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The applicability of Freundlich's isotherm model for the leaching of solidified hazardous waste using cementitious binders

Jong Ho Youn, Heon Mo Lee*, Byung Gon Jeong**
and Yong Hyun Chung***

Department of Environmental Engineering, Shinsung Junior College, Chung Nam, Korea
**Department of Environmental Engineering, Dongeui Technical Junior College, Pusan, Korea*
***Department of Marine Environment, Kunsan National University, Kunsan, Korea*
****Department of Environmental Engineering, University of Osaka, Japan*

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A laboratory study was conducted to investigate the immobilization of the laboratory waste sludge, mainly from chemical oxygen demand (COD) waste, using cementitious binders. The binders were: Ordinary Portland Cement (OPC), and lime-Rice Husk Ash (RHA) cement. The economic evaluation was done for three different kinds of cementitious binders, namely, OPC, Portalnd Rice Husk Ash Cement (PRHAC) which contained rice husk ash 50 percent by dry weight, and lime-RHA cement. The result showed that lime-RHA cement was the cheapest. The applicability of Freundlich's desorption isotherm was studied to assess the leachability of sludges. The leachability of cement mortars was found to follow the desorption isotherms. Therefore, it was concluded that based on this test, the leachate concentrations of the solidified heavy metals could be predicted, approximately by the Freundlich's isotherm desorption modeling.

1. Introduction

In the recent years, the hazardous waste production has increased with growing industrialization in the world. The wastes produced within a process and along the production line are dangerous to handle because of their inherent qualities. They are characterized by their corrosivity, ignitability, reactivity and toxicity.

Recent amendments to the 1976 Resource Conservation and Recovery Act (RCRA) have prohibited disposal of liquid or sludge wastes by landfill, which enjoyed dominance due mainly to its low cost. As a result, these wastes must be pretreated by a stabilization or solidification technique.

Landfill method has been the most widely used practice in the disposal of hazardous wastes. Krofchak (1978) reported that solidified waste has been used as a cover for garbage at a landfill site in Hamilton, England. Pojasek (1979) called for independent tests to confirm the credibility of solidified hazardous waste disposal by way of low leachate emanation.

Solidificaton and stabilization have been used together to define systems that would render all materials immobile and chemically un-reactive. Solidification is a process of treating hazardous wastes to limit its toxicity. Generally, the waste is either chemically bound or physically entrapped by mixing with chemical additives.

Stabilization technologies are usually categorized on the basis of similarity of the principal additives. Available technologies are:

1) Cement-silica based techniques,
2) Lime based techniques,
3) Thermoplastic techniques (including bitumen, paraffin and polyethylene),
4) Organic polymer techniques,
5) Encapsulation techniques.

Barnes et al. (1979) noted that all waste materials could be fixed by cement or pozzolanic techniques. However, he analyzed that some materials would not be economically managed in this manner. Cement is especially effective for wastes containing high amounts of heavy metals and acids because its neutral alkalinity neutralizes acid solutions and immobilizes many heavy metals.

Mehta (1975, 1977, 1981) reported the properties of Portland-Rice Husk Ash Cement (PRHAC) from three cements produced by blending the pulverized rice husk ash with TYPE II Portland cement in 30 : 70, 50 : 50, or 70 : 30, proportions by weight. The samples were designated as B-30, B-50, and B-70, respectively.

When compared with the control Portland cement, the PRHAC, and lime - rice husk ash cement containing 50 percent and 30 percent ash showed higher strength than the control Portland cement even at early ages of 3 and 7 days. He also found that an important characteristic of mortars and concrete made with rice husk ash cements is their superior durability in acidic environments. Portland cements contain 60 to 65 percent CaO and their hydration products contain about 25 percent $Ca(OH)_2$ which are primarily responsible for the poor resistance of Portland cement concretes when it is exposed to acidic attack. On the contrary, the rice husk ash cements containing either lime or Portland cement may have 20 to 40 percent CaO and practically no $Ca(OH)_2$ in the products of hydration. Due to their superior durability in acidic condition, PRHAC and lime-rice husk ash cement have been used mainly in the construction of acid resistant floors.

