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Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials

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Abstract

A circuit board printing factory sludge containing high concentrations of copper, zinc and lead was stabilized and solidified (S/S) with different portions of ordinary Portland cement (OPC) and pulverized fly ash (PFA). The chemical speciation and leaching behavior of heavy metals in these cement-based waste materials were studied by different sequential extraction procedures, standard toxicity characteristic leaching procedure (TCLP) and progressive TCLP tests. The sequential extraction results showed that more than 80% of Cu, Pb and Zn were associated with Fraction 2 (weak acid soluble, extracted with 1 M NaOAc at pH 5.0 with a solid to liquid ratio of 1:60). This indicated that the heavy metals could exist in the S/S matrix as metal hydrated phases or metal hydroxides precipitating on the surface of calcium silicate hydrates (C–S–H), PFA and sludge particles. The progressive TCLP test results and MINTEQA2 calculation also showed the importance of Cu and Zn oxides during the leaching process. The leaching behaviors of these metals in the S/S waste materials were mainly controlled by the alkaline nature and acid buffering capacity of the S/S matrix. During the progressive TCLP tests, the alkaline conditions and acid buffering capacity of the matrix decreased with the dissolution of calcium hydroxide and C–S–H, therefore, the leaching of heavy metals in the S/S waste materials increased. The leaching of heavy metals in the S/S materials can be considered as a pH dependent and corresponding metal hydroxide solubility controlled process.

Keywords: Heavy metals; Stabilization/solidification; Sequential extraction; Leaching; TCLP; MINTEQA2

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1. Introduction

Cement based solidification/stabilization (S/S) technology is a process in which waste materials are mixed with cement, small amounts of fly ash, sodium silicate and bentonite [1,2]. This technology is widely used because it can offer assurance of chemical stabilization of many contaminants and produce a mechanically stable waste form. Although the stabilization technology has been used for a long period of time, the chemical speciation and binding mechanisms of metal ions with cement and other reagents have not been fully characterized [3–7].

Previous researches addressed the chemical aspects involved in S/S processes [3,6]. Tashiro et al. [8] and Tashiro and Oba [9] investigated the effect of heavy metal oxides of Cr, Cu, Zn, As Ce, Hg and Pb on the physical properties of cement. It was found that metals could react with cement paste and affect the hardening and strength development during the early stage of cement hydration. Stepanova [10] reported that metal chlorides of Mn, Co, Ni, Cu and Zn interacted with the silicate and aluminate of cement to form complexes that could influence the strength development. Based on these studies, several types of interactions may occur simultaneously (and in some cases sequentially) in the solidified systems [5,11]. The waste component may react in one or more of the following ways: adsorption, chemisorption, precipitation, ion-exchange, passivation, surface complexation, inclusions (micro encapsulation) and chemical incorporation into the hydrated cement system.

The study of leaching behaviors of metals is an important way to obtain valuable information about the chemical speciation of contaminants in S/S waste matrix and their potential environmental risks [2,5,7]. Leaching is the process by which contaminants are transferred from a stabilized matrix to liquid medium, such as water or other solutions. However, most of the leaching procedures focused on one or two steps, without a detailed analysis of the chemical partitioning of the contaminants within the stabilized materials.

Sequential extraction methods have often been used to study the speciation and possible associations between metals and soil or sediment components [12–15]. The chemical partitioning of metals is operationally defined according to the reagents used and the matrix of the samples. For cement-based S/S waste, this method can be useful to evaluate the metal distribution in the different phases of the S/S waste matrix, potential binding mechanisms and leaching behaviors [16,17]. There may be some analytical limitations imposed by interference, selectivity, and sensitivity of the sequential extraction methods, which could affect the differentiation of metals between various physicochemical forms in the stabilized/solidified materials. At present, a number of schemes have been proposed to fractionate metals on the basis of extractability in various chemical reagents either discretely or sequentially [16,19,20]. Of these methods, the sequential extraction presented by Tessier et al. [12] has been widely used in soil and sediment studies.

In the present study, a raw waste material (an industrial copper sludge) was solidified and stabilized by different proportions of ordinary Portland cement (OPC) and pulverized fly ash (PFA). The chemical speciation of metal contaminants and major elements in the S/S waste materials were studied by using different sequential extraction procedures, standard toxicity characteristic leaching procedure (TCLP) and progressive TCLP tests. The speciation, binding mechanisms and leaching behaviors of heavy metals are evaluated based on the combined analytical results.

