

Research Article

Computer Modeling of Leaching of Heavy Metal from Cementitious Waste

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Abstract: Thermodynamic equilibrium model was used to simulate the results of leaching heavy metal from cementitious wastes. Modeling results of the leached major element concentrations for samples agreed well with the leaching test using the set of pure minerals and solid solutions present in the database. The model revealed Pb and Cd were predominantly incorporated within the calcium silicate hydrate matrix while a greater portion of Cd exist as discrete particles in the cement pores. Precipitation was found to be the dominant mechanism controlling heavy metal solubility with carbonate and silicate species governing the solubility of Pb and carbonate, silicate and hydroxide species governing the solubility of Cd. In the presence of acetic acid, at low pH values Pb and Cd acetate complexes were predominant whereas, at high pH values, hydroxide species dominated. In the presence of municipal landfill leachate, Pb and Cd organic complexes dominated the heavy metal species in solution.

Keywords: Computer modeling, heavy metal, leaching, Saturation Index (SI)

INTRODUCTION

There have been increased concerns regarding reusing the waste materials, as a result, an extensive array of leaching tests has been developed to assess the hazards of heavy metal-containing wastes. It is thus extremely important to understand the leaching behavior of the different elements.

A model capable of describing contaminant leaching from wastes can assist in improving the development of management options. Many studies are available on the modeling of extraction tests for different elements considering leaching from cement-based samples (Dijkstra *et al.*, 2006; Garrabrants *et al.*, 2004; Astrup *et al.*, 2006; Cornelis *et al.*, 2006). One dimensional reactive transport simulations were performed by a number of authors (Tiruta-Barna *et al.*, 2004), but only (DeWindt and Badreddine, 2007) developed a three dimensional model.

This study aimed at using PHREEQC to develop a model for simulating the leaching of Pb and Cd from cementations wastes and identify species governing the release of these contaminants. Model outcomes were assessed by comparison with leaching profiles obtained from procedures recommended by AS 4439.3-1997. Leaching fluids was Municipal Landfill (ML) leachate.

METHODOLOGY

Preparation of sample and leaching experiments: Heavy metal-containing cementitious wastes were

prepared by mixing Ordinary Portland Cement (OPC) with solutions of (Pb (NO₃)₂), (Cd (NO₃)₂·4H₂O) such that they contained 2.34% Pb, 1.3% Cd by weight, respectively. Detailed procedures are further described in Halim *et al.* (2004). The compositions of the cement samples were analyzed using X-Ray Fluorescence (XRF) and are shown in Table 1. Leachate samples were analyzed for metal ions using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES). Detailed descriptions are described elsewhere (Halim *et al.*, 2004).

Establishment of geochemical simulation for metal leaching from cement: PHREEQC was used to model the leaching of contaminants from cementations wastes. In the model simulation, cement was classified into four distinct groups: C-S-H matrix; portlandite; calcite (portlandite that had adsorbed atmospheric CO₂); and free heavy metal compounds. Mole percents of the compounds specified in the C-S-H matrix and their thermodynamic data are shown in Table 2.

Concrete dissolution can be described by several stages. The dissolution rates of the four matrices in cement are described in Eq. (1):

$$\frac{dM}{dt} = 50 \times 10^4 k_{system} \left(c_1 a_{H^+} + c_2 a_{H_2CO_3} + c_3 a_{OH^-} - c_4 a_{Ca^{2+}} a_{CO_3^{2-}} + c_5 \right) \quad (1)$$

where,

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Table 1: Compositions of the cement samples

Cement composition (mg/g of waste)	Element									
	Pb	Cd	Al	Ca	Fe	K	Mg	Na	Si	S
Pb cement	23	0.0	16	340	23	6.6	10	4.5	74	8.8
Cd cement	0.0	13	15	340	22	7.5	10	2.2	73	8.4

