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Journal of Hazardous Materials

Anomalous transient leaching behavior of metals solidified/stabilized by pozzolanic fly ash

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Abstract

This study presents observations on the transient leaching behavior of chromium, cadmium, and aluminum that were solidified/stabilized by pozzolanic fly ash. These three metals were selected since they were present in a simulated waste stream generated by an evaporator during plutonium purification and also because the minimum solubility of these metals occurs at significantly different pHs. The transient pH behavior of the toxicity characteristic leaching procedure (TCLP) leachate showed a monotonic increase for all cases, but the equilibrium value was affected by process conditions. The transient leachate concentration behavior showed curves with one or two local maxima for some cases and curves with a monotonic increase for other cases. Data from the leaching experiments was compared to the solubility curves for the hydroxides of each metal since it was assumed that the highly alkaline conditions inside the fly ash waste would cause the metals to precipitate as hydroxides after initially dissolving in the acidic leaching solution. It was found that of the three metals, only cadmium followed the solubility curve for pure hydroxide solutions or for fly ash systems currently reported in the literature.
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Keywords: Fly ash; Heavy metals; Leaching; Solidification/stabilization

1. Introduction

The use of fly ash as binder material in the solidification/stabilization of hazardous wastes is considered economically prudent since it is also a waste material which is produced in large quantities during coal combustion in thermal power plants [1]. In the solidification/stabilization process, the hazardous waste is combined with fly ash and, via the pozzolanic reaction of the fly ash, transformed into a solid waste form. Solidification involves blending the fly ash with the waste to create a solidified matrix. Stabilization involves chemically altering the waste to reduce the toxicity of hazardous constituents through chemical binding or altering the speciation of the hazardous constituents to less toxic forms [2]. During the process, metals are expected to precipitate as insoluble hydroxides or to combine with the components of the fly ash to form complex silicate forms [2]. To establish the environmental acceptability of the solidified/stabilized waste for land disposal, the U. S. Environmental Protection Agency [3] has developed the toxicity characteristic leaching procedure (TCLP). The test simulates the equilibrium behavior of the waste by contacting the waste with an acidic media and by measuring the concentration of material leached from the waste after 18 h of continuous agitation.

To determine the transient leaching behavior of metals from fly ash solidified/stabilized wastes under the assumption that they are encapsulated as hydroxides, it is necessary to establish a relationship between the pH behavior of the encapsulated waste and the concentration at which the metals would solubilize, both as a function of time. To do that, comparing measured data with existing solubility versus pH diagrams for the metal hydroxides is helpful. In the present study, results are presented on the transient leaching behavior of chromium, cadmium, and aluminum when they are encapsulated in fly ash matrices by applying a solidification/stabilization technology. These metals are important contaminants in the evaporator bottoms residues generated at the Los Alamos National Laboratory and since the pH at which their minimum solubility occurs is significantly different.

A review of available solubility constant data for chromium (III) in equilibrium with chromium hydroxide shows solubil-

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ity based on stability constants for individual species alone or for relative simple combinations [4–6]. Differences in solubility data for chromium hydroxide in pure solutions and in solutions in contact with fly ash were reported by Cote [7]. Cote presented an empirical relationship for the behavior of the metal hydroxide in a fly ash system with different dosages of cement. The relationship expressing the dissolved chromium concentration in g-mol/L was given as:

$$M_{Cr} = 10^{(3.081-2pH)} + 10^{(-5.425)} \tag{1}$$

Cote's solubility diagram shows less dependency on pH than the diagram for the hydroxide in pure solutions. The minimum solubility in Cote's plot of concentration versus pH is constant over a pH range of 4–14 while the minimum solubility for the hydroxide in pure solutions varies considerably, from a pH of 8 to 10 [4] or from a pH of 6 to 12 [6]. Also, the concentration for the minimum solubility is higher in the fly ash system than in pure solutions. In several fly ashes $Cr(OH)^{2+}$ is reported as the dominant aqueous species in equilibrium with chromium hydroxide at a pH range of about 2–6.3 [8]. Rai and Szelmeczka [8] suggested that chromium concentration in fly ashes in a pH range of 3–4.8 may be controlled by the solubility of $(Fe,Cr)(OH)_3$. No definite conclusions regarding the solubility-controlling solid of chromium at pH of 4.8–6.3 were reported since concentrations were near the detection limit. At pH higher than 6.8, solubility limitations due to chromium hydroxide is suggested. Sass and Rai [9] suggested that in materials that are relatively high in iron, such as the case of fly ash, an amorphous solid solution of composition $Cr_xFe_{1-x}(OH)_3$ is the compound most likely to control aqueous Cr(III) concentrations.