2. Material and methods

2.1. Sample preparation

The raw waste (copper sludge) was obtained from the industrial wastewater treatment process of a circuit board printing factory in Hong Kong. The plant utilized a sodium hydroxide precipitation and sedimentation process followed by a filter process for the treatment of its copper rich wastewater. The OPC and PFA were obtained locally from a cement plant and a coal fired power plant. Because of the heterogeneous nature of the raw waste sludge, it was dried in an oven at 105°C for 24 h, then ground to fine particles before the stabilization process. Measured amounts of OPC and PFA were added to the sludge, and distilled water was then added at a water to binder ratio of 0.4 to facilitate curing. The slurries were mixed manually by using a bowl and a rubber spatula. After mixing, the slurries were poured into plastic cylindrical molds. Air bubbles in the paste were removed by tapping the mold for about 1 min. The molds were then capped to retain moisture. The samples were cured at 20°C in the laboratory for 28 days. The cured samples were demolded and ground to pass through a 100 μm sieve before the total metal analysis and sequential extraction. The compositions of the stabilized waste samples are given in Table 1.

2.2. Analytical methods

2.2.1. Total metal concentrations and pH of the S/S waste materials

Total metal concentrations of the raw waste, PFA, OPC and S/S waste samples were analyzed using microwave-assisted leach method 3051A according to the United States Environmental Protection Agency (USEPA) [21]. About 0.5 g sample was digested with 10 ml concentrated HNO_3 in a microwave (CEM MSP 100) with an advanced composite vessel at 175°C for 5.5 min and hold at 175°C for 4.5 min. After cooling, the solution was filtered and analyzed by ICP-AES (Perkin-Elmer, OPTIMA 3300DV). The pH values of the samples were determined with a liquid-to-solid ratio of 4:1 after 48 h equilibrium [16] by using a Philip’s PW 9420 pH meter and an Ingold U455 glass electrode calibrated with buffer solutions of pH at 4, 7 and 10.

Table 1
The mix proportions of stabilized waste samples

Sample	OPC		PFA		Raw waste	
	%	Weight (g)	%	Weight (g)	%	Weight (g)
SW1	0	0	50	100	50	100
SW2	20	60	40	60	50	100
SW3	30	40	30	40	50	100
SW4	40	80	20	20	50	100
SW5	50	100	0	0	50	100

2.2.2. Sequential chemical extraction

Two sequential extraction procedures were used in this study, the original method of Tessier and coworkers [12,13] and the modified protocol. In Tessier's method, metals are partitioned into the following five operationally defined fractions:

1. Fraction 1 — exchangeable. The sample was extracted with 0.5 M $MgCl_2$ at pH 7.0 at a solid to solution ratio of 1:8, with continuous agitation for 5 h at room temperature;
2. Fraction 2 — bound to carbonates/specifically adsorbed. The residual from (1) was extracted with 1 M NaOAc (adjusted to pH 5.0 with HOAc) at a solid to solution ratio of 1:8. Continuous agitation was maintained for 5 h at room temperature;
3. Fraction 3 — bound to iron and manganese oxides. The residual from (2) was extracted with 0.04 M $NH_2 \cdot OH \cdot HCl$ in 25% (v/v) HOAc (initial pH 2.0 and a solid to solution ratio of 1:20) with occasional agitation for 6 h at 96°C;
4. Fraction 4 — bound to organic matter/sulfide. The residue from (3) was extracted with 30% H_2O_2 (initial pH 2.0 and a solid to solution ratio of 1:20) with occasional agitation for 6 h at 85°C, and then extracted with 3.2 M NH_4OAc in 20% (v/v) HNO_3 with continuous agitation for 30 min;
5. Fraction 5 — residual fraction. The residue from (4) was digested with concentrated HNO_3 and $HClO_4$ acids at 90–190°C for 18 h.

Considering the high alkalinity of S/S waste matrix, a modified Tessier's method at step 2 was adopted in order to make this method more suitable for S/S waste materials. To evaluate the optimum solid to liquid ratio for step 2, S/S waste samples were first extracted for 5 h for exchangeable fraction with 1 M $MgCl_2$ (pH 7.0), and then further leached with 1 M NaOAc (pH 5.0, adjusted with HOAc) with solid to liquid ratios ranging from 1:40 to 1:200 for 18 h. Finally, the solid to liquid ratio of 1:60 and constant pH adjustment (5.0) in step 2 was adopted in the modified procedure, which had the best extraction efficiency.

2.2.3. Standard TCLP test

The TCLP test used in this study followed the standard procedures described by USEPA [18]. About 10 g of samples was weighted into polypropylene bottles. About 200 ml of the TCLP No. 2 leachant (0.1 M HOAc, $pH = 2.88$) was added. The bottles were tumbled at 29 rpm in a rotary extractor at room temperature for 18 h. At the end of the extraction, the leachate was filtered with Whatmam GF/C glass fiber filter paper. The pH of the filtrate was measured and the leachate was acidified by a small amount of concentrated nitric acid to $pH < 2$ before being analyzed by ICP-AES.

2.2.4. Progressive TCLP test

In order to further study the leaching behavior of metal contaminants in the S/S materials, the progressive TCLP test was also used in this study. The test ran for a total of five progressive steps. The procedure of each step was the same as the standard TCLP test. After each extraction, the residues from the filtering process were returned to the extraction bottles to repeat the extraction using a fresh portion of the leachant.