From this point of view, the hazardous waste (mainly COD waste, Cr, Hg) was solidified with Ordinary Portland Cement (OPC) and lime - rice husk ash cement (lime - RHA). The solidified cement mortars were tested for compressive strength and leachability. From the leaching test, the leachability of the two cement binders were compared and the applicability of Freundlich's isotherm model for the leaching of the waste was studied

2. Experimental Approach

The waste used in this study was collected from the laboratory. The waste was mainly COD waste. After collection of waste, the concentration of Cr, Hg and other heavy metals were measured.

A soluble metallic ion in the waste is reduced through an oxidation-reduction reaction and then precipitated by conversion to an insoluble metallic hydroxide. This process is applied principally to reducing hexavalent chromium to a trivalent state. Sodium bisulfite and sodium hydroxide which increased the pH to 8.5, as reducing agents, were used.

Two laboratory samples, each with a volume of 20 L and 30 L, were used for this study and chromium and mercury contents were analyzed from the liquid waste and the dried sludge as follows:

1) measure chromium and mercury contents in the liquid waste and the supernatant,
2) calculate the total concentrations of chromium

and mercury in the sludge,

3) digest 1 g of the dried sludge using the nitric digestion method and measure chromium and mercury contents,

4) compare the total concentrations of chromium and mercury in the liquid waste and in the total dried sludge.

From this cross-checking, the dried sludges were found to contain 2.55 mg/g and 6.6 mg/g of chromium and mercury contents, respectively in sample I ; and 13.4 mg/g of chromium and 10.5 mg/g of mercury were found in sample II.

Each mixture was prepared by proportioning, on a dry weight basis, amounts of cement, sand, and water in the ratio 1 : 2 : 0.5 and 1.0 : 2.0 : 0.9 for OPC and lime-RHA cement mortar, respectively. Different amounts of dried waste sludge were added to different mixture. The amount of sludge was controlled in terms of sludge/cement ratio or sludge/(lime+RHA) ratio for OPC and lime-RHA cement mixture, respectively.

Experiments were conducted on four factors affecting the leachability of the hazardous waste.

The factors were:

a) Variation of waste amount in the sample,
b) Water/cement ratio in the sample,
c) pH of the extracted solution,
d) Curing time of the solidified samples.

The variation of waste sludge was controlled in terms of sludge/cement ratio. The ratios of 0.1, 0.2, 0.3, 0.5, and 1.0 were selected. Since the amount of dried sludge obtained was limited for each sludge/binder ratio, two samples were tested for leachability. All the samples for this test were cured for 24 hours. This time was selected to simulate the field conditions where a long interval may not be allowed between solidification of waste and its disposal to the dumping area.

The water/cement ratios were varied at 0.45, 0.50 and 0.6 for OPC mortar and 0.85, 0.90, and 1.0 for lime-RHA cement mortar by changing the quantity of water used for mixing the mortar. The ratio of sludge/cement was kept at 0.5.

During the extraction, the pH was varied at 2, 5, 7 and 10 to study its effect on the leachability. This was deviated from the US EPA Toxicity Extraction Procedure which specifies the pH of the extract solution to be in the range of 4.8 - 5.2. The sludge/cement ratio was kept at 0.5 and water/cement was also kept at the optimum ratio for each binder.

The curing time was varied from 1 day to 28 days. Samples were cured for 1, 3, 7, 14, and 28 days and then tested for leachability. These curing periods have been recommended by ASTM designation C 109 - 86 (ASTM, 1986) for testing the compressive strength of cement sand mortar. Moreover, since normal cement is expected to achieve most of its strength in 28 days, and the time provided for the study was also limited, the curing time was not increased beyond 28 days. The sludge/cement ratio was kept at 0.5 for this test.

For the extraction, about 150 g of the crushed samples of the solidified mass was needed. Since all the cubical samples were already tested for compressive strength, each cube was crushed further so as to convert the solid mass into much smaller forms to pass through 9.5 mm sieve. The US EPA Extraction Procedure was adopted with some modifications. The liquid to solid ratio was chosen as 4 : 1 as recommended by ASTM. This was helpful in detecting leachate from comparatively fewer leaching samples, as well as leachate from comparative analysis only, no serious harm was expected in the analysis by changing the ratio.

