

Evaluating the applicability of regulatory leaching tests for assessing the hazards of Pb-contaminated soils

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Abstract

Soil contamination is a major environmental problem due to the ecological threat it poses. In this work, electron probe microanalysis (EPMA), X-ray diffraction (XRD), and leaching studies were employed to explain the different leaching behaviors of non-stabilized and stabilized soils. The applicability of the leaching fluids used in the toxicity characteristic leaching procedure (TCLP) and Australian Standards, AS 4439.1-1997 for assessing the hazards of contaminated soils was investigated as was the leaching of lead from soil stabilized by cement and buffered phosphate techniques. The results showed Pb speciation in the soil highly influenced metal leaching. The synthetic leaching fluids were unable to provide a reliable estimation of Pb concentration in the municipal landfill leachate (ML) due to the absence of organic ligands capable of forming stable complexes with the lead. Water provided the closest representation of lead leaching from the non-stabilized and phosphate stabilized soils while sodium tetraborate buffer was found to be suitable for cement-stabilized soil in a non-putrescible landfill leachate system. A comparison of stabilization methods revealed that the buffered phosphate technique was more suitable for stabilizing the lead in the soil relative to cement stabilization.

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1. Introduction

The disposal of hazardous wastes in landfills is a major environmental issue worldwide. Heavy metals present in waste can leach into the surrounding soil and groundwater, posing a threat to the environment and to human health. Many leaching tests have been developed to assess the hazards of solid wastes [1–3] with failure to pass a leaching test typically necessitating waste stabilization prior to disposal. The Australian Standards, AS 4439.1-1997, AS 4439.2-1997, and AS 4439.3-1997, and the TCLP are used for waste classification in Australia. AS 4439.1-1997, AS 4439.2-1997, and AS

4439.3-1997 procedures are based on Method 1311 toxicity characteristic leaching procedure (TCLP), developed by the United States Environmental Protection Agency (USEPA). The TCLP was designed to simulate the worst-case scenario for disposal of waste in a co-disposed landfill environment. The TCLP recommends two leaching fluids; acetic acid solution at pH 2.88 and acetate buffer solution at pH 4.92 whereas, in addition to these fluids, the Australian Standards use water and sodium tetraborate buffer at pH 9.2 as leachants. The sodium tetraborate buffer is designed to simulate the leaching of contaminants from non-putrescible wastes while water is used for wastes disposed without any confinement (e.g. dispersed over land). Although the TCLP is widely used in the US and Australia, its applicability to assess the hazards posed by wastes disposed to landfill is questionable. For example,

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it has been argued that the use of an acidic leaching fluid is not appropriate to classify non-putrescible wastes that have not been co-disposed with municipal waste [4].

Stabilization has been widely applied to immobilize contaminants in soils. Many methods are available for soil stabilization, such as pH and redox control and precipitation of carbonates, sulfides, phosphates, or silicates which reduce metal solubility [5]. Techniques may either be capable of stabilizing a range of heavy metals such as cement stabilization or be designed to target specific heavy metals such as phosphate stabilization of lead. During cement stabilization, the contaminants in the soil can be retained either through adsorption onto the cement matrix, through precipitation as metal hydroxides due to the alkaline pH of cement, or through Pb incorporation into the cement matrix [6,7]. Phosphate stabilization has been widely used for wastes containing Pb as it involves the formation of very stable lead phosphate precipitates [8–14]. Pyromorphite compounds ($\text{Pb}_5(\text{PO}_4)_2\text{X}$; X = halide or hydroxide) have been the most common group of Pb phosphates detected in these studies [9–11], in addition to other Pb phosphate compounds such as drugmanite ($\text{Pb}_2(\text{Fe},-\text{Al})(\text{PO}_4)_2(\text{OH})_2$) and plumbogummite ($\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) [10]. The addition of a magnesium oxide buffer during phosphate stabilization maintains the leachate pH at a range where the phosphate compounds are insoluble. Successful large-scale application of this stabilization method to Pb-contaminated sediment has been investigated by Stolzenburg [14].

The main objective of this paper is to assess the applicability of the leaching fluids used in the TCLP and the Australian Standard test, AS 4439.3-1997, for classifying the hazards of selected non-stabilized and stabilized soils. This is achieved by examining the leaching of Pb from two Pb-contaminated soils (non-stabilized and stabilized) by leachants recommended in both tests and comparing these results with leaching by municipal and non-putrescible landfill leachates. Secondary to this is an assessment of the performance of cement and phosphate stabilization techniques at an Australian regulatory level when exposed to the synthetic and landfill leachates.