3. Results and discussion

3.1. The chemical characteristics of stabilized waste matrix

The basic chemical characteristics of the raw waste (RW) and S/S waste samples are listed in Table 2. The results show the highly alkaline nature of these samples. The raw waste contained very high Cu (387,000 mg/kg). In the S/S waste materials, the concentrations of Ca increased with the increasing percentage of OPC in S/S matrix as most of calcium came from OPC. The heavy metals, Cu, Pb and Zn mainly originated from the raw waste.

3.2. Sequential chemical extraction

The sequential extraction results (Tessier's method) of S/S waste materials are listed in Table 3. Cu, Zn and Pb were mainly distributed in Fraction 3 (bound to iron and manganese oxides) indicating that most of heavy metals had not entered the residual phase during S/S process. Most of the calcium was extracted within the first three steps (>80%).

The principle of sequential chemical extraction methods is that various chemical extractants are applied successively to a sample, dissolving the components of the sample matrix in sequential order. Ideally, a reagent should liberate all the metals from a particular matrix's component (i.e. exchangeable, carbonate, etc.), and should not affect the metals in other components. However, it is generally recognized that the partitioning of metals obtained by such procedures is always operationally defined as it is affected by many experimental factors especially the chemical composition of the sample matrix [14,15].

In the sequential extraction results of Tessier's original method, some possible overlap could exist between Fractions 2 and 3 due to the high pH of the S/S matrix, which could limit the reagent strength to dissolve the metals at Fraction 2. In order to validate the extraction protocol on S/S waste matrix and to optimize the sequential extraction procedures, the pH of the extract of Fraction 2 was measured and the concentration of calcium was also analyzed (see Table 4). The results showed that the pH of extractant increased to 8–9 after 30 min extraction. At this pH range, it was difficult to dissolve any heavy metals in carbonate or hydroxide forms from the S/S matrix. This might be the main reason why metal concentrations were low at step 2. Different solid to liquid ratios at step 2 also affected the concentrations of calcium (see Table 4). Therefore, the reagent used at this step was not strong enough for the high pH condition of these samples.

Table 2
The pH and total metal concentrations in the raw waste, OPC, PFA and S/S waste matrix (mg/kg)[a]

	RW	OPC	PFA	SW1	SW2	SW3	SW4	SW5
pH	9.39	13.3	12.7	12.1	13.3	13.4	13.5	13.5
Ca	2660	364000	36600	12100	57700	76000	119000	154000
Cu	387000	n.d.	n.d.	200000	191000	181000	189000	187000
Zn	4630	96.	32	2630	2480	2370	2400	2400
Pb	686	n.d.	n.d.	369	351	335	348	337

[a] n.d.: Not detected. Detection limits: Pb, 2 μg/kg; Cu, 0.85 μg/kg; Zn, 0.3 μg/kg.

Table 3
Results of sequential chemical extraction of the S/S waste materials[a]

	Step	RW		SW1		SW2		SW3		SW4		SW5	
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Ca	1	1120	66.6	5740	25.4	13500	17.7	14100	14.4	17100	16.2	19500	11.9
	2	325	19.4	8900	39.5	22000	28.9	26600	27.1	42200	40.1	41000	25.0
	3	183	10.9	4210	18.7	38000	49.8	55500	56.7	44300	42.1	101000	61.4
	4	24.9	1.5	1590	7.0	1550	2.0	1140	12.0	1130	1.1	2750	1.7
	5	27.7	1.7	2120	9.4	1270	1.7	722	0.7	543	0.5	58	0.0
Cu	1	n.d.	0.0	14.9	0.0	n.d.	0.0	n.d.	0.0	4.8	0.0	0.4	0.0
	2	28100	8.9	13000	6.9	n.d.	0.0	n.d.	0.0	2.3	0.0	0.8	0.0
	3	214000	67.3	154000	81.9	170000	91.6	173000	93.0	168000	96.1	214000	96.2
	4	75600	28.5	20100	10.7	14700	7.39	12200	6.6	6180	0.5	7880	3.5
	5	31.3	0.2	802	0.4	822	0.4	734	0.4	647	0.4	589	0.3
Zn	1	n.d.	0.0	n.d.	0.0	n.d.	0.0	n.d.	0.0	6.3	0.7	6.4	0.5
	2	344	9.1	149	7.7	n.d.	0.0	n.d.	0.0	n.d.	0.0	n.d.	0.0
	3	2590	68.5	1570	81.0	1660	90.5	1580	91.4	812	87.8	1130	89.5
	4	818	21.6	181	9.3	132	7.2	111	6.4	64.9	7.0	83.3	6.6
	5	30.6	0.8	39.0	2.0	41.4	2.3	37.5	2.2	42	4.5	43.6	3.4
Pb	1	n.d.	0.0	n.d.	0.0	n.d.	0.0	n.d.	0.0	n.d.	0.0	n.d.	0.0
	2	48.4	8.3	13.5	6.1	n.d.	0.0	n.d.	0.0	n.d.	0.0	n.d.	0.0
	3	365	63.0	174	78.3	182	87.2	182	89.0	104	85.9	142	88.2
	4	165	28.8	25.5	11.5	15.2	8.4	15.2	7.5	9.3	7.7	11.8	7.3
	5	1.0	0.2	9.4	4.2	7.2	4.4	7.2	3.5	8.0	6.4	7.3	4.5

[a] n.d.: Not detected. Detection limits: Pb, 2 μg/kg; Cu, 0.85 μg/kg; Zn, 0.3 μg/kg.

