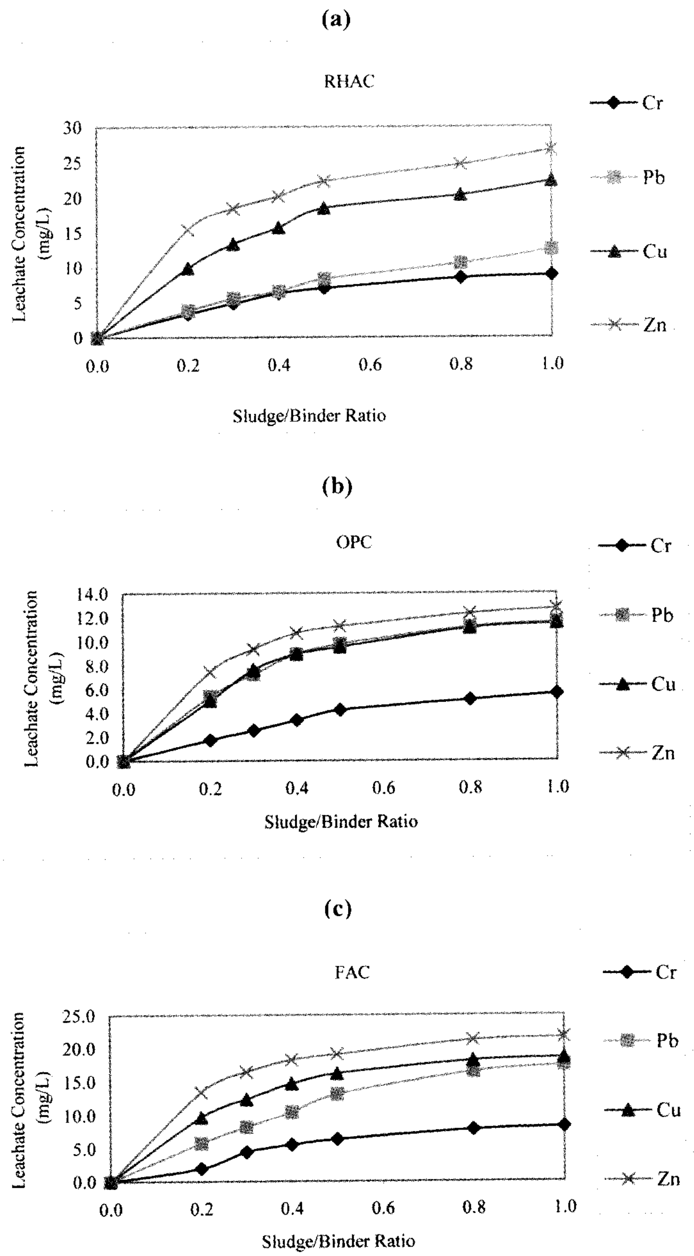


Figure 3. Effect of Sludge/Binder Ratio on Leachate Concentration for (a) RHAC, (b) OPC, and (c) FAC Binders.

Note: OPC = 1.00 OPC + Varied SL + 2.00 Sand + 0.55 Water/CMT;
RHAC = 0.70 OPC + 0.30 RHA + Varied SL + 2.00 Sand + 0.65 Water/CMT;
FAC = 0.85 OPC + 0.15 FA + Varied SL + 2.00 Sand + 0.60 Water/CMT;

Where: RHAC= Rice Husk Ash Cement, FAC = Fly Ash Cement, OPC = Ordinary Portland Cement, SL = Sludge, RHA = Rice Husk Ash, FA = Fly Ash, CMT = Cementitious Materials (OPC + RHA or FA) which are similar to that noted by Vipulanandan [24]. While studying the effect of curing period on solidified sludge samples, control samples were also performed side by side. It showed that the control samples exhibited higher compressive strengths than the corres-ponding test samples. OPC samples possesses the highest compressive strength while those made from RHAC gave the least compressive strength; the streng-th of RHAC samples were two-thirds of that shown by OPC samples.