2. Experimental procedure

2.1. Soil preparation and characterization

Two Pb-contaminated soil samples were taken from sites located in Sydney and surrounding regions. Pb in one sample (defined as *urban soil*) derived from paint flakes disposed at the site by a local resident. The paint flakes are readily visible, with a diameter of up to 5 mm. The second Pb-contaminated soil sample (defined as *industrial soil*) was obtained from land approximately 100 m from a lead and zinc smelter where the Pb source was dust windblown from the smelter area. The soil was taken to a depth of 20 cm below the surface.

Prior to stabilization, the soil samples were spread at a maximum thickness of 10 mm, air dried for 48 h, and then

Table 1
Characteristics of urban and industrial soils

Inorganic characteristics	Urban soil	Industrial soil
Soil pH (arbitrary unit)	7.8	7
Air dried moisture (%)	0.9	2.6
Conductivity ($\mu\text{S}/\text{cm}$)	140	180
Al	2.4	6.5
As	N/A	0.14
Ba	0.7	0.057
Ca	160	5.4
Cr	N/A	0.013
Cu	0.0	0.49
Fe	3.5	24
K	N/A	1.2
Mg	1.2	0.38
Mn	0.1	0.52
Na	N/A	0.23
Ni	N/A	0.033
Pb	12	3.2
Ti	0.1	0.018
V	N/A	0.023
Zn	1.6	9.4
Sulfur (acid extractable)	1.1	0.23
Total phosphorus	0.58	N/A

All values are in mg/g of soil except where otherwise stated. N/A: not available.

sieved through a 2.4-mm mesh-size sieve. The characteristics of the soil samples are shown in Table 1. The concentrations of metal ions in the soils were obtained by digesting the solid samples using an aqua regia solution. The samples were oven dried at 40 °C to remove moisture prior to the digestion process. One gram of dried sample was mixed with 5 mL of 70% nitric acid, 15 mL of 37% hydrochloric acid, and 0.5 mL of hydrogen peroxide, heated to 80–90 °C for 30 min, and then filtered through Whatman paper no. 4. The filtered solution was diluted to 100 mL and analyzed for metals using inductively coupled plasma atomic emission spectroscopy (ICP AES). Anion concentrations were measured using ion chromatography based on the methods described by the American Public Health Association (APHA) 4110 [15].

2.2. Preparation of cement-stabilized and phosphate-stabilized soils

Cement stabilization involved mechanically mixing 1 kg of the contaminated soil with water (approximately 700 g) and 100 g of Type GP Ordinary Portland Cement (supplied by Australian Cement, conforms to AS 3972-1991) until uniformly mixed. The mixture was cured for 28 days at ambient conditions. The cement-stabilized soil was then air dried for 2 weeks in a fume cupboard, crushed, and sieved through a 2.4-mm mesh-size sieve.

Buffered phosphate stabilization involved mixing 1 kg of the contaminated soil with 75 g of calcium dihydrogenphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) that had been previously dissolved in approximately 450 g of deionised water. Ten grams of magnesium oxide were added (to assist with buffering the solid at a pH where the newly formed phosphate species

Table 2
Metal concentrations in stabilized soil samples

Elements	Concentration of elements (mg/g of waste)			
	Urban soil		Industrial soil	
	Cement-stabilized soil	Phosphate-stabilized soil	Cement-stabilized soil	Phosphate-stabilized soil
Al	4.3	1.8	8.9	8.9
Ba	0.7	0.7	0.07	0.05
Ca	180	150	39	17
Cu	0.03	0.02	0.4	0.3
Fe	5.1	1.0	16	9.4
K	0.9	0.2	1.8	7.4
Mg	1.8	4.2	1.3	5.1
Pb	7.6	6.6	2.5	2.5
Zn	1.4	1.4	8.0	7.5
Si	3.5	0.2	0.5	0.2

were most insoluble), with further mixing for 5 min, after which the container was placed on a shaker table at a speed of 300 rpm for 2 h. After shaking, the soil mixture was placed on an aluminum tray and placed in an oven at 60 °C for 7 days. The samples were passed through a 2.4-mm mesh-size sieve prior to the leaching experiments.