An experiment was conducted with different solid to liquid ratios and a constant pH (5.0, adjusted with HOAc) during step 2 in order to optimize the experimental conditions (Fig. 1.) In Fig. 1, the metal concentrations in the extractants increased greatly when the solid to liquid ratio increased from 10 to 60. When the solid to liquid ratio was higher than 60, an equilibrium was reached and the metal concentrations in extractants remained constant. Based on this experiment, Tessier's method was modified in order to fit the matrix nature

Table 4
The pH and Ca concentrations at step 2 of the sequential extraction

Times (h)	S/L 1:8		S/L1:16	
	pH	Ca (mg/kg)	pH	Ca (mg/kg)
0.0	5.0	0.0	5.0	55600
0.5	9.6	27450	8.3	55900
1.0	9.7	29300	8.7	56600
1.5	9.7	29600	9.1	57300
2.5	9.7	33300	9.2	57300
4.0	9.8	32600	9.3	58900
5.5	9.8	34100	9.4	59500
8.0	9.9	35400	9.4	62900

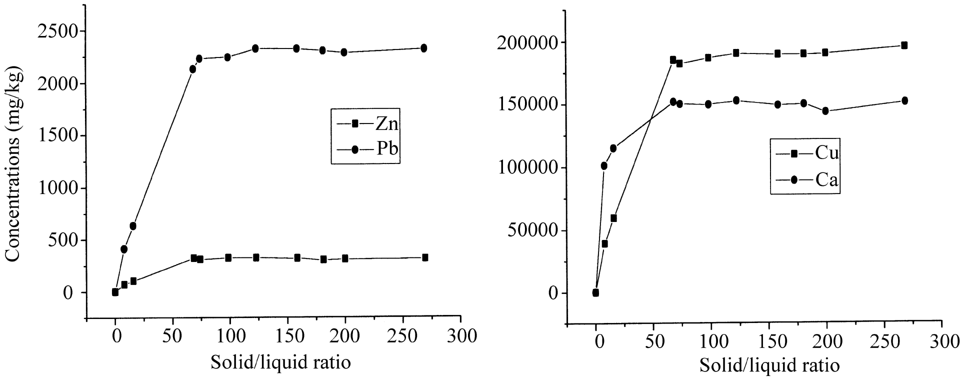

Fig. 1. The metal concentrations with different solid to liquid ratios at step 2 of the sequential extraction.

of the S/S waste samples. In the modified method, the solid to liquid ratio at step 2 was changed to 60 and the pH of the extractant was kept constant at 5.0 with HOAc adjustment during the extraction.

The sequential extraction results by the modified method are presented in Table 5. As shown in this table, Cu, Zn and Pb were mainly (>80%) distributed in Fraction 2

Table 5
Results of sequential chemical extraction of the S/S waste materials using the modified method

	Step	RW		SW1		SW4		SW5	
		mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Ca	1	1540	97.8	9360	42.3	52900	42.5	64000	40.5
	2	0.0	0.00	6620	29.9	65800	52.8	88300	55.8
	3	10.3	0.70	3220	14.5	5350	4.3	5760	3.6
	4	25.1	1.60	714	3.2	190	0.2	139	0.1
	5	0.0	0.00	2240	10.1	359	0.3	0.0	0.0
Cu	1	20.5	0.01	9.7	0.01	4.8	0.00	8.2	0.00
	2	288000	95.1	163000	96.5	153000	96.7	162000	96.4
	3	14600	4.80	5760	3.4	5060	3.2	5840	3.50
	4	352	0.1	109	0.1	84.9	0.10	166	0.10
	5	58.2	0.0	110.6	0.1	23.4	0.00	35.3	0.00
Zn	1	4.7	0.08	3.7	0.31	12.4	1.02	2.2	0.19
	2	5720	97.3	1120	94.3	1150	94.7	1110	94.2
	3	149	2.5	61.3	5.2	51.1	4.6	53.9	4.6
	4	8.5	0.10	2.6	0.2	0.9	0.1	1.6	0.1
	5	0.0	0.0	0.0	0.0	0.0	0.9	10.3	0.9
Pb	1	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
	2	736	97.4	384	95.1	364	97.3	374	97.4
	3	33.4	4.3	13.7	3.4	13.0	3.5	12.8	3.3
	4	16.2	2.1	0.9	0.2	0.0	0.0	0.3	0.1
	5	0.3	0.0	6.5	1.6	0.0	0.0	0.0	0.0

(weak acid soluble form). Comparing the partitioning patterns of this modified method and Tessier's original method, most of the metals that were originally associated with Fraction 3 in Tessier's method were changed to Fraction 2 (Tables 3 and 5) because of the change of extraction conditions (change in solid to liquid ratio and pH adjustment).

