

Comparison between Acetic Acid and Landfill Leachates for the Leaching of Pb(II), Cd(II), As(V), and Cr(VI) from Cementitious Wastes

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The Toxicity Characteristic Leaching Procedure (TCLP) has been widely used to characterize the suitability of solid wastes for disposal in landfills. However, the widespread application of this test for the assessment of wastes disposed in different landfill types is often questionable. This paper investigates the leaching profiles of cement-stabilized heavy metal ions, namely, Pb (II), Cd (II), As(V), and Cr(VI), using acetic acid and leachates from municipal and nonputrescible Australian landfill sites. The leaching profiles of Pb, Cd, As, and Cr using acetic acid were found to be similar to the nonputrescible landfill leachate and differed markedly from the municipal solid waste (MSW) leachate. The additional presence of high amounts of organic and inorganic compounds in the municipal landfill leachate influenced the leaching profiles of these metal ions as compared to the acetic acid and the nonputrescible systems. It is postulated that the organic compounds present in the municipal landfill leachate formed complexes with the Pb and Cd, increasing the mobility of these ions. Moreover, the organic compounds in the municipal landfill leachate induced a reducing environment in the leachate, causing the reduction of Cr(VI) to Cr(III). It was also found that the presence of carbonates in the municipal landfill leachate affected the stability of calcium arsenate, with the carbonate competing with arsenate for calcium at high pH, forcing arsenate into the solution.

Introduction

The long-term impacts of landfill leachates have increasingly raised public concerns. Many leaching tests have been developed to characterize the hazards of industrial wastes prior to their disposal to reduce contaminant release. Failure to pass these leaching tests usually requires solidification and/or stabilization of the wastes. In Australia, Australian Standards AS 4439.1-1997, AS 4439.2-1997, and AS 4439.3-1997 (1-3) or the Toxicity Characteristic Leaching Procedure (TCLP) are used to assess the hazardous nature of wastes.

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The development of the Australian Standards was based on the TCLP, which was designed by the United States Environmental Protection Agency (4), with a difference in the leaching fluid and the particle size reduction. The TCLP was intended to simulate the worst case scenario for codisposal of waste with municipal solid waste (MSW). Acetic acid (pH 2.88) and acetate buffer (pH 4.92) leaching fluids are used to simulate the presence of organic materials present in the municipal landfill leachate. Water and sodium tetraborate buffer are used in the AS 4439.3-1997 for wastes disposed on a site without any confinement and for nonputrescible materials, respectively. Because of the dependence of the TCLP on a single leaching result, it has been scrutinized due to its broad application in evaluating and regulating waste, including wastes codisposed with MSW and wastes disposed in a monofill (5, 6). The choice of leaching fluids used in the TCLP has received criticism. Both leaching fluids have an acidic pH, which is lower than the typical pH of MSW leachates in their mature stage (between 6 and 8.5). The aggressive leaching fluid used in the TCLP might overestimate the leaching of contaminants from wastes that are not codisposed with MSW wastes (7).

The TCLP has also been found to incorrectly classify highly alkaline wastes such as cementitious wastes (7, 8). In a previous publication (8), the high alkalinity of cement was found to rapidly neutralize the acidity of the leaching fluid, commonly resulting in a final leachate pH higher than 12. While this earlier work did not consider landfill leachates, such high pH values are seldom encountered in MSW landfills. In this work, it was found that the final pH controls the leachability of Pb and Cd. Hooper et al. (9) found the TCLP to underestimate the leaching of Sb, As, Mo, Se, and V as oxyanions when compared to MSW leachate. They proposed that this was due to complexation of the elements with organic materials in the MSW leachate. Similarly, Cecen and Gursoy (10) found strong complexation of cadmium and nickel with organic ligands in MSW leachate.

The use of the TCLP for the classification of wastes that are not codisposed with MSW, such as mineral processing wastes, has also been challenged. Legal proceedings have been undertaken against the U.S. EPA for its inadequate justification of waste classification by the TCLP (11). The acetic acid used in the TCLP has been claimed to overestimate contaminant leaching from mineral processing wastes as these wastes do not experience acidic conditions. Nonputrescible landfills can produce leachate with an alkaline pH, depending on the type of waste disposed in the landfill. For example, bottom ash landfills have leachate pH values ranging between 8 and 11 (12). Hence, the use of the TCLP for predicting the leaching in such environments can result in misclassification of these wastes, potentially resulting in unnecessary treatment.