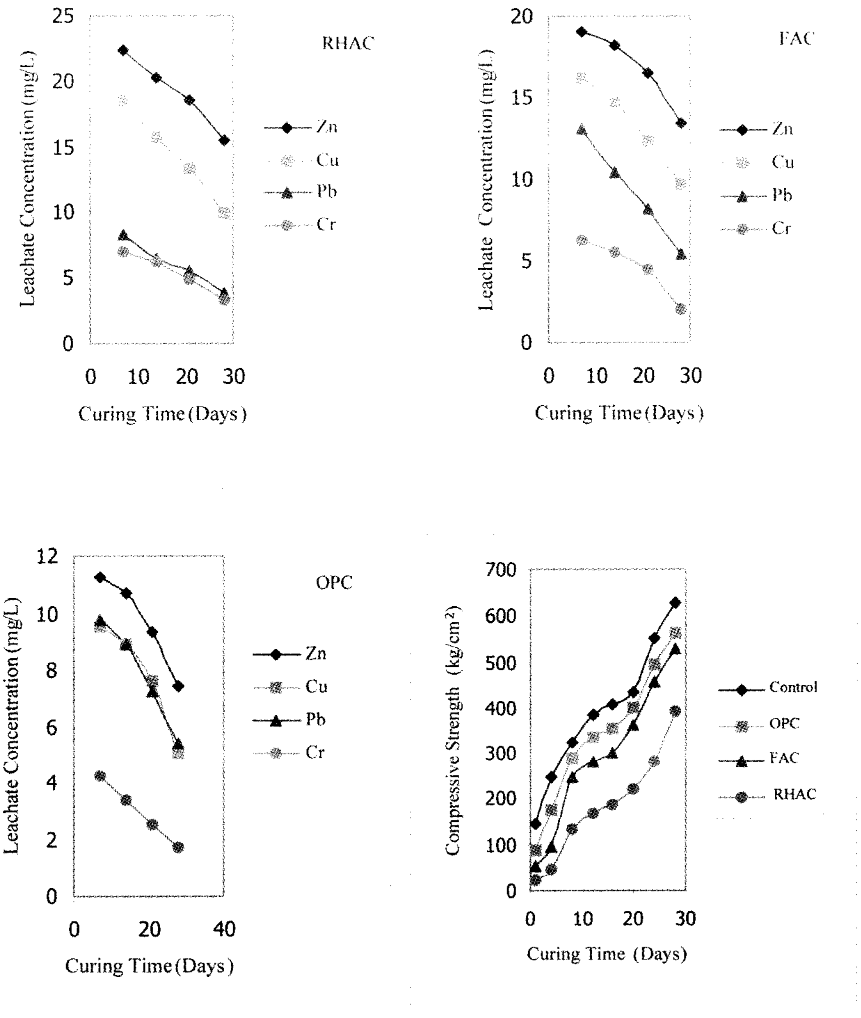


Figure 4. Effect of Curing Time on Leachate Concentration and Compressive Strength.

Note: OPC Binder = 1.00 OPC + 0.50 SL + 2.00 Sand + 0.55 Water/CMT; Control = Samples without Sludge;
FAC = (0.85 OPC + 0.15 FA) + 0.50 SL/CMT + 2.00 Sand + 0.60 Water/CMT;
RHAC = (0.70 OPC + 0.30 RHA) + 0.50 SL/CMT + 2.00 Sand + 0.65 Water/CMT;
Where: RHAC= Rice Husk Ash Cement, FAC = Fly Ash Cement, OPC = Ordinary Portland Cement, SL = Sludge, RHA = Rice Husk Ash, FA = Fly Ash, CMT = Cementitious Materials (OPC + RHA or FA)