Considering the highly alkaline condition of the S/S matrix, most of these metals might exist as metal hydrated phases, metal hydroxides and calcium-metal compounds [19]. Roy and Cartledge [20] studied the speciation of Cu in electroplating sludge stabilized with Portland cement. They found that the principal copper-bearing phase was a copper hydrated phase ($CuO{\cdot}3H_2O$) when Cu was added as copper nitrate in the matrix. Cu may also exist as hydroxides or react with calcium to form complex compounds in the S/S waste materials.

Zinc is expected to form hydroxides in the high pH condition (>8) of cement system [22]. Zinc hydroxide, a typical amphoteric hydroxide functions as both an acid and a base. The equilibrium is

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2 \rightarrow 2H^{+} + ZnO_2{}^{2-} \tag{1}$$

The hydroxy-complexes $Zn(OH)_4{}^{2-}$ and $Zn(OH)_5{}^{3-}$ can be present in a strong alkaline solution. Their anionic properties preclude their adsorption onto the negative surface of the C–S–H, but they may form the calcium zinc complex hydrated compound $CaZn_2(OH)_6{\cdot}H_2O$ with Ca. This has been confirmed by the FTIR investigations of Zn doped Portland cement [23,24].

For lead, the dissolved species in solution are Pb^{2+}, $PbOH^{+}$, $Pb(OH)_2{}^{0}$, and $Pb(OH)_3{}^{-}$. At low pH condition, $PbOH^{+}$ is the dominant dissolved Pb(II) species, but with the increase of pH, Pb can form hydroxide precipitate and then become the more insoluble PbO. Considering the relatively low concentration of Pb in these S/S materials, Pb may be adsorbed onto the Ca hydrate or C–S–H phase.

Most of calcium was extracted within the first three steps. This may be due to the dissolution of calcium hydroxide (CH), nearly amorphous calcium silicate hydrates (C–S–H) and complex calcium metal compounds. Calcium hydroxide can dissolve at comparatively high pH condition during extraction [25,26]. The following equilibria exist in a C–S–H–H_2O system:

$$Ca_2H_2Si_2O_73H_2O = \{H_3SiO_4{}^{-}\}^2\{CaOH^{+}\} = K_{CS} \tag{2}$$

$$Ca(OH)_2 = \{CaOH^{+}\}\{OH^{-}\} = K_{CH} \tag{3}$$

where K_{CS} and K_{CH} are the solubility products.

In the sequential extraction, with the dissolution of calcium hydroxide (C–H) and C–S–H phases, the matrix lost its buffering capacity. For heavy metals, their hydrated phases, and metal hydroxides precipitated on the surface of C–S–H and PFA particles or encapsulated in C–S–H phases could dissolve into solution. From the results, it seems that most of the heavy metals might exist as metal hydrated phases and metal hydroxides in the S/S waste matrix. The extraction of these metals with different reagents was related to the dissolution of C–H and C–S–H phases in the S/S matrix.

Table 6
The results of TCLP test in the S/S waste matrix (mg/l)[a]

	RW (0[b])	SW1 (0[b])	SW2 (20[b])	SW3 (30[b])	SW4 (40[b])	SW5 (50[b])
Cu	2060	927	n.d.	n.d.	n.d.	n.d.
Pb	27.7	11.8	n.d.	n.d.	n.d.	n.d.
Zn	3.15	1.33	n.d.	n.d.	n.d.	n.d.

[a] n.d.: Not detected. Detection limits: Pb, 2 μg/l; Cu, 0.85 μg/l; Zn, 0.3 μg/l.
[b] OPC%.

3.3. TCLP test

The concentrations of heavy metals in the leachates of the standard TCLP test are shown in Table 6. These results can be compared to the USEPA standards to determine whether or not the samples can be classified as hazardous wastes. No stipulated standards are available for Cu and Zn. The stipulated standard in the US regulation for Pb is 5 mg/l [2]. Pb concentrations in the standard TCLP test were all below this level except for the raw waste and SW1 sample (only PFA was added). The concentrations of Cu in the TCLP test were high for the raw waste and SW1 sample. There was also small amount of Zn in the leachate for these two samples. For other S/S waste samples, the concentrations of Cu and Zn in the standard TCLP test were all below the detection limits. The results show that the standard TCLP test was unable to differentiate the leachability of metal contaminants in various cement-based waste materials due to the strong buffering capacity of the waste matrix, which could neutralize the extraction solution and limit metal leaching process.