The cement-to-soil and phosphate-to-soil ratios used were based on values typically employed within the Australian industry. Metal ion compositions of the stabilized soils were obtained by aqua regia dissolution and are presented in Table 2. The total amount of Pb in the phosphate-stabilized soil may be lower than the actual level present as not all the Pb may be extracted from the soil by this technique.

2.3. Landfill leachate collection

Two landfill leachates were collected for use as leaching fluids. The municipal landfill leachate (ML) was taken from a landfill which accepted both putrescible and non-putrescible wastes. This was collected in 20-L plastic drums from pipes leading to a leachate pond. The non-putrescible waste landfill leachate (NP) was obtained from a landfill that received only non-putrescible wastes, including construction and demolition waste, wood, and industrial wastes. This leachate was located in a well 15–30 m underground and was collected using a 38-mm diameter bailer and stored in 20-L plastic drums. Both landfills were approximately 20 years old. Both collected leachates were stored at 4 °C to minimize microbial activity.

The leachate characteristics are shown in Table 3. A summary of the organic species present and their concentrations are given in Table 4. The elemental, anion, and organic concentrations were analyzed using the same procedures described for the soil samples. Total organic and inorganic carbon contents were analyzed using an ANATOC Series II TOC Analyzer. The pH, electrical conductivity, biological oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSS) were analyzed using methods de-

scribed elsewhere [15]. It should be noted that the organic species presented in Table 4 contained only semi-volatile organics detected with extracted by US EPA methods 3510 [16] and 3550 [17]. Analyses for other organic compounds such as humic or fulvic acids were not undertaken.

Table 3
Composition of landfill leachates [23]

Characteristics	Municipal landfill (ML) leachate	Non-putrescible (NP) landfill leachate
pH (arbitrary unit)	7.8 ± 0.1	7.4 ± 0.4
BOD ₅	840 ± 230	50 ± 2
COD	3850 ± 130	930 ± 30
Conductivity (µS/cm)	24,000 ± 3500	33,000 ± 0
Total inorganic carbon	2700 ± 400	295 ± 20
Total organic carbon	1000 ± 200	185 ± 10
Total suspended solids	79 ± 29	110 ± 30
Aluminum	0.9 ± 0	<0.5
Arsenic	<0.2	<0.2
Barium	0.2 ± 0.0	3.8 ± 0.0
Cadmium	<0.1	<0.1
Calcium	92 ± 25	180 ± 3
Chloride	2900 ± 400	10,600 ± 200
Chromium	0.3 ± 0.1	<0.1
Cobalt	<0.1	<0.1
Copper	<0.2	<0.2
Iron	14 ± 1	22 ± 1
Lead	<0.2	<0.2
Magnesium	120 ± 5	N/A
Manganese	0.3 ± 0.0	0.4 ± 0.0
Molybdenum	<0.05	<0.05
Nickel	0.2 ± 0	<0.1
Phosphate	16 ± 4	<3
Potassium	1400 ± 300	N/A
Selenium	<0.2	<0.2
Sodium	1700 ± 300	N/A
Sulfate	32 ± 33	5.4 ± 2.0
Titanium	0.1 ± 0.03	<0.05
Vanadium	0.06 ± 0	<0.05
Zinc	1.2 ± 0.2	0.8 ± 0.1

All values are in mg/L unless otherwise stated. N/A: not available.

Table 4
Summary of organic species present in landfill leachates

Organic characteristics	Municipal landfill (ML) leachate	Non-putrescible (NP) landfill leachate
Alcohols/phenols	3200 ± 500	110 ± 20
Alkyl ketones		69 ± 24
Acids	2300 ± 1000	2 ± 4
Benzenes and toluenes	260 ± 200	
Amides	1700 ± 2500	22 ± 2
Phthalates	1100 ± 300	57 ± 9
Others	1100 ± 400	
Total	9700 ± 2500	260 ± 50

All values are in µg/L.

2.4. Electron probe microanalysis of the soil samples

Microanalysis of the soil was achieved using a Cameca SX50 microprobe. The soil samples were mounted at 80 °C in araldite D/HY-951 epoxy resin and hardener (resin:hardener ratio 10:1). The polishing was performed on a Kent Mk 3 polishing machine at a speed of 140–160 rpm using 3 µm Engis diamond paste on a Ceramic Lap and 1 µm diamond paste on a Texmet Lap. The epoxy resins containing the samples were carbon coated for the analysis [18]. Quantitative analysis for elements at different points across the samples was performed and electron images were acquired [19].