Recent studies reported the possibility of formation of a Cr(VI)/Fe(III) hydroxide precipitate under environmental acidic conditions [10]. Rodriguez-Piñedo et al. [11] reported the presence of Cr(VI) in the leaching solution of a solidified/stabilized waste which was previously pretreated to reduce the Cr(VI) present to concentrations much lower than 0.5 ppm. Rodriguez-Piñedo et al. [11] suggested that the increase in the Cr(VI) concentration may be caused by the contribution of this element from the Portland cement used as an additive. Fruchter et al. [12] conducted oxidation-state analysis on leaching solutions of a 1:1 fly ash to water mixtures and reported that the soluble chromium is present as Cr(VI).

Cadmium exists as a very stable hydroxide in pure and other systems only in the (II) oxidation state [4,13]. Differences in solubility data for cadmium in equilibrium with pure cadmium hydroxide and in fly ash systems were reported by Cote [7]. Cote presented an empirical relationship for the behavior of the metal hydroxide in a fly ash system. The relationship expressing the dissolved cadmium concentration in g-mol/L was given as:

$$M_{Cd} = 10^{(3.808-pH-9.52/pH)} + 10^{(-8.06)} + 10^{(pH-20.0)} \tag{2}$$

In this equation, the first term corresponds to a species, not identified by the author, responsible for the limited solubility of cadmium at a pH range of 4–11. The second and the third terms are assumed to correspond to the $Cd(OH)_2$ (aq) and $Cd(OH)_3{}^{-1}$ species, respectively. These two last species are reported as

responsible for the limited solubility of the metal at pH values higher than 11. The pH for the minimum cadmium solubility ranges between 10.5 and 13 for the fly ash system in contrast to the pH range of 11 and 12 for the pure system. Concentration at the minimum solubility is also lower in the fly ash system.

Solubility constant data available for aluminum species in equilibrium with aluminum hydroxide vary considerably [4,13,14]. In fly ash, aluminum has been reported both as oxide and as hydroxide [15]. It has also been suggested that aluminum forms a complex with silica in the fly ash giving aluminium–silicate mixtures [16]. Talbot et al. [16] suggested that although the alumino–silicate phases are primarily responsible for controlling the bulk solution composition, incipient phases such as $Al(OH)_3$ may play an important role in controlling the dissolved concentration of species such as trace metals. Although $Al(OH)_3$ (s) is the most frequently reported species in fly ash systems, amorphous $Al(OH)_3$ has also been found, specially in alkaline fly ash extracts [17]. Roy and Griffin [17] suggested that small amounts of Al^{+3} persisted in the leaching solution as a result of having exhausted the hydrogen ions in the leaching solution that are responsible for the metal hydrolysis. Roy and Griffin [17] also suggested that alumino-silicate phases act as the source of the Al^{+3} that forms the aluminum hydroxide precipitates in the extracts. However, no definite conclusions were drawn in this report since aluminum and silicon exist in other solids in the ash particles in addition to the alumino-silicate phase.

2. Samples and experimental techniques

Fly ash and fly ash solidified/stabilized waste samples were prepared and analyzed to study their solubility behavior during the leaching process. The fly ash used was a ASTM type Class C provided by the Plain Scalante Generation Station from New Mexico. Its composition is presented in Table 1. Formation of the waste samples was based on the simplified formulation of an original radioactive evaporator-bottoms waste provided by Los Alamos National Laboratory [18]. This evaporator bottoms

Table 1
Inductively coupled-plasma atomic emission spectroscopic analysis of fly ash in mg/kg digest of solids

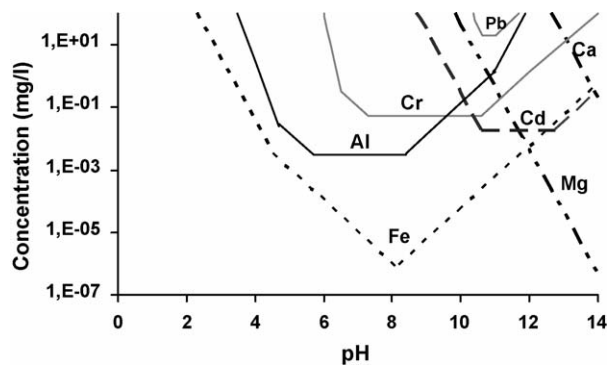| Test parameter	Content	Detection limit
Aluminum	93700	10
Arsenic	3.8	0.3
Barium	4644	1
Cadmium	2	1
Calcium	138400	200
Chromium	26	1
Iron	25400	20
Lead	40	5
Magnesium	18300	10
Mercury	35	20
Total P	3720	1
Selenium	1	1
Silver	Less than	1
Sodium	7480	10
Titanium	1250	5