3.4. Progressive TCLP test

3.4.1. The metal concentrations of leachates during each extraction step

The metal concentrations in the leachant of the progressive TCLP test are shown in Fig. 2. Cu, Zn and Pb show similar leaching behaviors during the extractions. Two different types of leaching curves were observed. One was for the raw waste and SW1, in which the highest metal concentrations in the leachate occurred at the second TCLP extraction. The other type was for SW2 to SW5, in which the metal concentrations in the leachate solutions increased with the successive TCLP extractions. These two types of leaching behaviors might be caused by the different OPC contents in the waste matrix. For the raw waste and SW1, the maximum extraction could be reached at the second TCLP extraction due to the low buffering capacity (no OPC added).

For calcium, there were also two different types of leaching curves. For the raw waste (RW) and SW1, the highest concentrations were in the first TCLP extraction and the concentration decreased gradually in the following extraction. The second type of leaching curves was for the samples SW2 to SW5. Calcium concentrations in the leachates increased and reached the maximum at the second TCLP test and then dropped gradually afterwards. The calcium concentrations in the leachate of different samples at the same step increased with the increasing OPC content of the S/S waste matrix, reflecting the contribution of Ca from OPC.

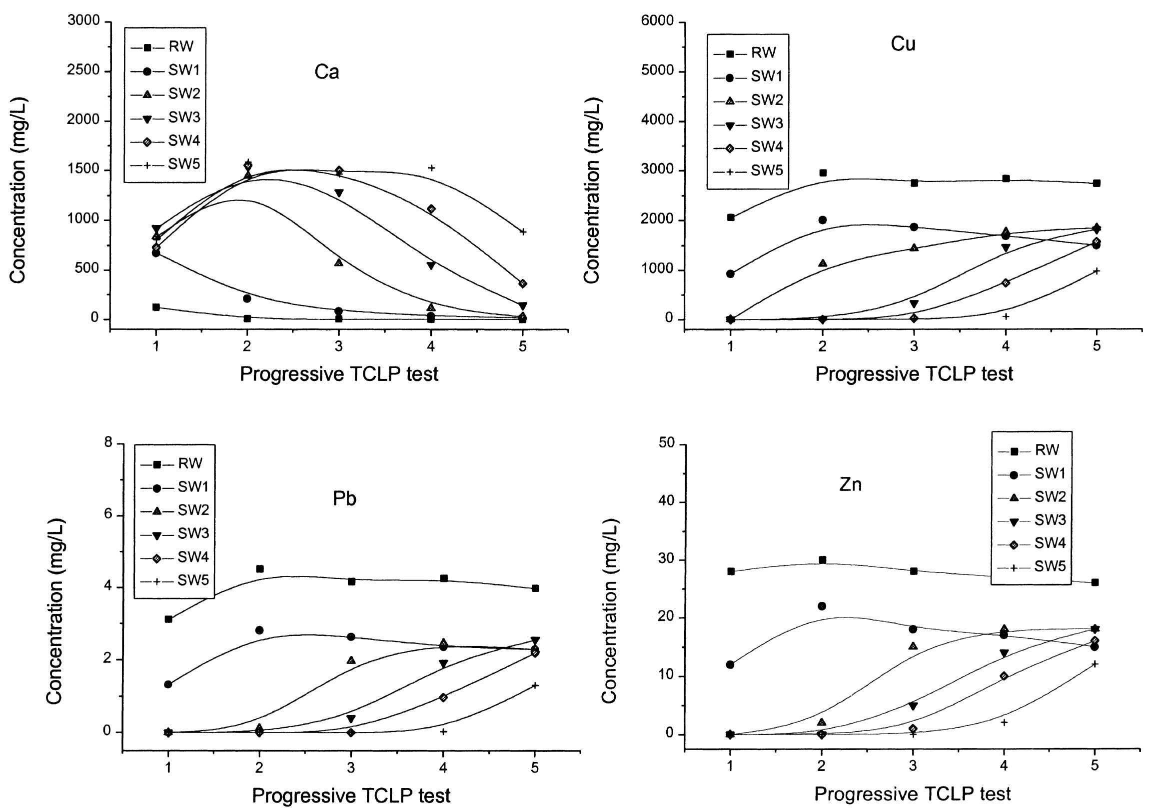

Fig. 2. The metal concentrations in leachate during each extraction step of the progressive TCLP test.