The aims of this paper are to investigate and compare the leaching of the metal ions Pb, Cd, As, and Cr from cementitious wastes using the TCLP leaching fluid (acetic acid) and landfill leachates from a MSW landfill and a nonputrescible landfill. The results will be used to assess the applicability of the TCLP leaching fluid for examining the hazards of cementitious wastes.

Experimental Section

Preparation of Cementitious Wastes. Metal salts (lead nitrate (Pb(NO₃)₂), cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O), sodium arsenate (Na₂HAsO₄·7H₂O), and sodium chromate (Na₂CrO₄) were mechanically mixed with approximately 0.5 L of water and blended with approximately 4 kg of Ordinary

Portland Cement (OPC). Additional water was added until the paste reached similar consistency with the resulting mixture cured for 28 days. The water-to-cement ratios used during blending were 0.38, 0.44, 0.38, and 0.31 for Pb, Cd, As, and Cr, respectively. The cured cementitious wastes were sequentially crushed using a jaw crusher, cone crusher, and roller crusher and passed through a 2.4 mm mesh sieve according to the Bottle Leaching Procedure of the Australian Standard AS 4439.3-1997 (3). The particle size differed slightly to that described in the TCLP (9.5 mm). The concentrations of Pb, Cd, As, and Cr were determined by Phillips PW2400 X-ray fluorescence (XRF) spectrometer to be 23, 13, 13, and 20 mg/g of waste. These concentrations were chosen such that they gave detectable concentrations during the leaching process and were within the levels used in the literature (13–15). The wastes also contained 340 mg/g Ca and approximately 74 mg/g Si.

Landfill Leachate Collection. Landfill leachates were collected from two landfills, both of which have operated for almost 20 years. The MSW landfill (ML) accommodated both putrescible and nonputrescible wastes, including household chemicals, health care facility wastes, asbestos, dusty wastes, and untreated timber and garden organics. The leachate was collected from pipes leading to a leachate pond in the landfill. Leachate from all areas of this landfill was directed to the same leaching pond for discharge or treatment. The nonputrescible landfill leachate (NP) was collected from a well leading to an underground leachate pipe using a bailer. This landfill received nonputrescible wastes such as construction and demolition wastes, wood, and industrial waste. Approximately 160 L of ML leachate and 140 L of NP leachate were collected and stored in 20 L plastic drums with no headspace at 4 °C to minimize bacterial activity. Four liters of leachate was taken from each drum for constituent analysis.

Elemental concentrations of the landfill leachates were determined by an Optima 3000 inductively coupled plasma-atomic emission spectroscope (ICP-AES) after digestion with nitric acid, hydrochloric acid, and hydrogen peroxide. Anion concentrations were determined using ion chromatography as described by U.S. EPA method 0300.0.600/4 79-020 and the *Standard Methods for the Examination of Water and Wastewater* method 4110 (16). Total organic carbon (TOC) and total inorganic carbon (TIC) were analyzed using an ANATOC Series II TOC analyzer. The initial pH of these samples was reduced to 3.5 to measure TIC followed by irradiation of solution (photocatalysis) to measure TOC. The pH, conductivity, BOD, COD, and total suspended solids were analyzed using methods described in the *Standard Methods for the Examination of Water and Wastewater* (16). The organic scan, which screens semivolatile organic compounds, was performed on a Varian-Chrompack Saturn 2000 Gas Chromatograph/Mass Spectrometer (GC/MS) based on U.S. EPA method 8270 (17) with extraction procedures based on U.S. EPA methods 3510 (18) and 3550 (19). The compositions of the leachates in each drum were averaged, and the standard deviations determined with the overall results shown in Table 1 and a summary of the organic compositions described in Table 2 are shown. The organic scan results describe only a portion of the total organic composition of the ML and NP leachates. For instance, the dark color of the landfill leachates implies the presence of humic and fulvic acids which, while not directed analyzed, are accounted for in the total organic carbon values shown in Table 1. It can be seen from Table 1 that the ML composition was comparable to the range of constituent levels in the literature.