Fig. 1. Solubility–pH diagram for metals present in the original (all metals) and simplified (chromium, cadmium and aluminum) simulated formulation as obtained from theoretical metals solubility [4,13,14].

waste was produced during the plutonium purification process. The simplified formulation was developed by selecting the three metals of the original formulation whose minimum solubility as a function of pH overlapped the least. The principle contaminants in the original waste formulation were chromium, cadmium, and lead while other metals present in that formulation included aluminum, iron, calcium, and magnesium; all of them at concentrations higher than 10^{-3} mg/L. Aluminum and iron overlap with chromium, cadmium, and lead due to their similar amphoteric characteristics. The hydroxide limited solubility for these five metals is at a pH between 6 and 13 (Fig. 1). Iron (III) is present as a stable hydroxide at almost every pH value and in a broad range of concentrations; therefore, it may be assumed that this metal will not be easily removed under leaching circumstances. Four of the other metals, namely Al(III), Cr(III), Pb(II) and Cd(II), are soluble at relatively higher concentrations than iron, lead being the most soluble, therefore any change of pH would cause them to leach from the waste. Based on these considerations, the metals selected for the simplified waste formulation were chromium, cadmium, and aluminum.

A total of 80 leaching tests were conducted following a mixture design combined with a 2^{6-3} fractional factorial. The mixture design used the concentration of the three metals, expressed in terms of relative mole fractions of these three metals independent of all the other constituents present. Thus, the sum of these three metal mole-fractions equaled one. The six process parameters used as the independent factors for the fractional factorial were strength of acid added to the metal nitrates to form the slurry, pH of the slurry, slurry to fly ash ratio, pressure applied to form the waste matrix, aging effect on the waste matrix, and concentration of metal in the waste. The high and low level of the process parameters are given in Table 2 while a complete, detailed description of the experimental design and procedure is given by Camacho [19].

To prepare each sample, 100 g of nitric acid were combined with the metal nitrates (the ratio of nitrates was dictated by the mixtures design while the total amount of nitrates was dictated by the fractional factorial design). Sodium hydroxide was added slowly with continuous stirring until the desired pH was reached. This slurry was then placed in a conventional mixer and mixed with sufficient fly ash to obtain a 300 g mixture. This mixture

Table 2
Process parameters levels for the fractional factorial design

Process parameter	Low level	High level
Acid strength (M)	1	4
Slurry pH	5	10
Ash:slurry ratio	1:7	1:8
Applied pressure (psi)	600	3000
Aging time (days)	1	28
Acid:waste ratio	19:1	1991:1

was compressed for 5 s to form a 6.35 cm × 12.7 cm × 2.54 cm solidified waste matrix. The solidified matrix was sealed in a plastic bag and allowed to age at room temperature. From the 80 samples, 24 were taken as control samples since the metals contained on them was only the one originally present in the fly ash.

After aging, 94 g of the aged waste sample were pulverized using a mortar and placed into the TCLP extraction vessel. To this sample, 1880 g of acetic acid solution of pH 2.88 ± 0.10 was added. The amount of extraction fluid corresponded to 20 times the weight of the solidified material as specified by the TCLP test [3]. The suspension was tumbled at 30 rpm. Based on previous observations of non-equilibrium conditions after 18 h of leaching [18], the TCLP test was extended to 100 h and run under a semi-batch mode, instead of the standard batch mode, to extract samples for concentration analysis. Four milliliter leachate aliquots were collected every hour at the beginning and then with decreasing frequency until the 100 h had elapsed. The leachate pH was also recorded with the same frequency during the 100 h. Collected aliquots were filtered with TCLP filters of 0.6–0.8 μm and stored at 4 °C for subsequent analysis. Samples were analyzed for chromium, cadmium, and aluminum concentration using inductively coupled-plasma atomic emission spectroscopy.

3. Results and discussion

To understand the transient leaching behavior of these materials, it is necessary to analyze the change in pH of the leachate during the test as well as the changes in concentration of the metals in the leachate. In this section, we initially discuss the evolution of the pH before considering the leaching behavior of the metals.