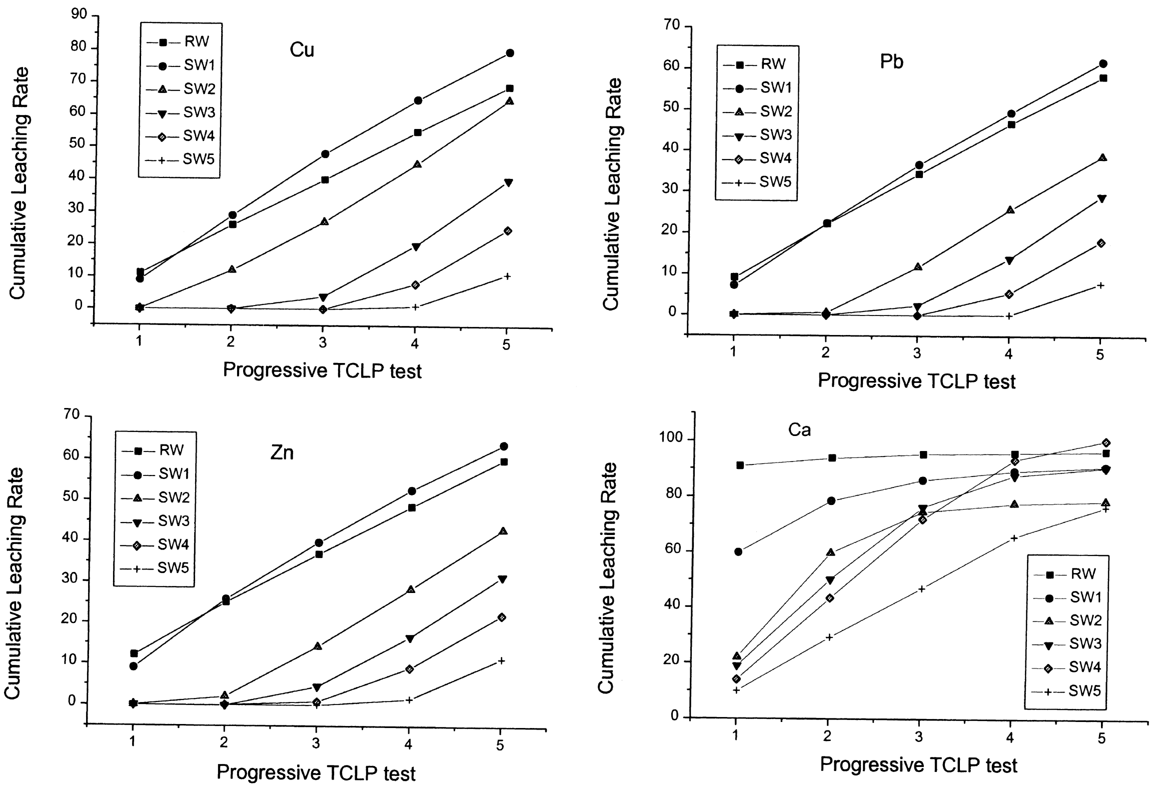

Fig. 3. The cumulative leaching efficiency (rate) of metals in S/S waste materials during the progressive TCLP test.

3.4.2. Cumulative leaching rate in progressive TCLP test

Cumulative leaching rate is often used to evaluate the leachability of the waste matrices. It is defined as a ratio of the cumulative amount of metal concentrations leached out to the total metal concentrations in S/S waste matrix and can be calculated according to the following equation:

$$\mathrm{CLR\%} = \sum \left(\frac{\text{leachate content}}{\text{total content}} \right) \times 100 \qquad (4)$$

The cumulative leaching rates (CLR) of each metal during the progressive TCLP test are shown in Fig. 3. Cu, Zn and Pb were leached in increasing amounts from the first TCLP extraction to the end of the progressive extraction. The cumulative leaching rates (CLR) of these metals were from 10 to 80% for different S/S samples. The samples with more OPC percentage had lower cumulative leaching rates (CLR), indicating the addition of OPC can facilitate the binding of heavy metals in S/S waste matrix. It should be pointed out that the main reason of heavy metal immobilized in cement-based S/S waste matrix is due to the alkaline nature and buffering capacity provided by calcium hydroxide and C–S–H.

3.4.3. The pH of the leachate in the progressive TCLP test

The pH values of the leachate in the progressive TCLP test are plotted in Fig. 4. The pH values at the end of each extraction were much higher than the initial pH (2.88) of the leachant. The alkaline nature of the waste matrix could significantly change the initial pH of the leachant. The pH decreased with the progressive TCLP extraction, showing the decrease of the buffering capacity of the S/S waste matrix after leaching. The differences in pH values of various S/S waste materials at the same TCLP extraction were also significant. The pH decreased with the increasing of PFA content in the samples. This result shows that replacement of OPC by PFA can reduce the alkaline nature and the buffering capacity of the waste materials, which can in turn increase the leachability of heavy metals from the S/S matrix.

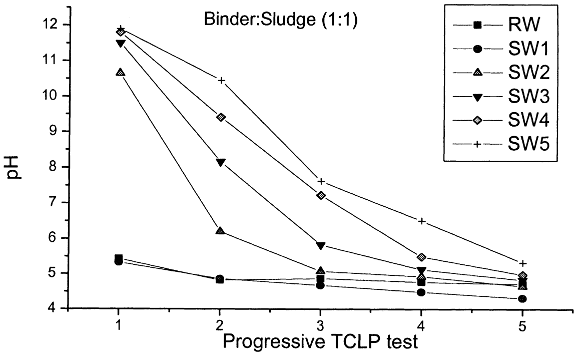

Fig. 4. The pH changes of leachate in the progressive TCLP test.