3.6 Effect of pH on Extract Solution

Among the chemical factors influencing leaching processes and leachate concentrations, pH is so far the one studied most. In order to determine the influence of pH on leachate concentration, leaching experiments were conducted on three mortars. The hardened cement pastes were ground at an age of 28 days and leached at pH values of 2 - 10. Figure 5. shows pH dependent of leaching behavior for Cr, Cu, Pb and Zn. The concentrations of heavy metals are shown as functions of leachate throughput for applied pH conditions. As expected, the highest leachate concentrations were attained at pH 2. Stable leachate throughput was obtained at pH 4 to 5. At higher pH condition of 7 to 10, the leaching amounts declined with increasing pH value; only very slight leaching amounts were detected for the various elements at pH 10. Cementitious binders provide a strong alkaline internal environ-ment owing to the presence of calcium oxide as a main cons-tituent. When exposed to an acidic solution, the surface tends to be eroded and thus exposing a greater area for the leaching of heavy metals. The solubility of the metal ions plays an important role because the distribution of species is a function of pH. At low pH, the metal ion or its hydroxocomplex has to compete with hydronium ion for the active desorption site and usually optimum pH favors the desor-ption of the metal ions. Gen-erally, heavy metal concen-trations decreased dramatically and then reached nearly constant concentration with the change in the pH condition from acidic to neutral and basic. The leach-ability in neutral solution was 30 to 60% of that in acidic solution. Under exposure to neutral and basic solutions, the leachability change was very little. Many metals are relatively insoluble in an alkaline aqueous environment. From these experiments, it is concluded that critical pH for Cr, Cu, Pb and Zn is 4 to 5.

3.7 Effect of Grain Size

Leaching studies were conducted at pH 4 and a leaching time of 24 hours to determine the influence of grain size on leachability. The hardened mortars at an age of 28 days were ground at different grain sizes of 2 to 8 mm. Figure 6. shows the effect of grain size on the leachability of the heavy metals. It can be observed that leaching rates rise with decreasing grain size. The grain size of the binder is an important para-meter in the leachability. The extracting solutions, which in practice can cause a greater corrosion to the samples that, have smaller grain sizes. Conse-quently, they shall exhibit a greater leachability and possibly samples shall be weaker than those having larger grain sizes. In this study, the leachability of -+OPC binders was about 40% of that obtained by RHAC and FAC binders.

3.8 Effect of Isothermal Desorption

Freundlich's equation is often used to describe the experimental desorption isotherm data. This simple mathematical relationship was also used to determine the variation of waste amount on the leachability data. An evaluation of desorption capability was carried out using model para-meters which were graphically determined. Desorption isoth-erms for four metals were plotted by log transformed data as shown in Figure 7. Freundlich's desor-ptive capacity (K_{des}) for Cr and Zn in RHAC mortars were of much smaller than their respective K_{des} in OPC and FAC mortars. Likewise, the desorption rate ($1/n_{des}$) in RHAC mortars were much larger than the ($1/n_{des}$) values in OPC and FAC mortars. This indicated that RHAC mortars had smaller desorptive capacity and faster desorption rate for Cr and Zn than those in OPC and FAC mortars. There was no the significant difference in the Cu and Pb desorption rate ($1/n_{des}$) for all mortars; however, the significant difference in Cu desorptive capacity (K_{des}) was observed among FAC mortars. This was probably due to lower affinity for Cu binding sites in FAC mortars.