3.1. Leachate pH

Initial pH of fly ash samples without waste, before addition of the extraction fluid, showed basic characteristics with an average value of 11.3. This value may be attributed to the high content of calcium present in the fly ash (Table 1). After adding the extraction fluid the leachate pH was 4.0. At this point the leaching process began and the pH of the leaching solution increased slowly (Fig. 2). After about 25 h of leaching the pH of the fly ash began to stabilize. After 100 h the leaching solution reached the original pH value of the fly ash (pH 11.3), showing the relatively high neutralization capacity of this material.
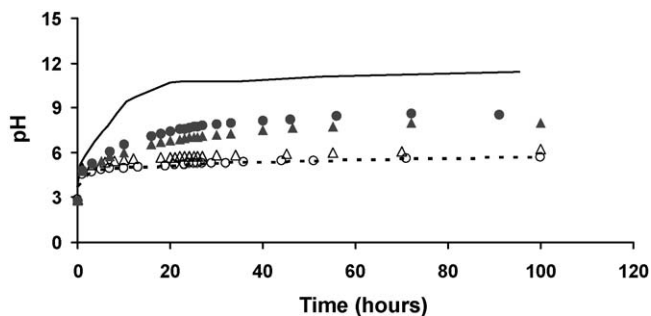
Fig. 2. Illustrative pH of leaching solutions for fly ash-waste samples with simplified formulation tested 1 day (empty markers) and 28 days (filled markers) after stabilization. pH of leaching solutions for fly ash samples with no waste and fly ash-waste samples with original formulation tested after 24 h of stabilization are represented by solid and dotted lines, respectively.

During the first hours of leaching, the fly ash samples mixed with original evaporator-bottoms waste showed pH behavior similar to the fly ash sample in absence of waste. Initial pH was about 11.0 and after addition of the extraction fluid its pH dropped to 4.0. Once the leaching process began, the pH increased and required about 5 h to start to equilibrate. The final leachate pH after 100 h was 5.6 (Fig. 2). This final pH may suggest that most of the alkalinity originally present in the fly ash was used for the formation of calcium silicate hydrates in the presence of water and for the combination of the fly ash components with the metals present in the waste to form chemical complexes or other stable species.

Of the composition and process parameters studied, the only one that significantly affected the final leachate pH of fly ash samples with simulated waste formulation was the aging time. The pH of the leachate from samples with 24 h of stabilization were similar to results from fly ash samples with original waste formulation and, regardless of the concentration of metal or the specific processing conditions, were essentially the same at the end of the test at 5.6. However, the leachate from samples with 28 days of stabilization showed a faster rise in pH as well as a final pH that was higher than the samples that had only 24 h of aging. Furthermore, the leachate from the samples aged for the longer period also showed more variation, ranging from 7.0 to 8.5 (Fig. 2). X-ray diffraction analysis showed that the effect of aging time was related to the formation of calcium silicate hydrates [19]. Since very little variation was observed with respect to the different mixture compositions for all the conditions tested, it might be assumed that the pH behavior of solidified/stabilized wastes is independent of the metal composition. That is not to say that the concentration of the metal was unimportant since this factor was included as one of the process factors (i.e. within the fractional factorial portion of the design) and not part of the simplex-centroid design, which was only concerned with composition.

3.2. Leaching behavior of chromium

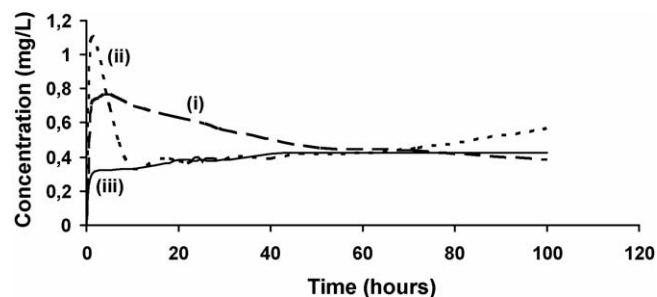Three different behaviors were observed during the 100 h of leaching (Fig. 3):

Fig. 3. Examples of chromium concentration observed during the transient tests in the leachate.

(i) A peak in the first hours of the leaching process followed by a slow decrease until reaching a final concentration of about 0.5 ppm. A 33 of the 40 samples subjected to the test 24 h after solidification showed this behavior. The same behavior was observed by Valles [18] when running a semi-batch TCLP test on solubilized/stabilized fly ash-waste with original formulation.

(ii) A sharp peak which occurred much earlier than for samples with 24 h of stabilization. This behavior was observed for 8 of the 40 samples tested after 28 days of stabilization.

(iii) A monotonic increase in the concentration reaching equilibrium after about 25 h of leaching. This behavior was observed in the remaining seven samples tested after 24 h and in 32 samples of the 40 tested after 28 days of stabilization with a final concentration of about 0.5 ppm.