2.5. X-ray diffraction analysis of soil samples

A Phillips PW 3710-based X-ray diffractometer (XRD) was used to analyze the crystal line forms present in the non-stabilized and stabilized soil samples with a Cu tube anode, a generator tension of 40 kV, and a current of 20 mA.

2.6. Leaching experiments

The leaching experiments were conducted based on the Australian Standard method, AS 4439.1-1997 [20]. Eighty grams of non-stabilized or stabilized soil sample was mixed with 1600 g of leaching fluid in a high-density polyethylene (HDPE) bottle. The leaching fluids used were municipal landfill leachate, non-putrescible waste landfill leachate, and synthetic leaching fluids. The synthetic leaching fluids used for the non-stabilized and phosphate-stabilized soils were acetate buffer (AB, pH 4.9) and water, while for cement-stabilized soil, 0.1 M acetic acid (AA, pH 2.9) and sodium tetraborate buffer (borax, pH 9.2) were used. The bottle containing the soil and leaching fluid was tumbled at a speed of 30 rpm for a predetermined leaching duration. During the experiment, air was not purged from the system. After the tumbling process, the leachate was filtered through a 0.8-µm pore-size membrane filter. Nitric acid (2%) was added to the leachates recovered from the synthetic leaching fluid (acetic acid or water) experiments for preservation purposes. The leachates were stored at 4 °C to minimize microbial activity.

Investigations into the effect of leachate pH involved mixing the soil samples with different concentrations of acetic acid or NaOH. Investigations into the leaching duration involved tumbling the waste between 0 h and 7 days. The 0-h measurement in the leaching duration studies corresponded to the case where the leaching fluid and the cementitious waste were briefly agitated (~5 s of shaking) before being filtered. Sampling involved taking a 10 mL aliquot (using a plastic syringe) at different time intervals upon which the leaching bottles were placed back into the tumbler. A total of approximately 10 samples at different times during the leaching period were collected. Leaching results collected after 24 h were used for the comparison of Pb concentration in the leachate with TCLP threshold values [21].

3. Results and discussion

3.1. Electron probe microanalysis and X-ray diffraction results of soils

3.1.1. Urban soil

The XRD (Fig. 1(a)) and microstructure (Fig. 2) analyses indicated the urban soil contained mostly calcite (CaCO₃) and quartz/sand (SiO₂), small amounts of kaolinite (Al₂Si₂O₅(OH)₄), and traces of dolomite (CaMg(CO₃)₂) and portlandite (Ca(OH)₂). High levels of Pb (up to 60%) were observed in the black particles (Pb-rich particles) in Fig. 2 and corresponded to the paint flakes present in the soil. XRD analysis of the paint flakes upon manual isolation from the soil (Fig. 1(b)) revealed the presence of calcite (CaCO₃), zincite (ZnO), hydrocerussite (Pb₃(CO₃)₂(OH)₂), rutile (TiO₂) and small amounts of lead oxide sulfate hydrate (Pb₄O₃SO₄·H₂O), barite (BaSO₄), quartz (SiO₂), and anatase (TiO₂). Lower levels of Pb (3.6 ± 5.1 wt.%) were found to be evenly distributed throughout other small particles within the sample. These small particles contained low amounts of Ca (6.0 ± 7.7 wt.%), Al (5.5 ± 3.6 wt.%), Si (12 ± 8 wt.%) and O (31 ± 12 wt.%), with the remainder likely to comprise of organic components of the soil.

The back-scattered image of the cement-stabilized urban soil (Fig. 3) indicated that cement was bound the soil particles. Moreover, the cement matrix was found to contain an even distribution of Pb (1.8 + 0.5 wt.%) suggesting partial dissolution of Pb from the paint flakes. This is believed to have been followed by reprecipitation and/or incorporation of Pb in the cement structure [7].

Visually, the back-scattered electron image of the phosphate-stabilized soil was similar to that of the non-stabilized urban soil. However, in the phosphate-stabilized soil the Pb-rich particles contained approximately 55 wt.% Pb and 6.0 wt.% P indicating the formation of a Pb phosphate compound. Other small particles in the phosphate-stabilized soil also contained Pb (10%) and P (8.3%). The variation in Pb and P contents of the particles points to the formation of Pb phosphate compounds of varying stoichiometry. It is

also possible that some Pb compounds remained unreacted. It has been reported that the pyromorphite mineral family ($Pb_5(PO_4)_2X$; X = halide or hydroxide) rapidly forms when soluble phosphorus compounds, or apatite ($Ca_{10}(PO_4)_6(X)_2$) are mixed with a solution containing Pb [9]. The weight ratio of Pb to P in the hydroxypyromorphite compound ($Pb_5(PO_4)_3OH$) is 11:1, while the Pb-rich particles in the phosphate-stabilized soil exhibited an average Pb/P ratio of 9.2:1, suggesting the formation of hydroxypyromorphite in the soil. Due to the low overall concentration of Pb in the soil