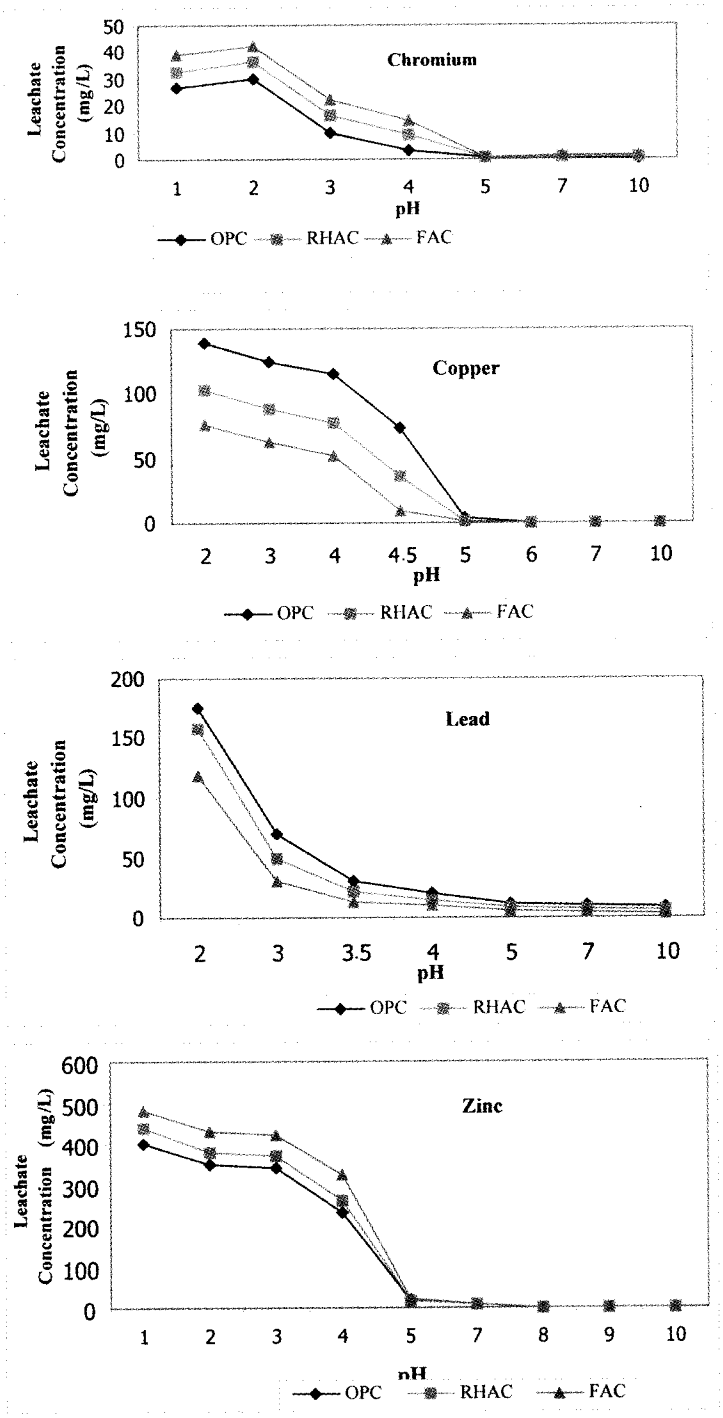


Figure 5. pH Dependent of Leaching Behavior for Cr, Cu, Pb and Zn.