Chromium was also released from control samples made with fly ash, cadmium and aluminum but no chromium, i.e. chromium mole-fraction equal zero, since chromium was originally present in the fly ash. The final chromium concentration for these samples was also about 0.5 ppm. Neither mixture composition nor process parameter conditions applied during the solidification/stabilization process seem to affect the final solubility behavior of the metal.

In order to determine if the observed concentrations of chromium in the leaching solution could be explained by the theoretical chromium hydroxide curves, the metal concentration of samples with 28 days of stabilization was plotted as a function of pH and compared to theoretical chromium hydroxide solubility diagrams. When compared to Baes and Mesmer's diagrams [4], a significant difference was observed (Fig. 4). Over the pH range of 5–9, our data indicated a relatively constant concentration of chromium regardless of whether the sample showed an asymptotic change as a function of time or a local maximum. In contrast, the data of Baes and Mesmer [4] showed approximately a four-decade decline in concentration over that pH range.

Even with the discrepancies observed in the literature for the chromium solubility data [5,6], our experiments resulted in a higher solubility than that predicted theoretically for the pH range of 7–9. Therefore, the concentration of chromium in the leaching solutions could not be explained based on solubility data for chromium hydroxide when present as individual species. When comparing the observed concentrations with reported
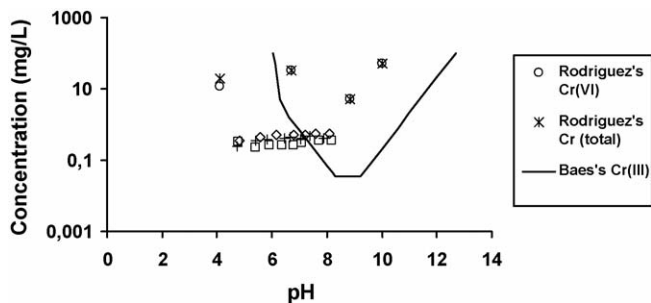
Fig. 4. Examples of experimental chromium solubility as compared to theoretical Cr(III) and Cr(VI) systems [4,11]. The symbols (□, ◊, +) represent data from the current study.

chromium concentrations for a fly ash system [7], it was found that that system behaves more similar to the chromium hydroxide in a pure system [4] than to the observed data. For either systems [7,4], the concentration at the minimum solubility pH is about 10^{-2} to 10^{-1} mg/L, which is lower than the solubility observed in the present case.

Observed chromium concentrations also could not be explained by the chromium (III)–iron (III) hydroxide coprecipitate $(Fe, Cr)(OH)_3$. This compound has been suggested to control the aqueous Cr(III) concentrations when high amounts of iron are present in the fly ash [8], as in the present study. Our data were present in a pH range of about 5–8.6 and showed no pH dependence while the data suggesting the presence of the $(Fe, Cr)(OH)_3$ complex have been identified at a pH range of 3.0–4.8 and decreased approximately two orders of magnitude for each unit increase in pH [8].

Since the ICP analysis method used to measure the chromium concentrations released to the leaching solution measures the metal as total chromium with no differentiation between oxidation states, the possibility that the measured chromium corresponds to the oxidation state of (VI) could not be dismissed. Two possible cases were taken into consideration: (1) the oxidation of chromium (III) through a highly oxidized species present in the solubilized/stabilized waste or (2) the chromium originally present in the fly ash was in that oxidation state. Support for both of these hypotheses is found in the literature [20,10,11]. For the first case, iron (III) could serve as the electron acceptor for the oxidation of chromium (III) since this metal was present in relatively high amounts in the fly ash used to solidify the waste, ca. 34,000 ppm in total digest of solids [19], and it can coexist under these experimental conditions as the trivalent (III) or bivalent (II) hydroxide form. The second case can also be possible since the ICP analysis of the fly ash used reported a total chromium concentration of 26 ppm and the metal was also found in the leaching solution of the samples to which no chromium was added. Neither of the two possible cases could be experimentally confirmed due to lack of sufficient aliquots for redox analysis. However it was found that the trend followed by our data is in relative agreement with Rodriguez-Piñedo et al. [11] data. Rodriguez-Piñedo et al. [11] plotted the Eh–pH experimental data of a fly ash sample with an iron content of 10% by weight in a Pourbaix diagram of chromium, which was developed for a chromium concentration of 1 ppm. At the same time

the authors measured the chromium (VI) and chromium (total) concentration in the extract. Rodriguez-Piñedo et al. [11] concentration data points are included in Fig. 4. From the analysis of the Pourbaix diagram, Rodriguez-Piñedo et al. [11] determined that when the pH is above 6.0, chromium (VI) predominated since no differences existed between Cr (total) and Cr (VI). The content of iron in our fly ash was about 8% by weight [19] with respect to the 10% by weight of Rodriguez-Piñedo's fly ash sample [11] therefore we may conclude that the chromium present in the solidified/stabilized wastes in the pH range of 5.0–8.5 is most likely in the hexavalent form. From Fig. 4 we may also conclude that an increase in the iron content in the fly ash causes an increase in the concentration of Cr (VI) leached.