Each of the two 100 g of identical samples was placed in a 1000 mL plastic bottle, in which 400 mL of deionized water was added. The deionized water was preadjusted to a pH of 4.8 to 5.2 by the addition of 2400 mg/L (0.04 M) acetic acid. The bottles were placed on an orbital shaker (GALLENKAMP - SD - 125) at a speed of 90 cycles per minute at ambient conditions for 24 hours. Continuous agitation for 24 hours was taken to provide for better assurance of a homogeneous water/extraction mixture.

The US EPA Extraction Procedure was again modified to study the effect of the pH of leachability. The pHs of the extract solutions were varied at 2, 5, 7, and 10. The pH adjustment was made by the addition of concentrated nitric acid for acidic codition, and 40,000 mg/L (1 N) sodium hydroxide solution for neutral and alkaline solutions.

The leachate, obtained after the end of extraction for 24 hours, was vacuum filtrated by using 0.45 μm filter. The leachate was acidified with nitric acid solution to less than pH 2 for metal analysis and then two drops of H_2O_2 was added to avoid interference of other heavy metals. Reagent blanks and sample blanks were tested and no significant metal concentrations were detected in the elutants from the blank binder samples.

3. Result and Dicussion

3.1 Mathematical Model for Leachability

A desorption isotherm, developed by Freundlich, was applied to correlate the sludge concentration in the mortar and the leachability. This simple mathematical relationship was also used to find the coefficients of leachability constants.

Freundlich's desorption isotherm is given by:

$$S = K \times C^{\frac{1}{n}} \qquad \text{(Eq. 1)}$$

where,

S = Weight of Cr and/or Hg in the mortar, mg for both the OPC and lime - RHA mortar,

C = Concentration of sludge leaching out, μg/L for both the OPC and lime - RHA mortar,

K & C = Empirical constants

For the present study, S was measured as mg of Cr and/or Hg of cement mortar and C was measured in μg of Cr and Hg per L of extractant.

Converting the isotherm to the linear form:

$$\text{Log}\,S = \text{Log}\,K + \left(\frac{1}{n}\right) \times \text{Log}\,C \qquad \text{(Eq. 2)}$$

The input data were taken from Table 1 and 2 to fit the Eq. 2 into the Table 3. Regression was carried out for Eq. 2 by fitting the observed data for S and C (Fig. 1 - Fig. 4), and the correlation coeffiecients were determined (Table 4 and 5). The results showed that the values of correlation coefficients (r^2) of Cr leachability for OPC and lime - RHA cement mortar were 0.872 and 0.902 respectively. For Hg leachability, the correlation coefficients (r^2) for OPC and lime - RHA cement mortars were 0.969 and 0.958 respectively. This result implied that the observed data were fit closely into the line of regression or the Freundlich's desorption isotherm. Therefore, the leachate concentrations of the solidified heavy metals could be predicted, approximately by the Freundlich's desorption isotherm modeling.

Table 1. Effect of addition of sludge on compressive strength and leachability for OPC mortar.

Ws/c ratio	Initial amount mg/mould		Compressive strength, kg/cm^2		Final pH in leachate		Leachability			
							Cr (mg/L)		Hg (mg/L)	
	Cr	Hg	sample	average	sample	average	sample	average	sample	average
0.00	0.0	0.0	184.8	194.6	12.6	12.6	N.D	N.D	N.D	N.D
			204.4		12.6		N.D	N.D	N.D	N.D
0.10	25.5	66.0	233.6	231.9	12.9	12.9	0.37	0.43	28	23
			230.1		12.9		0.48		19	
0.20	51.0	132.0	206.4	206.0	13.0	13.0	1.38	1.30	40	40
			205.6		13.0		1.22		40	
0.30	76.5	198.0	244.0	246.2	13.0	13.0	1.68	1.77	115	108
			248.4		13.0		1.85		100	
0.50	127.5	330.0	74.4	78.8	13.0	13.0	2.20	2.18	430	410
			83.2		13.0		2.16		390	
1.00	255.0	660.0	12.8	15.2	13.1	13.1	2.78	2.83	495	502
			17.6		13.1		2.88		510	

condition :

1) Period of curing = 1 day
2) Water/cement ratio = 0.5
3) pH of water before extraction = 4.8 - 5.2
4) Test conducted on 5 × 5 × 5 cm^3 sized cubes
5) Initial amount of Cr in 1 g of dried sludge = 2.55 mg
   Initial amount of Hg in 1 g of dried sludge = 6.6 mg

Table 2. Effect of addition of sludge on compressive strength and leachability for lime - RHA mortar.