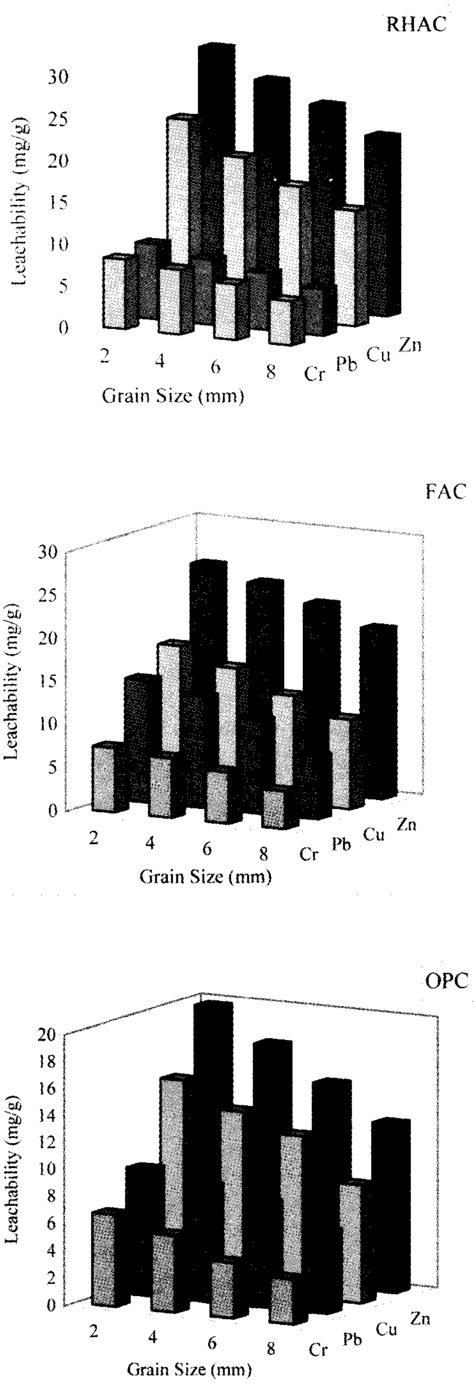


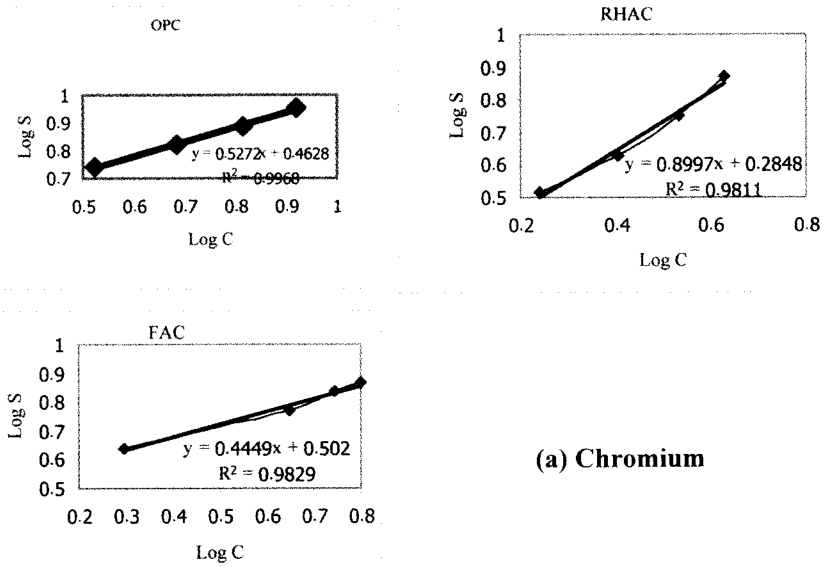
Figure 6. Influence of Grain Size on the Leachability of Leached Elements.

4. Conclusion

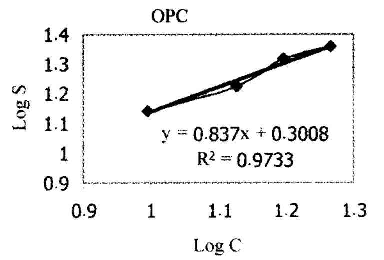
Solidification/stabilization can be an alternative technology for the ultimate disposal of heavy metal sludge wastes. In condition of sanitary landfill environment, numerous interacting factors can simultaneously affect desorption of heavy metal in the binder. The desorption of trace metals conta-minants in binder are affected by pH, electrode potential (Eh), cation exchanger capacity (CEC), Cl^-, ionic strength, organic matter, and some other factors [25]. These may be works for future research.

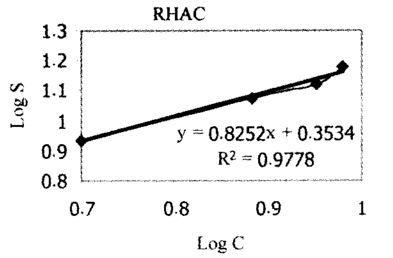
The findings indicate that: (a) detoxic ash-sludge mixture has potential agricultural application for increasing soil alkalinity and provide plant nutrients (nitrogen and phosphorus), (b) tested mortars possess significant com-pressive strength, which may be used as a construction aggregate. This can be considered as envir-onmentally sound, as well as assisting in the disposal of troublesome wastes and (c) RHAC mortars are of larger desorptive capacity and slower desorption rate for Cr and Zn than those in OPC and FAC mortars.

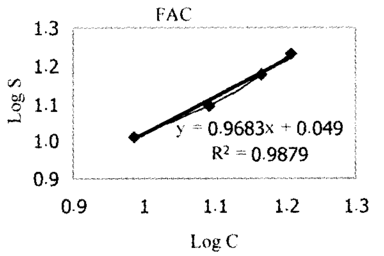
However, before applications, long term evaluation on the behavior of heavy metals in ash-sludged aggregate are needed. Perhaps the best that can be said from the presented data is that ash-sludge mixture could be an effective non-environmentally harmful method for the disposal of both ash and sludge wastes.