If the chromium is present as Cr (VI), it is likely that once the solidified/stabilized material is mixed with the acidic TCLP solution, the metal in the hexavalent form moves easily into solution. Once in contact with other species, its concentration is reduced since it combines with those species to form stable complexes [11]. This behavior is in agreement with the peak observed at the beginning of the process (pH range of 5.0–6.0). Other samples not showing a peak may be explained as a more rapid formation of complexes occurring during the first hours of the leaching process.

3.3. Leaching behavior of cadmium

Three different behaviors for the cadmium concentration in the leaching solution as a function of time were observed (Fig. 5):

(i) A maximum in the cadmium concentration after about 10 h of leaching. This behavior was observed for 8 of the 40 samples that had been aged for 24 h and for 14 of the 40 samples that had been aged for 28 days.

(ii) A monotonic increase in the cadmium concentration, which became constant after approximately 10 h of leaching. This behavior was observed in only 11 of the samples that had been aged for 24 h.

(iii) A very low concentration during the entire test, less than 1 mg/L, compared to the concentration of the rest of the samples. This behavior was observed for 9 of the samples aged for 24 h and for 14 of the 40 samples aged for 28 days.
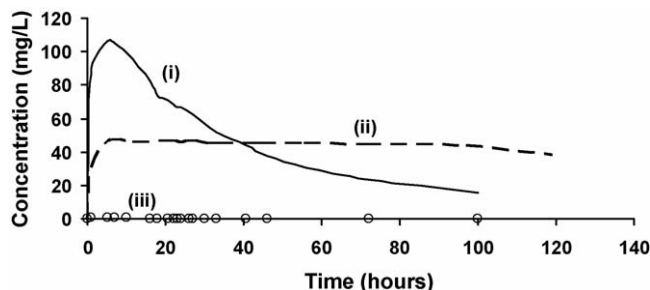

Fig. 5. Examples of cadmium concentration observed during the transient tests in the leachate.

From all the samples, the ones with final low metal concentration were affected only by the process parameter acid to waste ratio and their behavior seemed to be independent of the mixture composition. Contrary to chromium, none of the samples with no addition of cadmium, i.e. cadmium mole-fraction equal zero, but with an original amount of it in the fly ash, leached cadmium during the test.

The concentration of samples tested after 28 days of stabilization was plotted against the measured pH and compared to Lindsay's theoretical cadmium hydroxide solubility diagram [13] to explain the observed concentrations in the leaching solution. It was assumed that the samples tested after 1 day of stabilization haven't completely stabilized yet. Lindsay's curve [13] was selected among the cadmium hydroxide solubility diagrams available in the literature since his data were the most complete. Lindsay's constant values at the ionic strength $I = 1.0$ in general do not vary greatly from others [4,21]. It was observed that depending on the molar fraction of the metal in the waste, the experimental points were located two or more orders of magnitude lower than the Cd^{+2} species, which is the species representing the limiting solubility of cadmium at pH 8.5–10.5 in Lindsay's diagram (Fig. 6a–d). Also, the points did not follow exactly the trend of that curve. By observing other complex species present in the cadmium hydroxide solubility diagram [13], it was found that the $Cd(OH)^{+1}$ species, with a slope of one, could better represent the declining trend of the experimental curves. Fig. 6 clearly shows the displacement of the cadmium curves from the $Cd(OH)^{+1}$ line as a function of the metal mole-fraction (x). As the cadmium mole-fraction reduced, the cadmium was not completely controlled by that species even though the slope was still the same. Since the increase of the chromium or aluminum mole fraction did not show any effect on the cadmium solubility behavior, it may be suggested that cadmium has to compete with the other metals originally present in the fly ash to reach saturation as cadmium hydroxide. The
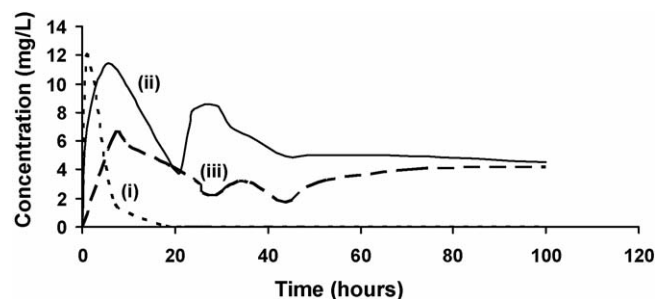