Ws/c ratio	Initial amount mg/mould		Compressive strength, kg/cm^2		Final pH in leachate		Leachability			
							Cr (mg/L)		Hg (mg/L)	
	Cr	Hg	sample	average	sample	average	sample	average	sample	average
0.00	0.0	0.0	8.8	8.8	12.4	12.5	N.D	N.D	N.D	N.D
			8.8		12.5		N.D	N.D	N.D	N.D
0.10	25.5	66.0	14.4	14.8	12.7	12.7	0.13	0.13	3	3
			15.2		12.7		0.13		3	
0.20	51.0	132.0	16.0	16.0	12.7	12.7	0.15	0.15	12	15
			16.0		12.7		0.15		18	
0.30	76.5	198.0	16.0	16.4	12.8	12.8	0.22	0.23	31	26
			16.8		12.8		0.24		22	
0.50	127.5	330.0	50.4	50.8	12.9	12.9	0.51	0.53	95	95
			51.2		12.9		0.54		95	
1.00	255.0	660.0	104.0	106.0	12.9	12.9	0.62	0.63	170	175
			108.0		12.9		0.63		180	

condition :

1) Period of curing = 1 day
2) Water/cement ratio = 0.9
3) pH of water before extraction = 4.8 - 5.2
4) Test conducted on 5 × 5 × 5 cm^3 sized cubes
5) Initial amount of Cr in 1 g of dried sludge = 2.55 mg
   Initial amount of Hg in 1 g of dried sludge = 6.6 mg
6) Water/cement ratio = 0.9

Table 3. Modified leachability data used to develop desorption isotherm.

A) Chromium Leachability

Type of mortar	No.	Sludge/cement ratio	"S" in mg	"C" in μg/L
OPC motar	1	0.00	-	-
	2	0.10	25.5	430
	3	0.20	51.0	1300
	4	0.30	76.5	1770
	5	0.50	127.5	2180
	6	1.00	255.0	2830
lime - RHA motar	1	0.00	-	-
	2	0.10	25.5	130
	3	0.20	51.0	150
	4	0.30	76.5	230
	5	0.50	127.5	530
	6	1.00	255.0	630

B) Mercury Leachability

Type of mortar	No.	Sludge/cement ratio	"S" in mg	"C" in μg/L
OPC motar	1	0.00	-	-
	2	0.10	66	23
	3	0.20	132	40
	4	0.30	198	108
	5	0.50	330	410
	6	1.00	660	502
lime - RHA motar	1	0.00	-	-
	2	0.10	66	3
	3	0.20	132	15
	4	0.30	198	26
	5	0.50	330	95
	6	1.00	660	175

Table 4. Regression outputs on Cr leachability for OPC and lime - RHA mortar.

No.	Parameters of regression output	OPC motar	lime - RHA motar
1	constant	- 1.62499	- 0.94985
2	standard error of Y estimated	0.157664	0.137836
3	R squared (r^2)	0.871520	0.901665
4	No. of observation	5	5
5	degrees of freedom	3	3
6	X coefficient	1.117309	1.169723
7	standard error of coefficients	0.247679	0.223024
8	K	0.0237	0.1122
9	n	0.8950	0.8549