Leaching Experiments. Batch leaching experiments were conducted according to Australian Standard AS 4439.3-1997 (3). Investigating the effect of leaching duration involved mixing 80 g of crushed cementitious waste (<2.4 mm) with 1600 g of leaching fluid in high-density polyethylene (HDPE)

TABLE 1. Compositions of the Landfill Leachates as Compared to Literature Values^a

leachate characteristics	municipal landfill leachate (ML)	nonputrescible waste leachate (NP)	literature values (38–42)
pH (–)	7.8 ± 0.1	7.4 ± 0.4	1.5–9.5
BOD5	840 ± 230	50 ± 2	6.8–57000
COD	3850 ± 13	930 ± 30	140–152000
conductivity (μS/cm)	24000 ± 3500	33000 ± 0	470–72500
total inorganic carbon	1900 ± 700	295 ± 20	
total organic carbon	500 ± 300	185 ± 10	30–29000
total suspended solids	79 ± 29	110 ± 30	26–605
aluminum	0.9 ± 0	<0.5	
arsenic	<0.2	<0.2	0–70.2
barium	0.2 ± 0.0	3.8 ± 0.0	0–22.5
cadmium	<0.1	<0.1	0–1.16
calcium	92 ± 25	180 ± 3	5–7200
chloride	2900 ± 410	N/A ^b	40–11375
chromium	0.3 ± 0.1	<0.1	0–22.5
cobalt	<0.1	<0.1	
copper	<0.2	<0.2	0–10
iron	14 ± 1	22 ± 1	0–42000
lead	<0.2	<0.2	0–14.2
magnesium	120 ± 5	N/A	30–15000
manganese	0.3 ± 0.0	0.4 ± 0.0	0–1400
molybdenum	<0.05	<0.05	
nickel	0.2 ± 0	<0.1	0–13
phosphate	16 ± 4	<3	0.01–154
potassium	1400 ± 300	N/A	0.16–3700
selenium	<0.2	<0.2	0–1.85
sodium	1700 ± 300	N/A	0–8000
sulfate	32 ± 33	5.4 ± 2.0	0–7750
titanium	0.1 ± 0.03	<0.05	
vanadium	0.06 ± 0	<0.05	
zinc	1.2 ± 0.2	0.8 ± 0.1	0–1000

^a All values are in mg/L except where indicated. ^b N/A = not available.

TABLE 2. Organic Compositions of Landfill Leachates Obtained from Organic Scan using GC/MS^a

organic characteristics	municipal landfill (ML) leachate	nonputrescible (NP) landfill leachate
alcohols/phenols	3200 ± 500	110 ± 20
alkyl ketones		69 ± 24
acids	2300 ± 1000	2 ± 2
benzenes and toluenes	260 ± 200	
amides	1700 ± 2500	22 ± 2
phthalates	1100 ± 300	57 ± 9
others	1100 ± 400	

^a All values are in μg/L.

bottles. The bottles were tumbled at a speed of 30 rpm for 7 days with ten 10 mL samples taken at different time intervals using a syringe. The 0 h measurement corresponded to brief agitation (~5 s of shaking of the slurry). Liquid to solid (L/S) ratios of 10, 20, 40, and 60 were investigated whereby the slurry was tumbled for 18 h at a speed of 30 rpm. All samples were filtered through a 0.8 micron membrane filter (in accordance with AS 4439.3-1997) prior to analysis.

The leaching fluids used included 0.1 M acetic acid (as described in the TCLP and AS 4439.3-1997) and the ML and NP leachates. Clarification of the effect of carbonate ions on the leaching of As involved tumbling the waste for 2.5 min with 0.1 M acetic acid until the leachate pH reached 7. A 0.05, 0.1, or 0.2 M sodium carbonate solution was then added to the waste. This procedure was adapted to avoid the conversion of the carbonate into carbon dioxide under acidic pH conditions. Samples were taken for analysis at the same time intervals as mentioned earlier.

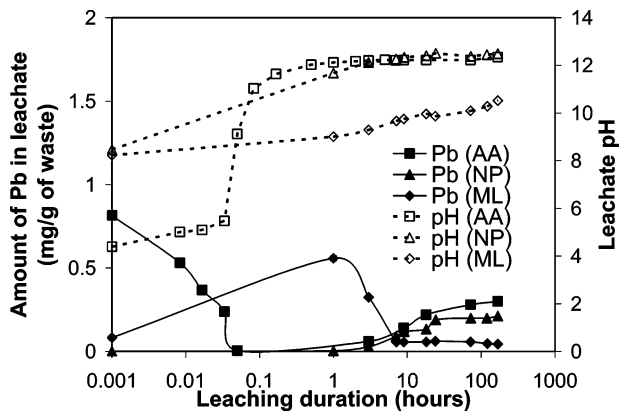


FIGURE 1. Amount of Pb as a function of leaching duration. Cementitious waste containing 23 mg of Pb/g of waste was tumbled with 0.1 M acetic acid (AA), nonputrescible landfill leachate (NP), and municipal landfill leachate (ML) at a liquid-to-solid ratio of 20:1 for up to 18 h.