Fig. 7. Examples of aluminum concentration observed during the transient tests in the leachate.

main difference between the sample points that were only a little displaced from the $Cd(OH)^{+1}$ line and those that were far displaced was the initial cadmium concentrations in the fly ash solidified/stabilized brick. The first had an initial cadmium concentration of 50,000 ppm whereas the second had 500 ppm only. This behavior was in agreement with the maximum and the small concentrations observed in the solution as a function of time, respectively. The experimental curve obtained when cadmium was a mole fraction of 0.33 ($x = 0.33$) was in agreement with the non-identified species presented in Cote's empirical diagram for the limited solubility of cadmium in a fly ash system at pH lower than 11 [7] (Fig. 6c). For pH higher than 11, Cote's empirical diagram [7] was in agreement with Lindsay's theoretical solubility diagram [13]. We may conclude that at pH lower than 10.5 the $Cd(OH)^{+1}$ species is responsible for the limiting solubility of cadmium as cadmium hydroxide in the fly ash-waste system.

3.4. Leaching behavior of aluminum

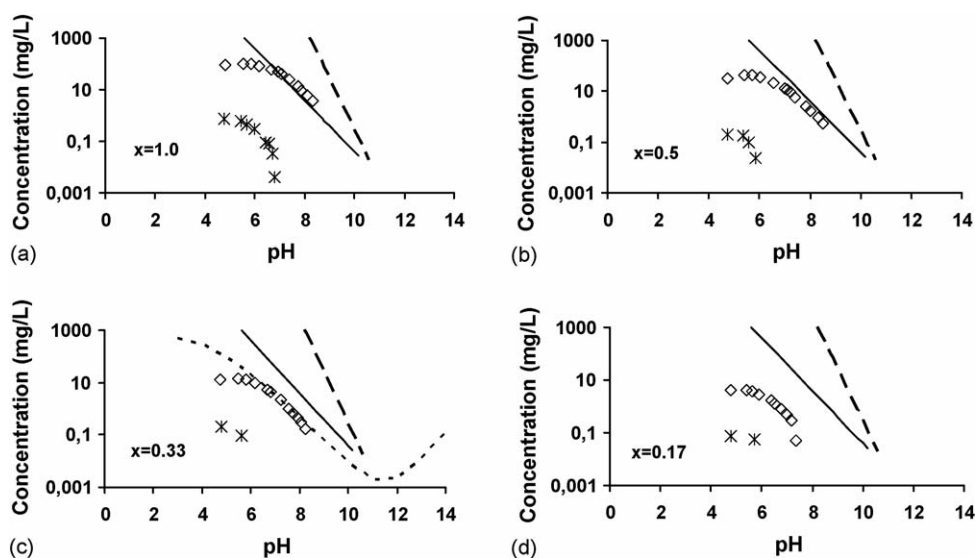The aluminum concentration in the leachate showed three behaviors (Fig. 7).

Fig. 6. Examples of experimental cadmium solubility based on its molar fraction as compared to $Cd(OH)^{+1}$ and Cd^{+2} lines in Lindsay's diagram [13] (solid and spaced lines, respectively), and Cote's empirical diagram [7] (dotted line). The symbols ($\diamond$, $\ast$) represent data from the current study. X: mole fraction of cadmium among chromium, cadmium, and aluminum.
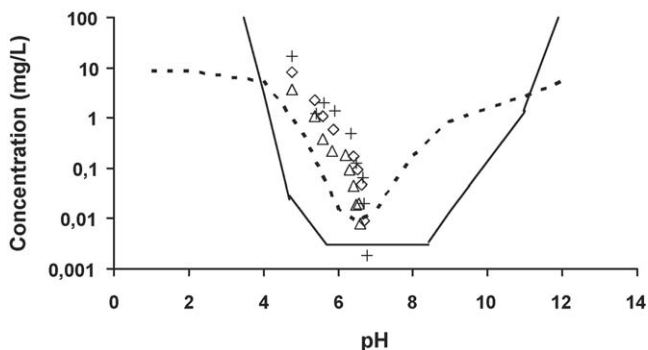
Fig. 8. Examples of experimental aluminum solubility as compared to theoretical solubility of aluminum hydroxide for pure systems (solid line) [13] and fly ash system (dotted line) [16]. The symbols ($\square$, $\lozenge$, +) represent data from the current study.