Table 2: Mole percents of metal compounds in the C-S-H matrix

Compounds	Mol% in the matrix		Log solubility constant (Ksp) or neutralization constant (Kn)
	Pb cement	Cd cement	
C-S-H gel (CaH ₂ SiO ₄)	64.5	66.6	Kn = 15.30
Hydrogarnet (Ca ₃ Al ₂ (H ₄ O ₄) ₃)	2.2	2.2	Kn = 81.45
Brownmillerite (Ca ₄ Al ₂ Fe ₂ O ₁₀)	5.1	5.1	Kn = 140.51
Gypsum (CaSO ₄ ·2H ₂ O)	6.7	6.7	Ksp = -4.31
Pb (OH) ₂ in C-S-H	2.3	-	Kn = 12.64
Cd (OH) ₂ in C-S-H	-	1.3	Kn = 13.74

Table 3: SI's of selected compounds at different stages of leaching for Pb-contaminated cement

Formula	ML leachate			
	30 sec	180 sec	73 h	
pH	8.70	8.90	10.90	
pe	1.80	1.30	-4.20	
Dominant Pb species in solution	Pb Organic X ⁺ (95%) Pb Organic X ₂ (5%)	Pb Organic X ⁺ (95%) Pb Organic X ₂ (5%)	Pb Organic X ⁺ (89%) Pb (CO ₃) ₂ ²⁻ (7%) Pb Organic X ₂ (4%)	
Alamosite	PbSiO ₃	-6.20	-4.20	0.77
Anglesite	PbSO ₄	-6.60	-5.90	-7.00
Brownmillerite	Ca ₄ Al ₂ Fe ₂ O ₁₀	-74	-71	-51
CaH ₂ SiO ₄ (gel)	CaH ₂ SiO ₄	-8.70	-7.50	-2.00
Calcite	CaCO ₃	0.75	0.75	0.75
Cerussite	PbCO ₃	-0.92	0.00	-0.62
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O	-42	-40	-25
Hydrocerussite	Pb ₃ (CO ₃) ₂ (OH) ₂	-4.60	-1.60	0.00
Hydrogarnet	Ca ₃ Al ₂ (H ₄ O ₄) ₃	-38	-35	-19
Lanarkite	Pb(SO ₄)O	-8.50	-6.60	-4.90
Litharge	PbO	-7.10	-5.90	-3.10
Massicot	PbO	-7.30	-6.10	-3.30
Pb ₂ SiO ₄	Pb ₂ SiO ₄	-13	-9.80	-2.00

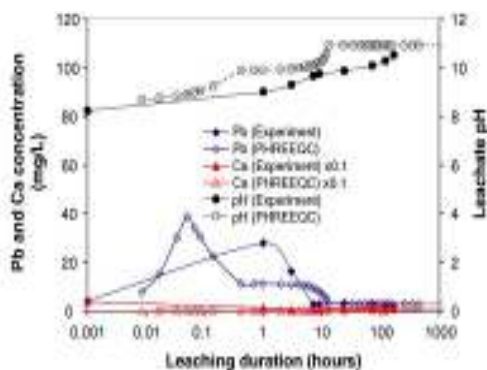


Fig. 1: Experimental and modeling results for cementitious waste containing Pb tumbled with ML leachate; Ca concentrations are multiplied by 0.1

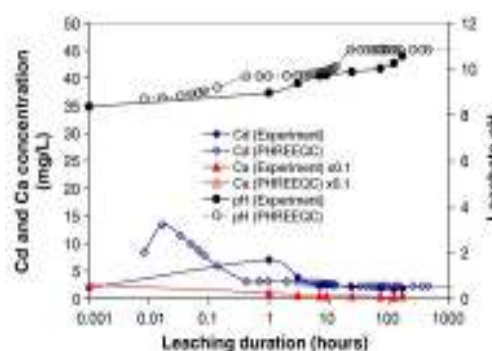


Fig. 2: Experimental and modeling results for cementitious waste containing Cd tumbled with ML leachate; Ca concentrations are multiplied by 0.1