The filtered samples, where acetic acid was the leaching fluid, were preserved with 2% HNO₃ while the filtered samples of the landfill leachates were stored at 4 °C prior to heavy metal analysis by ICP–AES. Lower detection limits for Pb, Cd, As, and Cr were 0.1 mg/L, corresponding to 0.002 mg/g of waste. All leaching experiments were performed in duplicate. The relative percentage of difference between the duplicates was approximately 10%. A single analytical measurement was performed for every sample.

Arsenic and Chromium Reduction. Arsenic speciation involved the determination of the oxidation state of As in the ML leachate taken after 7 days of leaching using ion chromatography in conjunction with an inductively coupled plasma mass spectrometer (IC–ICPMS) (20).

Studies on chromium reduction during leaching involved analysis of Cr in both the solid and the leachate, following extraction. X-ray absorption spectroscopy (XAS) with a bending magnet beamline, 20B, Si (111) channel-cut monochromator, and a storage ring delivering 250–400 mA current at 2.5 GeV was used for leachate analysis. Three leachant conditions were investigated: ML leachate, NP leachate, and NP leachate acidified to pH 8.5 by HNO₃ following tumbling. All samples were tumbled at 30 rpm for 2 h at a L/S ratio of 20:1. X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG ESCA LAB 220 I-XL instrument with a photon source of Al K α for determining the Cr phase present in the solid sample after leaching with ML leachate.

As a comparison, the potential for 0.1 M acetic acid to reduce Cr(VI) was studied. The Cr(VI)-contaminated waste was tumbled under the same conditions described previously and then acidified by HNO₃ to a pH of approximately 9. Cr(VI) in the leachate was determined using a Cary 400 Varian UV–vis spectrometer and the colorimetric method described in the *Standard Methods for the Examination of Water and Wastewater* method 3500 (16), while total Cr content in the leachate was determined by ICP–AES.

Results and Discussion

Leaching of Pb and Cd. Figures 1 and 2 show the amounts of Pb and Cd, respectively, in the leachate as a function of leaching duration. The figures show that the pH profiles of the acetic acid and the NP leachates rapidly increase to 12, due to the alkalinity release by cement. However, the pH of the ML leachate increased only to 10. The observed difference is due to the types of organics and nutrients present in the ML leachate, which buffer the leachate pH, as suggested in several studies (21, 22). The ML leachate contained ap-

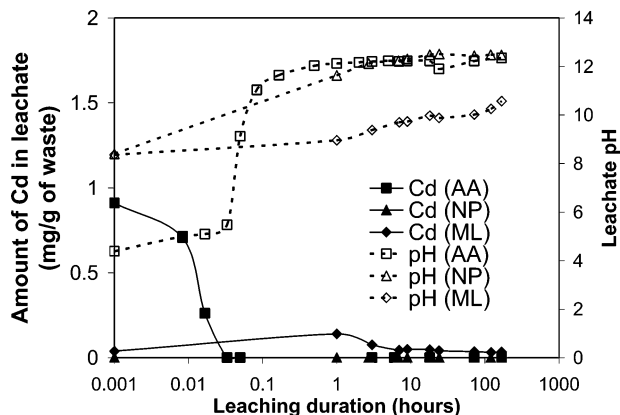


FIGURE 2. Amount of Cd as a function of leaching duration. Cementitious waste containing 13 mg of Cd/g of waste was tumbled with 0.1 M acetic acid (AA), nonputrescible landfill leachate (NP), and municipal landfill leachate (ML) at a liquid-to-solid ratio of 20:1 for up to 18 h.

proximately 500 mg/L total organic carbon (Table 1) as compared to 200 mg/L in the NP leachate. Despite the 0.1 M acetic acid leachant exhibiting the highest concentration (6000 mg/L), it is apparent that the various organics present in the ML leachate impart a higher buffering capacity as compared to the acetic acid, but it should be noted that this was only done using one leachate sample, and further studies need to be done to achieve a generic conclusion.

Pb and Cd release by the acetic acid may be dominated by the effect of pH on the solubility of their hydroxide and silicate species, as described elsewhere (8). Similarly, the Pb and Cd profiles of the NP leachate were governed by pH, with the amphoteric nature of Pb (23) leading to its presence under alkaline conditions (Figure 1). However, the elevated release of both Pb and Cd particularly at the initial stages of the leaching using the ML leachate is believed to be due to the complexation of these heavy metals with organic constituents of the ML leachate. Pb and Cd complexation with organic matter in landfill leachate has been widely reported (24–26). The subsequent decrease in the concentrations of Pb and Cd after 1 h of leaching is thought to be due to the tendency of many of the formed complexes to convert to thermodynamically more favorable precipitates, such as hydroxide, sulfide, or possibly silicate (27). Similar findings were reported by Pagenkopf and Whitworth (28), who found that metals that form stable complexes would preferentially precipitate, and Christensen et al. (24), who found that 5% of the soluble Cd formed stable organic complexes in landfill leachate, while 95% of Cd was labile and could form a precipitate.