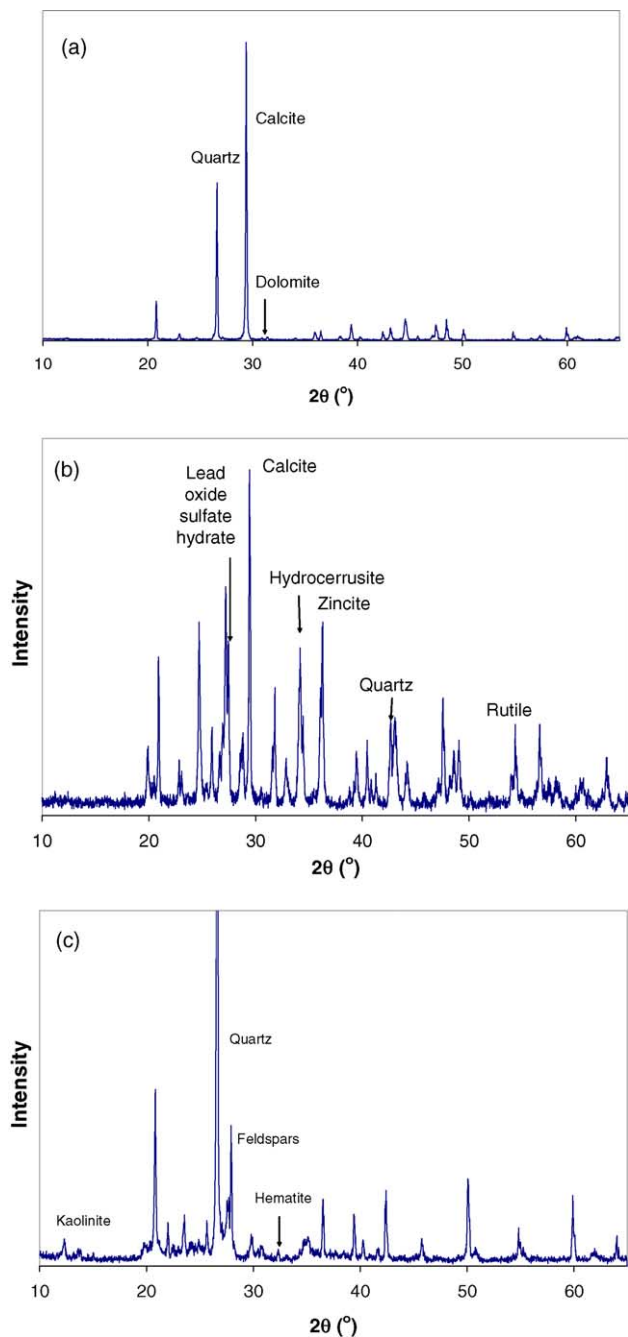


Fig. 1. XRD spectra of (a) urban soil, (b) paint flakes isolated from urban soil, and (c) industrial soil.

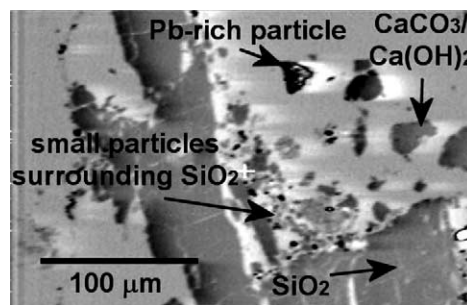


Fig. 2. Back-scattered image of non-stabilized urban soil containing 12 mg Pb/g of soil.

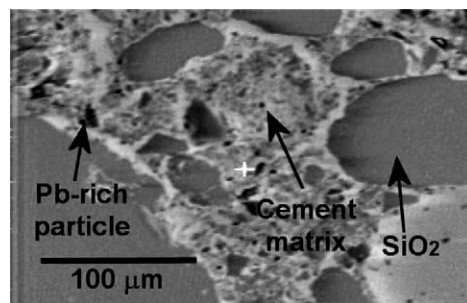


Fig. 3. Back-scattered image of cement-stabilized urban soil containing 7.6 mg Pb/g of soil.

sample, detection of crystalline Pb compounds by XRD was not possible, hence the presence of $Pb_5(PO_4)_3OH$ could not be confirmed.