RESULTS AND DISCUSSION

Leaching of Pb: Pb, Ca and pH profiles as a function of leaching duration in the presence of ML leachate are provided in Fig. 1, with the SI's of various compounds at different stages of leaching by the ML leachate presented in Table 3. The initial increase in Pb is due to complexation of Pb with Organic X. This is illustrated in

dM/dt : The dissolution rate of above four matrix

k_{system} : A constant

A : The surface area of the matrix (in $m^2 g^{-1}$ of waste)

a_{H^+} , $a_{H_2CO_3}$, a_{OH^-} , $a_{Ca^{2+}}$ & $a_{CO_3^{2-}}$: The activities of H^+ , H_2CO_3 , OH^- , Ca^{2+} and CO_3^{2-} , respectively

Table 4: SI's of selected compounds at different stages of leaching for Cd-contaminated cement

Formula		ML leachate		
		30 sec	180 sec	73 h
pH		8.70	8.90	10.70
pe		2.30	2.00	-2.70
Dominant Cd species in solution		Cd Organic X ⁺ (96%)	Cd Organic X ⁺ (96%)	Cd Organic X ⁺ (95%)
		Cd Organic X ₂ (3%)	Cd Organic X ₂ (3%)	Cd Organic X ₂ (3%)
		Cd Organic X ₃ (1%)	Cd Organic X ₃ (1%)	Cd Organic X ₃ (1%)
Brownmillerite	Ca ₄ Al ₂ Fe ₂ O ₁₀	-66	-65	-52
CaH ₂ SiO ₄ (gel)	CaH ₂ SiO ₄	-8.80	-7.70	-2.20
Calcite	CaCO ₃	0.75	0.75	0.75
Cd (OH) ₂	Cd (OH) ₂	-6.10	-5.60	-2.40
Ettringite	Ca ₆ Al ₂ (SO ₄) ₃	-34	-34	-26
	(OH) ₁₂ ·26H ₂ O			
Hydrogarnet	Ca ₃ Al ₂ (H ₄ O ₄) ₃	-30	-29	-19
Otavite	CdCO ₃	-0.25	0.00	0.00
CdSiO ₃	CdSiO ₃	-6.10	-4.70	0.74
CdSO ₄	CdSO ₄	-12	-12	-13

the model (Table 3), which shows complexation of Pb with Organic X dominates Pb speciation in the solution below pH 10. At 180 sec of leaching, the pH of the leachate had increased to 8.9, with Pb indicated to be precipitating as cerrusite. A further increase in pH to above 11 saw hydrocerussite and lead silicate precipitates likely to be the solubility controlling species.

Leaching of Cd: The modeling and experimental results for the leaching of Cd and Ca from cementitious waste by ML leachate are shown in Fig. 2. SI values are provided in Table 4. The model findings imply complexation of Cd with organic ligands increased the soluble Cd early in the leaching process. The increase in pH with time gives rise to the precipitation of Cd as carbonate and silicate species. Cd concentration was not experimentally monitored between 0 and 1 h, such that existence of the peak described by PHREEQC over this time frame cannot be confirmed here.

CONCLUSION

This study has illustrated the capacity of PHREEQC for providing greater insight into the leaching of Pb, Cd from cementations waste in the presence of simple and complex leachants. In the presence of acetic acid, at low pH values, acetate complexes were predominant in solution whereas hydroxide species dominated at high pH values.

The model has indicated the same major phase dissolution rates are valid for Pb and Cd, contaminated wastes, illustrating its potential adaptability to cement containing different heavy metals. It also served to highlight the importance of hydroxide ions during dissolution of the C-S-H matrix and indicated carbonate and silicate species governed the solubility of Pb, silicate and hydroxide species governed the solubility of Cd. Ultimately, information provided by the model may be valuable by assisting in decisions regarding choice of appropriate waste stabilization techniques and conditions.

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