The effects of variations in the liquid to solid (L/S) ratio on the release of Pb (Figure 3) and Cd (Figure 4) by the acetic acid and NP leachates were found to be dominated by the impact of pH on precipitate formation (8). The observed decrease in Pb concentration with an increasing L/S ratio stems from the alkaline conditions and its amphoteric nature. That is, the increased acid volume promotes a decrease in the pH of the leachate to a region where the Pb is less soluble. The effect of the L/S ratio on the Pb and Cd profiles was markedly different from the ML leachate in which the observed increase was a direct result of the higher loadings of potential organic complexing agents introduced by the higher L/S ratios.

Leaching of As(V). The leaching of As as a function of leaching duration is presented in Figure 5. Arsenic was seen to decrease to undetectable levels within the first hour for

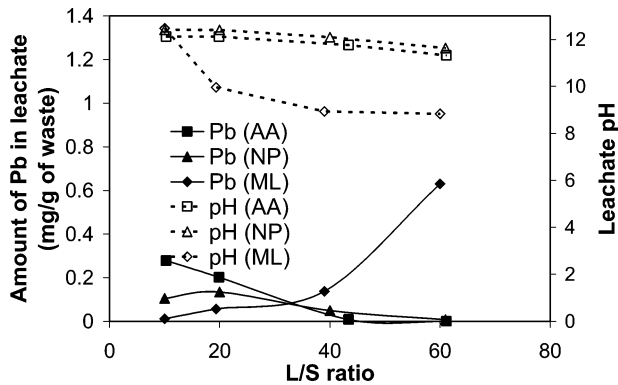


FIGURE 3. Amount of Pb as a function of liquid-to-solid ratio. Cementitious waste containing 23 mg of Pb/g of waste was tumbled with 0.1 M acetic acid (AA), municipal landfill leachate (ML), and nonputrescible landfill leachate (NP) for 18 h.

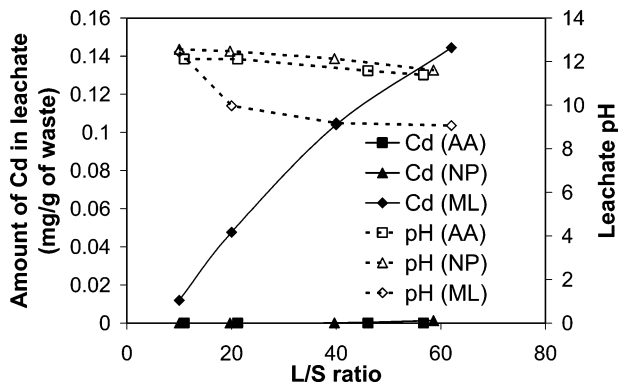


FIGURE 4. Amount of Cd as a function of liquid-to-solid ratio. Cementitious waste containing 13 mg of Cd/g of waste was tumbled with 0.1 M acetic acid (AA), municipal landfill leachate (ML), and nonputrescible landfill leachate (NP) for 18 h.

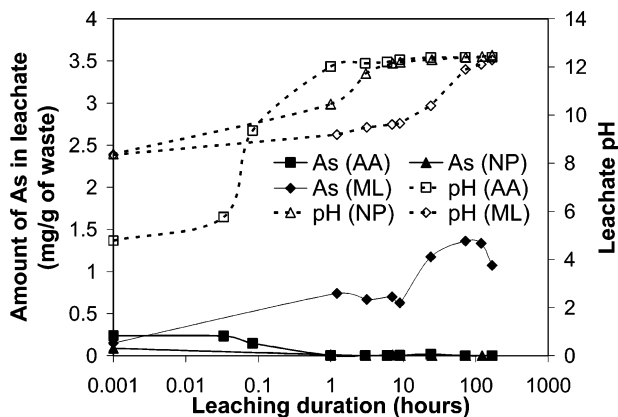


FIGURE 5. Amount of As as a function of leaching duration. Cementitious waste containing 13 mg of As/g of waste was tumbled with 0.1 M acetic acid (AA), nonputrescible landfill leachate (NP), and municipal landfill leachate (ML) at a liquid-to-solid ratio of 20:1.

the AA and NP leachants. It is postulated that this decrease is due to the coprecipitation of As with Ca released from the cement matrix to form of calcium arsenate $\text{Ca}_3(\text{AsO}_4)_2$. Calcium arsenate precipitates at a pH greater than 7 ($\log K_{sp}$ of $\text{Ca}_3(\text{AsO}_4)_2$ is -18.9 (29)). Alternatively, the As profile for the ML leachate increased to approximately 1.4 mg/g of waste over the 70 h. Analysis of the leachate revealed that most As (>99%) existed as As(V). It is postulated that the elevated levels of inorganic carbon in the ML leachate (Table 1) are responsible for the increased As leaching as the carbonates compete with the As to form calcium precipitates.