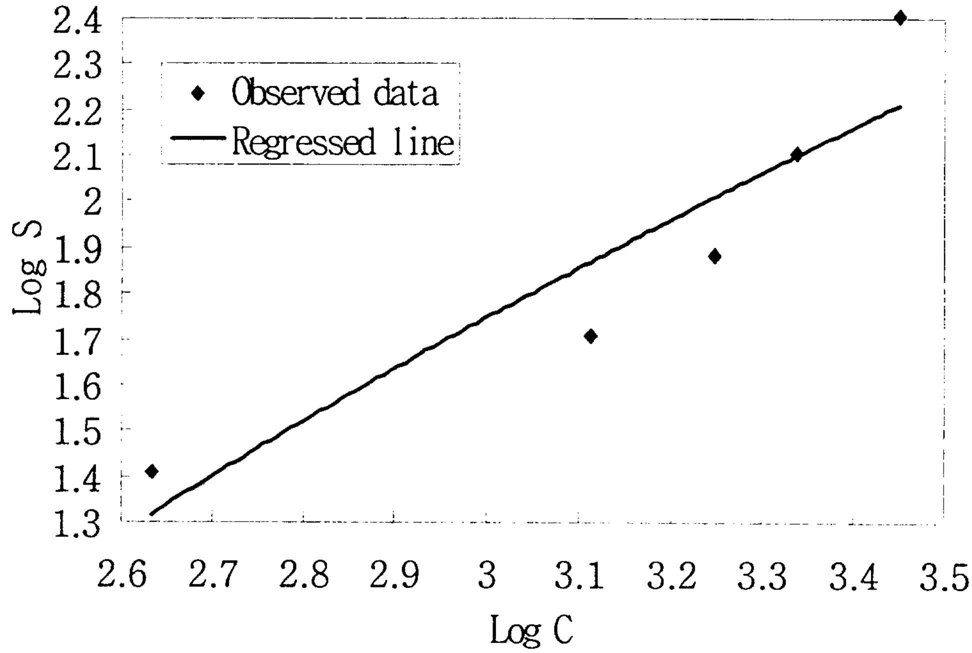

Fig. 1. Variation of Log S with Log C and the Line of Regression for OPC Mortar on Cr Leachability.

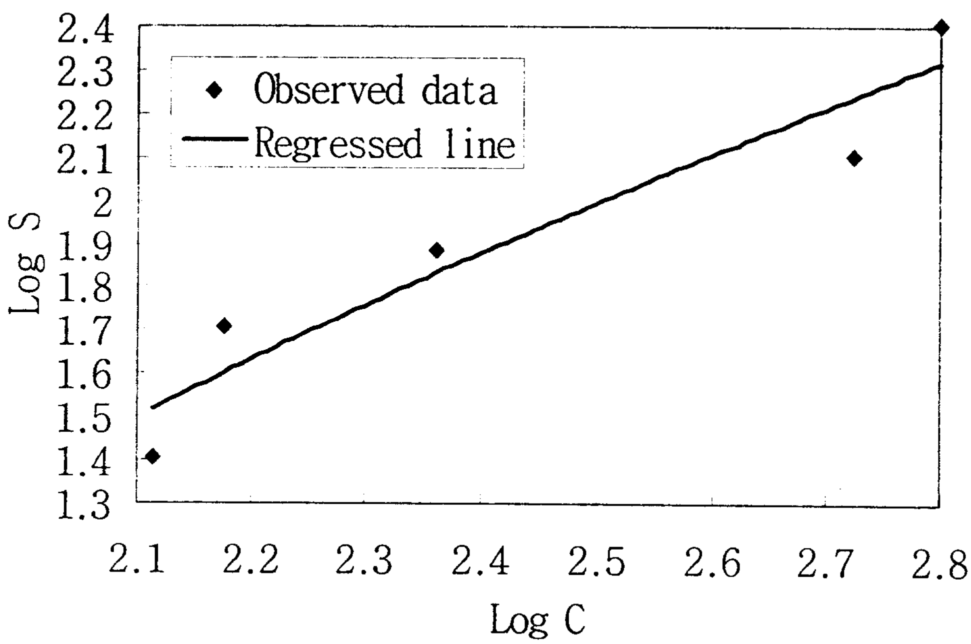

Fig. 2. Variation of Log S with Log C and the Line of Regression for Lime - RHA Mortar on Cr Leachability.