 (i) A single peak within the first 5 h followed by a rapid decrease to levels below the detection limit.
 (ii) Two peaks, the first occurring after about 10 h and the second (which was slightly lower) after about 25 h with a smooth decrease reaching a final equilibrium value of approximately 5 mg/L.
(iii) Two peaks, both of them lower than in the second trend, the first occurring after about 10 h of leaching and the second after about 30 h and followed by an asymptotic increase until reaching a final concentration of 5 m/L.

The single peak behavior was seen in all 40 samples aged for 28 days and in five of the samples aged for 24 h. The double peak behavior with smooth decrease was seen in 25 of the samples aged for 24 h, with the sharpness and magnitude of the peaks being dependent on the concentration of aluminum in the waste as well as the stabilization/solidification process conditions. The double peak behavior with asymptotic increase was observed in 10 of the samples aged for 24 h. Control samples for which there was no aluminum added to the waste, i.e. aluminum mole-fraction equal zero, but with an initial amount of aluminum in the fly ash also showed the single and the double peak behavior as the aluminum initially present in the fly ash was leached. The two last trends reflect instabilities of the aluminum behavior due to a short leaching period.

A plot of the experimental concentration data for 28 days of aging versus pH was performed to see if the observed aluminum behavior was consistent with the theoretical solubility of the metal as aluminum hydroxide, $Al(OH)_3$ (Fig. 8). In this case Lindsay's data [13] were also selected as the most reliable among the different diagrams reported in the literature [4,21,14]. Results showed solubility several orders of magnitude higher than the maximum solubility reported by Lindsay, which suggest that aluminum does not behave as aluminum hydroxide when it is encapsulated in fly ash solidified/stabilized wastes. However, the observed behavior was similar to that reported by Talbot et al. [16]. Based on the formation of aluminium–silica complexes suggested by Talbot, it might be assumed that aluminum in the present study combines with the silica of the fly ash to form such aluminium–silicate mixtures instead of precipitating as aluminum hydroxide. However, more studies will be

required in order to be able to draw definite conclusions about the behavior of aluminum in the leaching process.

4. Summary

In this paper, results obtained from the analysis of transient metal leaching behavior of a waste solidified/stabilized using pozzolanic fly ash were presented. The toxicity characteristic leaching procedure test was applied under semi-batch conditions during 100 h of leaching to analyze non-equilibrium behaviors. The transient pH data all exhibited a monotonic increase in pH from an initial value of approximately 3 to an equilibrium value. The final equilibrium value was dependent on the aging time; samples aged for 24 h had an equilibrium pH of approximately 6.0 while samples aged for 28 days had an equilibrium value between 7.0 and 8.0. The transient leachate concentrations of the three metals studied (chromium, cadmium, and aluminum) showed five distinct trends: (1) a monotonic increase to an equilibrium value, (2) an initial peak followed by a decrease to an equilibrium value, (3) an initial peak followed by a decrease to a value below the detection limit, (4) twin peaks followed by a decrease to an equilibrium value, and (5) twin peaks followed by an asymptotic increase to an equilibrium value. The first two trends were seen in both the chromium and cadmium data while the last three were seen in the aluminum data. From all the concentrations measured, only the final chromium concentration was not affected by the process parameter conditions applied during the solidification/stabilization process.

Analysis of the experimental leachate data showed that the solubility behavior of chromium, cadmium, and aluminum could not be explained by the saturated solubility of their hydroxides. Chromium solubility may also not be controlled by a $Fe,Cr(OH)_3$ complex species even though high iron amounts were present in the fly ash used. Behavior of that metal seemed to be best represented by the solubility of Cr(VI) species. This implies that reprecipitation of the metal can not be expected in real environmental conditions since Cr(VI) remains soluble over a broad range of pH concentrations. The behavior of the cadmium samples showed the most variations with respect to leachate concentration as a function of pH, but there may have been insufficient cadmium in the samples for the leachate to become saturated and the results may reflect an equilibrium situation between stabilized cadmium and solubilized $Cd(OH)^{+1}$. Cadmium solubility behavior was mostly affected by its metal mole fraction in the waste. The same did not occur with the other two metals. Solubility of aluminum was several orders of magnitude higher than the solubility reported by Lindsay [13]. Its behavior in the leachate showed a four order-of-magnitude decrease over the pH range of 5.0–7.0 which was similar to data reported by Talbot et al. [16] even though Talbot's decrease occurred over the pH range of 4.0–6.0. Further study to explain the observed aluminum behavior is required.

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