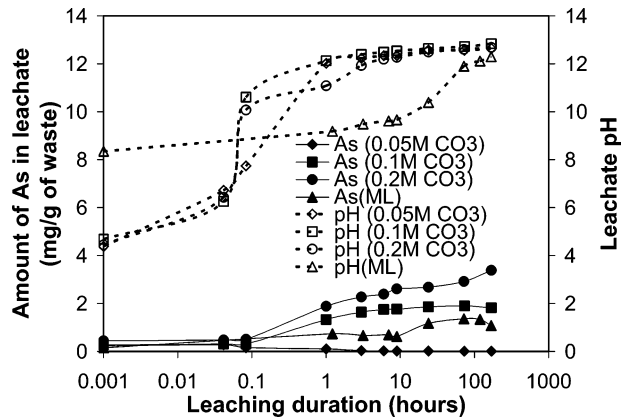


FIGURE 6. Amount of As in leachate as a function of leaching duration. The waste used was cement containing 13 mg of As/g of waste. The leaching fluids used were 0.1 M acetic acid solutions that were mixed with 0.05 M (0.05 M CO_3), 0.1 M (0.1 M CO_3), and 0.2 M (0.2 M CO_3) sodium carbonate and municipal landfill leachate (ML). The waste and leaching fluid was tumbled for 7 days at 30 rpm at an L/S ratio of 20:1.

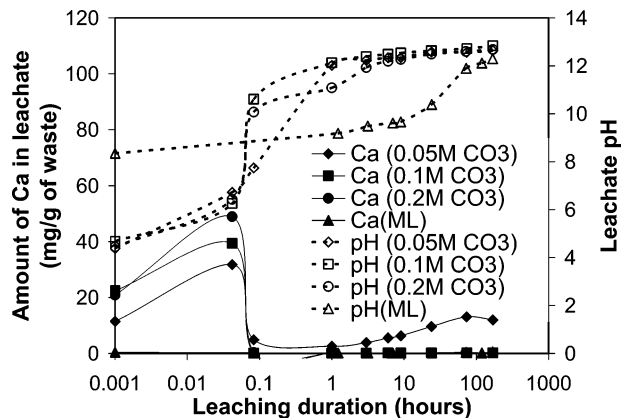


FIGURE 7. Amount of Ca in leachate as a function of leaching duration. The waste used was cement containing 13 mg of As/g of waste and 340 mg of Ca/g of waste. The leaching fluids used were 0.1 M acetic acid solutions that were mixed with 0.05 M (0.05 M CO_3), 0.1 M (0.1 M CO_3), and 0.2 M (0.2 M CO_3) sodium carbonate and municipal landfill leachate (ML). The waste and leaching fluid was tumbled for 7 days at 30 rpm at an L/S ratio of 20:1.

The addition of carbonate ions to the acetic acid leachate increased the extent of As release from cementitious waste (Figure 6), which is coincident to a decrease in the release of calcium into the leachate (Figure 7). The average concentration of total inorganic carbon in the ML leachate corresponded to 0.16 ± 0.06 M. Figure 6 shows that the As concentration released to the ML leachate lies within the As concentrations obtained for the 0.05 and 0.1 M carbonate leachates. These results provide strong evidence to support the competitive precipitation between calcium carbonate and calcium arsenate.

The concentrations of As as a function of the L/S ratio are given in Figure 8 with the ML leachate providing a greater extent of As leaching as compared to the AA and NP leaching fluids. The increase in the L/S ratio of the ML system led to a higher availability of carbonate for precipitation with calcium and hence a greater soluble As concentration. A similar effect was observed for the NP leachate however the lower carbonate concentration resulted in As release only occurring at a higher L/S ratio.