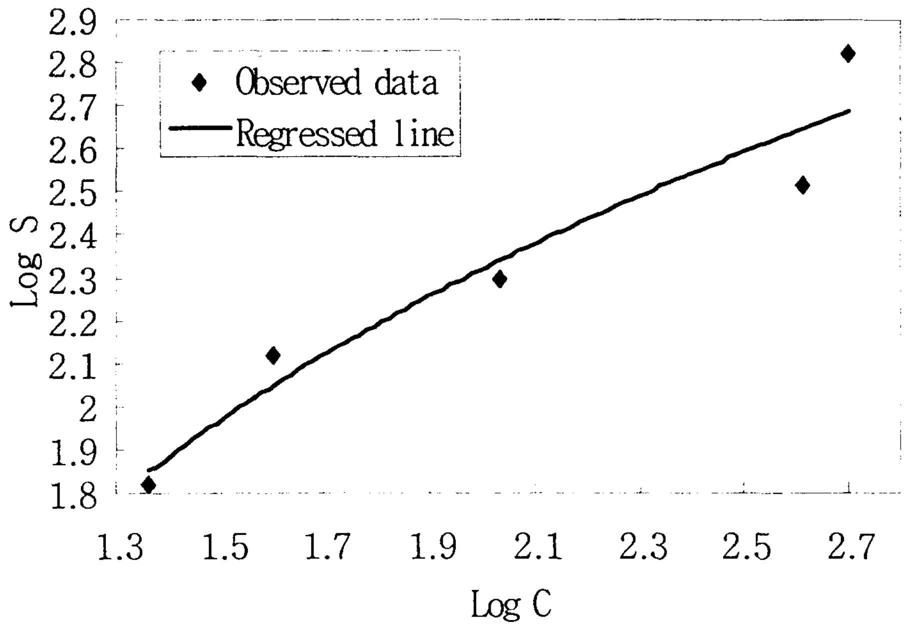

Fig. 3. Variation of Log S with Log C and the Line of Regression for OPC Mortar on Hg Leachability.

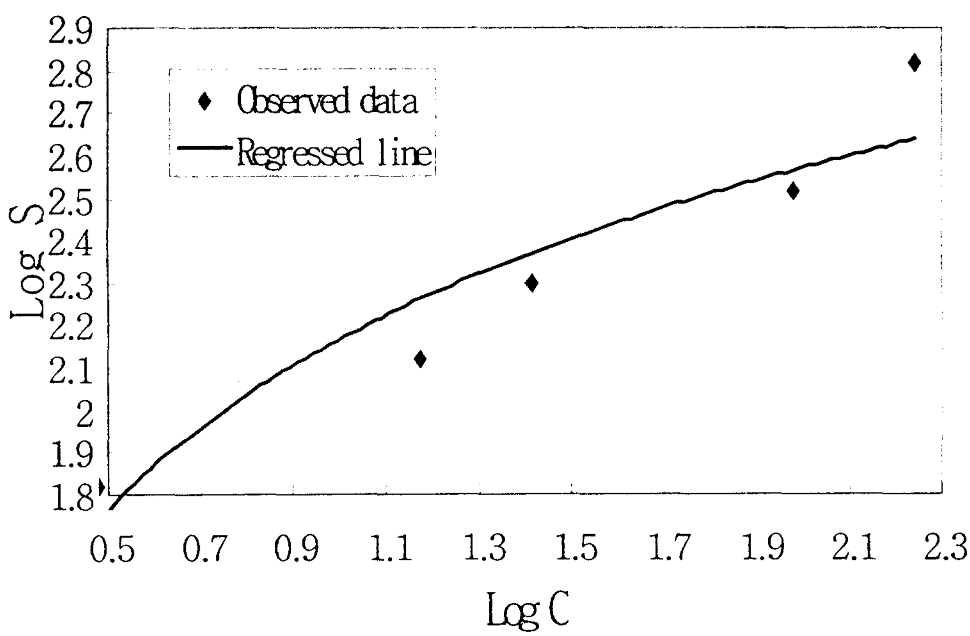

Fig. 4. Variation of Log S with Log C and the Line of Regression for Lime - RHA Mortar on Hg Leachability.

Table 5. Regression outputs on Hg leachability for OPC and lime - RHA mortar.

No.	Parameters of regression output	OPC motar	lime - RHA motar
1	constant	1.298250	1.519379
2	standard error of Y estimated	0.078006	0.091319
3	R squared (r^2)	0.968716	0.957128
4	No. of observation	5	5
5	degrees of freedom	3	3
6	X coefficient	0.466680	0.555494
7	standard error of coefficients	0.048418	0.067876
8	K	19.8724	33.0658
9	n	2.1428	1.8002

3.2. Effect of Variation on Sludge/Cement Ratio

It was observed that the OPC mortars which contained less amount of sludge possessed higher compressive strengths than those samples that contained higher amounts of sludge. This results is in close conformity with the results of previous researches on this aspect. The decrease in compressive strength of the OPC mortar with the increase in sludge/cement ratio could probably be attributed to the interferences of the sludge on the properties of hardened cementitious binders (Bahadir, 1987).