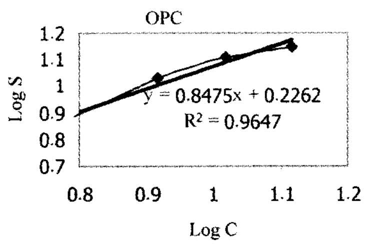
(a) Chromium

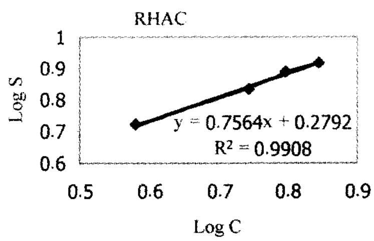


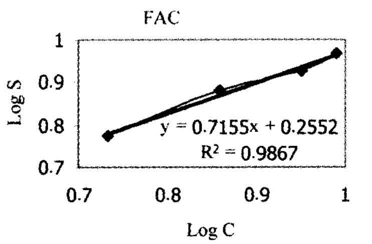




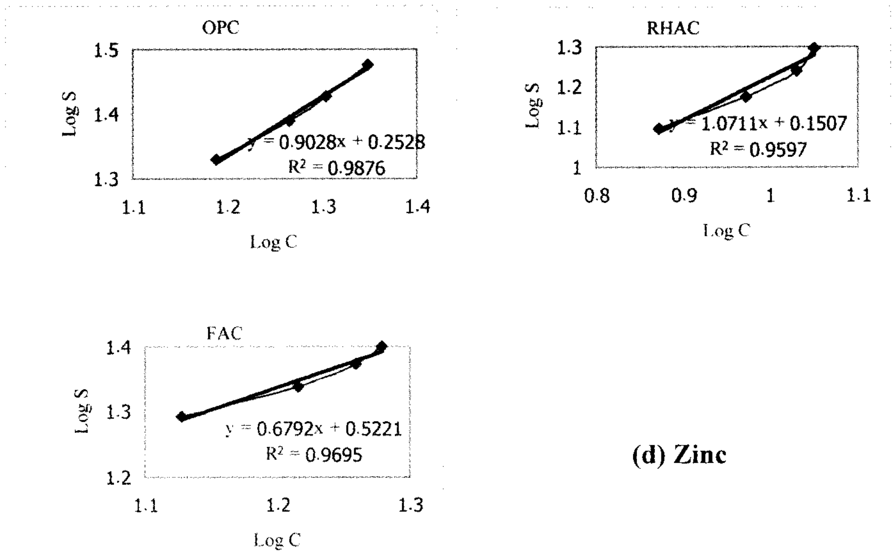
(b) Copper







(C) Lead



(d) Zinc

Figure 7. Regression Relationship of Leachability (Log S) with Leachate Concentration (Log C) for Cr, Cu, Pb and Zn in OPC, RHAC and FAC Mortars.

Note: Freundlich's Desorption Isotherm: Log S = Log k + (1/n) Log C, where S is the Leachability in mg/g, C is the Leachate Concentration in mg/L,

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Foreword: Special Section

The 2002 International Technical Conference on Circuits/Systems, Computers and Communications (ITC-CSCC 2002), which was the 17th annual conference, was successfully held at Phuket (Thailand) in July 2002, with the technical cooperation of the IEICE, Japan, the IEEK, Korea, and the IEEE Thailand section. The number of papers presented in the conference was over 600 papers covering a broad range of technical subjects. They were about orally presented 317 papers in 8 parallel tracks of 54 lecture sessions and about 300 papers in 3 tracks of 23 poster sessions. Four (4) invited keynote speeches and 3 special sessions were also arranged.

After the conference, the guest editor called for papers from those presented. We received 8 submissions from the response and, through the regular review process of the journal, we selected 4 papers for publication in this special section.

As the guest editor of this special section, I greatly appreciate the effort of the editorial committee members of this special section. Finally, I would like to thank all the authors of the submitted papers and all the reviewers for their valuable cooperation.

Wanlop Surakampontorn