The As leaching results for the cementitious waste is in agreement with findings by Hooper et al. (9), who showed that the TCLP (using 0.1 M acetic acid) underestimated the

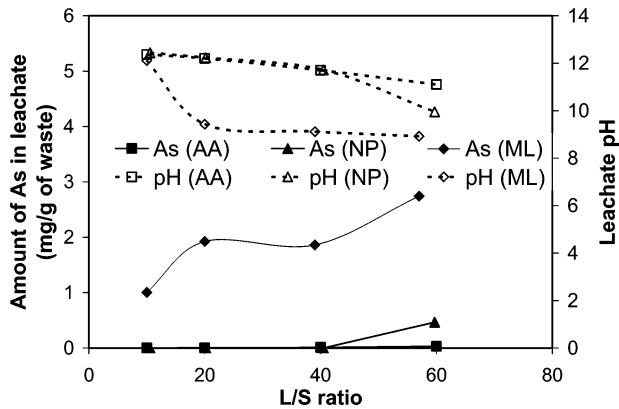


FIGURE 8. Amount of As as a function of liquid-to-solid ratio. Cementitious waste containing 13 mg of As/g of waste was tumbled with 0.1 M acetic acid (AA), municipal landfill leachate (ML), and nonputrescible landfill leachate (NP) for 18 h.

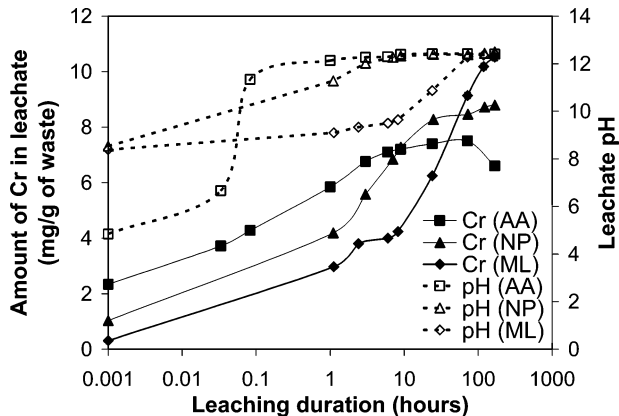


FIGURE 9. Amount of Cr as a function of leaching duration. Cementitious waste containing 20 mg of Cr/g of waste was tumbled with 0.1 M acetic acid (AA), nonputrescible landfill leachate (NP), and municipal landfill leachate (ML) at a liquid-to-solid ratio of 20:1.

leaching of elements that form oxyanions, such as arsenate, in neutral and slightly alkaline conditions when compared to leaching by a municipal landfill leachate. However, Hooper et al. (9) suggested that the formation of organic complexes was the primary reason behind the elevated arsenic levels. Our studies have indicated that the inorganic carbon plays a significant role in the leaching of As.

Leaching of Cr. The Cr profiles in Figure 9 indicate that cement stabilization is a poor method for stabilizing Cr(VI), as approximately 50% of the Cr was leached out from the cementitious waste after 7 days of leaching. A comparison of the AA and NP results indicates that while the pH profiles were similar, the amount of Cr leached out by NP was slightly greater. For both leaching fluids, Cr was present as CrO_4^{2-} , as indicated by a yellow coloring of the leachate. However, the leaching profile of Cr in the presence of ML differed as compared to AA and NP in that the Cr leaching in the ML leachate was significantly lower for the first 60 h of tumbling. Beyond this, the Cr concentration in the leachate increased to a level higher than the other two leachates.

It is apparent the extent of chromium release is a function of the buffering capacity of the leachate. A greater buffering capacity increases cement matrix destruction and subsequently Cr release. Similar effects have been observed in earlier work (8, 30). It is thought that the lower Cr concentration in the ML leachate over the first 60 h is due to the reduction of Cr(VI) to Cr(III) and subsequent precipitation as $\text{Cr}(\text{OH})_3$. Chromium reduction is known to be facilitated

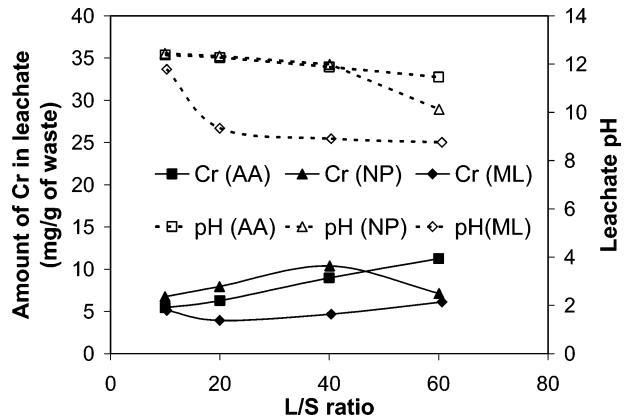


FIGURE 10. Amount of Cr as a function of liquid-to-solid ratio. Cementitious waste containing 20 mg of Cr/g of waste was tumbled with 0.1 M acetic acid (AA), municipal landfill leachate (ML), and nonputrescible landfill leachate (NP) for 18 h.