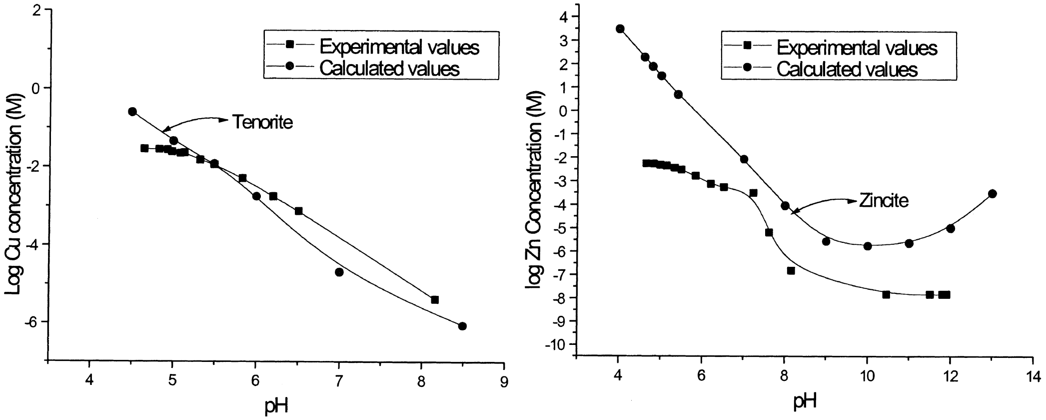

Fig. 5. Laboratory determined copper and zinc concentrations presented as a function of pH (solution equilibrium with 0.1 M HOAC and calculated by MINTEQA2).

3.4.4. The pH dependent and solubility controlled leaching behaviors of Cu, Pb and Zn

A number of studies proved that the leachability of metals in waste materials is controlled by the solubility of metal compounds in the leachate [19]. Mechanisms that limit solubility are complex and have been described by Stumm and Morgan [27]. The study of the dissolution processes of precipitated pure solid phases, such as hydroxides and carbonate under leaching test conditions is the most commonly used method in the leaching behavior assessment.

Based on the results of the sequential extraction, Cu in the S/S waste materials may exist as copper hydrated phase or copper hydroxide precipitated on the surface of C–H and C–S–H particles. Zinc can also form the hydroxide precipitation during cement hydration process. The solubility of copper hydroxide (tenorite) and zinc hydroxide (zincite) were studied in the medium of 0.1 M HOAc of the progressive TCLP test in order to examine the leaching behaviors of these two metals. MINTEQA2 [28] was also used to calculate the solubility of the hydroxides in the leachate at different pH conditions. The calculated equilibrium results with 0.1 M HOAC at 25°C in a closed system are shown in Fig. 5. The experimental values obtained by the progressive TCLP test are also presented for comparison. For Cu, within the experimental pH range (4–9), both the experimental values and theoretical calculated values all decreased gradually with the increasing pH of the leachate. The experimental values were very similar to the predicted lines. This results indicates that copper hydroxide (tenorite) could be the dominant species formed in cement hydration process, which controlled the leaching behavior of Cu in the progressive TCLP test.

Zn leaching in cement systems is more complex. Some investigators [24] postulated that the Zn was fixed by a reaction, forming a metallic calcium silicate hydrate (almost certainly not a stoichiometric form). Others regarded that zinc hydroxide was formed which was encapsulated in the silicate matrix [5,7]. The experimental leaching values of Zn were lower when compared with the predicted values for zincite (ZnO). The chemical forms of Zn in the S/S materials were more complicated than that of pure ZnO, although the leaching behavior was also pH dependent.

4. Conclusions

The sequential chemical extraction results of the S/S waste materials indicated that the chemical speciation of heavy metals was strongly dependent on their chemical behaviors during cement hydration process and the potential binding mechanisms within the cementitious matrix. Different sequential extraction results suggested that Cu and Zn might exist in the S/S matrix as metal hydrated phases or metal hydroxides precipitating on the surface of calcium silicate hydroxide (C–S–H) phase, and PFA particles. The results were also supported by the progressive TCLP tests and MINTEQA2 calculation of Cu and Zn hydroxides.

The leaching behaviors of metals in S/S waste matrix were mainly controlled by the alkaline nature and acid buffering capacity of the S/S matrix. During the leaching process, with the dissolution of calcium hydroxide and C–S–H, the pH value and buffering capacity of the matrix decreased and the leachability of heavy metals in S/S waste materials increased. The leaching of metal contaminants in these S/S materials can be considered as a pH dependent metal hydroxide solubility controlled process.

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