On the contrary, the compressive strength of lime-RHA cement increased slowly up to the sludge/cement ratio of 0.3, however after that, the compressive strength increased at a much faster pace. Several studies have been reported on the effects of heavy metals on cementitious binders.

Eaton et al. (1990) studied the effect of a heavy metal sludge and various interference substances on cementitious binders - portland cement, a portland cement/sludge F fly ash mixture, and a lime/class C fly ash mixture - by scanning electron microscopy, energy dispersive x-ray microanalysis and x-ray diffractometry. According to them, the addition of some interferences led to an increase in crystallinity and thus considerably changed the microstructure, which can have an important effect on mechanical strength. They also suggested that an inorganic interferences chemically reacted with the binders.

Although the reason for the increasing trend of compressive strength of the lime-RHA mortar with the increase of sludge/cement ratio can not be determined at the present, it seemed that a chemical interaction might have happened between the sludge and lime-RHA cement.

Cassell (1970) commented that the heavy metals either get precipitated by the cement hydration product $Ca(OH)_2$ or enmeshed and/or adsorbed in the cement matrix in the calcium silicates present in the binder. As every solidified sample possessed the same capacity of adsorption-precipitation, the total amount of Cr and Hg in the leachate increased when their initial amounts in sludge were increased. The leachability of lime-RHA cement mortar was found to be much less than that of OPC mortar. Moreover, in this case the rate of increase of leachability with sludge/cement ratio was also lower than that of the OPC mortar.

This result can be interpreted in two ways. Firstly, as demonstrated in table 3, silica(SiO_2) constituted more than 90% of RHA. This silica helped in reducing the leachate. Primarily, it combined with the cement to form more quantity of semi-crystalline C-S-H gel which helped in absorbing heavy metals by entrapping them into their semi-crystalline structure (Cook, 1982).

The chemical reaction can be represented as,

$$3Ca(OH)_2 + 2SiO_2 \rightarrow 3CaO_2SiO_23H_2O$$

Secondly, RHA increased the impermeability of lime-RHA cement mortars. This is due to the continuing formation of hydrates which fill the pores and also the absence of free lime which could be leached out (Neville, 1981).

3.3 Economic Evalution

The economic study of three kinds of cementitious binders - OPC, PRHAC (cement/RHA = 1:1), and lime - RHA cement - was done for 100 kg of binding materials. The comparative study considered only the material cost, while the production method, equipment, labour and other related expenditures are the same.

Table 6 shows the cost analysis of the three kinds of cements. The prices of sand, cement, lime and sodium aluminate were the local market prices. The result of this study shows that the price of lime - RHA cement is the cheapest among the three kinds of cements, and the use of lime - RHA cement is more economical than the OPC and PRHAC.

4. Conclusion

Based on the results obtained in this study, the following conclusions were drawn:

1) The leachability of both OPC and lime - RHA cement mortars was found to follow the desorption isotherm developed by Freundlich.
2) The leachability of both OPC and lime - RHA cement mortars decreased with increasing curing time.
3) Both OPC and lime - RHA cement mortars showed a better immobilization effect for Hg than Cr.
4) Material cost of lime - RHA cement was cheaper than OPC and PRHAC.

Table 6. Material cost analysis of OPC, PRHAC, and lime - RHA cement for 100 kg.

Cementitious binders		OPC		PRHAC		lime - RHA	
Components	Cost/kg US $	Quantity kg	Cost US $	Quantity kg	Cost US $	Quantity kg	Cost US $
sand	0.0024	200	0.48	200	0.48	200	0.48
cement	0.068	100	6.8	50	3.4		
RHA	0.024			50	1.2	76	1.608
lime	0.04					33	1.32
sodium aluminate	0.96					1.5	1.44
total cost US $			7.28		5.08		4.848

condition :

1) cement/sand = 1 : 2 for all cementitious binders
2) cement/RHA = 1 : 1 for PRHAC
3) lime/RHA = 1 : 2 for lime - RHA

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