TABLE 3. Comparison of TC Threshold Values and Concentrations of Metals Obtained after Tumbling Cementitious Wastes Containing 23 mg of Pb/g of Waste and 13 mg of Cd/g of Waste with 0.1 M Acetic Acid (AA), Nonputrescible Waste Landfill Leachate (NP), and Municipal Landfill Leachate (ML) at an L/S Ratio of 20:1 for 18 h^a

metals	metal concentration (mg/g of waste)			
	TC threshold	AA	NP	ML
Pb	0.1	0.20	0.13	0.06
Cd	0.02	<0.002	<0.002	0.05
As	0.1	0.004	<0.002	1.9
Cr	0.1	6.3	3.9	6.6

^a TC threshold values for Pb, As, and Cr are 5 mg/L, while that of Cd is 1 mg/L (37).

by pH, organic matter, and microbial activity as well as other species such as sulfides (31–36). Cr(VI) was found to undergo 24% reduction in the ML leachate (pH 9.3) and 10% reduction in the NP leachate (pH 12.2). A decrease in pH of the NP leachate to 8.5 increased the extent of Cr(VI) reduction to 23%. Evidence of CrOOH was also found in the precipitated solid extracted from the ML leachate. No reduction was observed in an acetic acid leachate at pH 8.8, indicating more than one factor is associated with the reduction process.

The L/S ratio (Figure 10) influenced the release and reduction of Cr(VI) through variations in the leachate pH and loadings of reducing species. A decrease in pH with increasing L/S ratio increases damage to the cement matrix but also provides for greater Cr(VI) reduction. Higher L/S ratios of the ML and NP leachates lead to an increase Cr(VI) reduction by introducing greater levels of reducing agents and microbial activity.

Applicability of AS 4439.3-1997 on the Leaching of Metals in Landfill Leachates. Table 3 compares the heavy metal (Pb, Cd, As, and Cr) concentrations with the Toxicity Characteristic (TC) threshold values (37). In the instance of Pb leaching, both the AA and NP leachates gave values above the TC threshold, whereas ML fell below this threshold. Alternatively, the AA and NP leachates were found to release Cd at concentrations lower than the TC threshold values with ML exceeding the limit. As exhibited a similar effect to Cd, and in the case of Cr, all leachate concentrations were in excess of the threshold limits.

These results and the leaching profiles have shown that acetic acid is a poor mimic for the leaching of cementitious wastes by municipal landfill leachate. To improve the applicability of this leaching procedure, the leaching fluid needs to contain compounds of significant influence present

in the MSW leachate. For example, an organic ligand capable of forming more stable complexes with Pb and Cd than acetic acid can be used to better describe Pb and Cd leaching, while the addition of carbonate to the leachant will improve As leaching predictions. For Cr, the leaching fluid should be able to mimic the reducing condition present in a landfill leachate. While it may be easy to incorporate carbonate into the leaching fluid, the identification of organic ligands that can form stable complexes with Pb and Cd and the simulation of reducing conditions present in an MSW leachate are more difficult to attain. To incorporate these in the development of a new leaching procedure, more studies are required.

While it has previously been claimed that the TCLP is too harsh for simulating leaching in a monofill (11), our study has found that acetic acid leachant, which is used in both the TCLP and AS 4439.3-1997, is capable of simulating the nonputrescible landfill leachate for the leaching of metals from cementitious waste. This is predominantly due to the lower loadings of organic and inorganic carbon in the NP leachate that may act as a pH buffer or complexing agents.

A further critical point requiring consideration is the validity of the use of a single result taken at one leaching time (18 h) in the AS 4439.3-1997 for the determination of the hazard of waste. From the previous sections, it is clear that the metal concentration changes with time depending on the kinetics of the chemical reactions and thus leachate pH. For example, the concentration of Pb in the ML leachate was much higher during the initial stages of leaching (<2 h) than after 18 h of leaching due to organic complexation (see Figure 1). This illustrates that a one-point leach test does not give a complete picture of the leaching profile and ultimately may result in an incorrect assessment of the waste.

The findings indicate that the applicability of AS 4439.3-1997 to assess the hazards of cementitious waste is questionable. However, the diversity of leachate compositions from landfill to landfill would require more rigorous studies of a similar nature to be undertaken before any general conclusion could be formed.

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