3.1.2. Industrial soil

The XRD analysis (Fig. 1(c)) and EPMA imaging (Fig. 4) indicated the industrial soil mainly comprised of quartz/sand (SiO_2), feldspars ($XAl_{(1-2)}Si_{(3-2)}O_8$ where X may be Na, K, or Ca) and small amounts of kaolinite ($Al_2Si_2O_5(OH)_4$) and hematite (Fe_2O_3). A large number of Fe-rich particles were observed by EPMA, while only a small presence of hematite was observed by XRD, suggesting the industrial soil contained a large amount of poorly crystalline Fe particles. The wavelength dispersive (WDS) analysis showed the Fe-rich particles contained approximately 52% Fe, 0.6% Pb, 0.2% Zn, and 0.2% as evenly distributed within the particle, with the balance mostly oxygen. The association of Pb with the

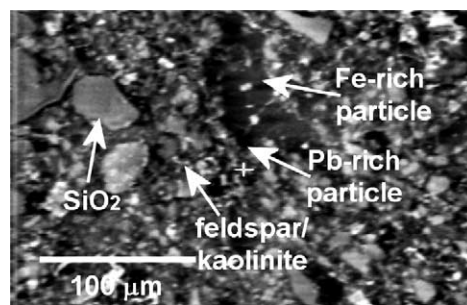


Fig. 4. Back-scattered image of non-stabilized industrial soil containing 3.2 mg Pb/g of soil.

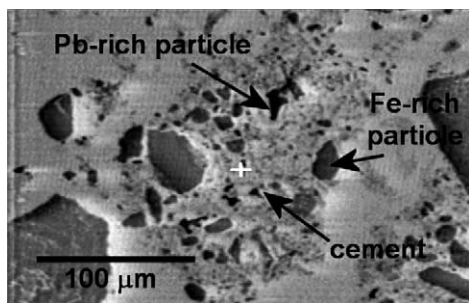


Fig. 5. Back-scattered image of cement-stabilized industrial soil containing 2.5 mg Pb/g of soil.

Fe-rich particles agrees with the findings by Lin et al. [22], who observed that Pb was associated with poorly crystalline Mn and Fe oxides in soil. The isolated black particles (Pb-rich particles) present in Fig. 4 contained 8.9% Pb, 22% Fe, and 3.6% Zn. These black particles may be windblown dust from the smelter.

Similar to the cement-stabilized urban soil, cement bound the industrial soil particles (Fig. 5). This matrix contained a uniform distribution of approximately 0.5 wt.% Pb again providing evidence of possible dissolution and reprecipitation and/or incorporation in the cement matrix of a portion of the Pb-containing particles upon cement addition.

The visual appearance of the phosphate-stabilized industrial soil was similar to the non-stabilized industrial soil. However, the Pb-rich particles were found to contain Pb levels ranging from 0.1 to above 50 wt.% and phosphorus levels of 3.3 ± 1.6 wt.%, suggesting that Pb again formed phosphate precipitates.

3.2. Leaching results

The Pb concentration profiles of the non-stabilized urban soil (Fig. 6(a)) show an initial elevated presence of Pb in the acetate buffer leachate, primarily due to the solubilization of PbCO_3 precipitate in the sample. A subsequent increase in the leachate pH, provided by a release of alkalinity from the soil, led either to the reprecipitation of Pb possibly as lead hydroxide, which typically begins to form around pH 5.0 [23], and/or Pb chemical inclusion during pozzolanic product formation. The Pb and pH profiles for the water and NP leachates are similar and possess the lowest Pb levels of the four leachants. While it is apparent the Pb presence in the leachate is a function of pH, the ML leachate exhibited a similar final pH to the water and NP leachate systems however gave an elevated Pb release over the 7-day leaching period. The higher Pb level in the ML leachate was postulated as due to Pb complexation with organic materials in the ML leachate, in agreement with previously published results on the leaching of Pb from cementitious wastes [39]. From both Tables 3 and 4, the ML leachate contained higher levels of organic carbon than the NP leachate. Numerous studies [24–30] have shown the ability of lead to complex with organic compounds. For example, Weng et al. [30] observed Pb complexation with dissolved or-

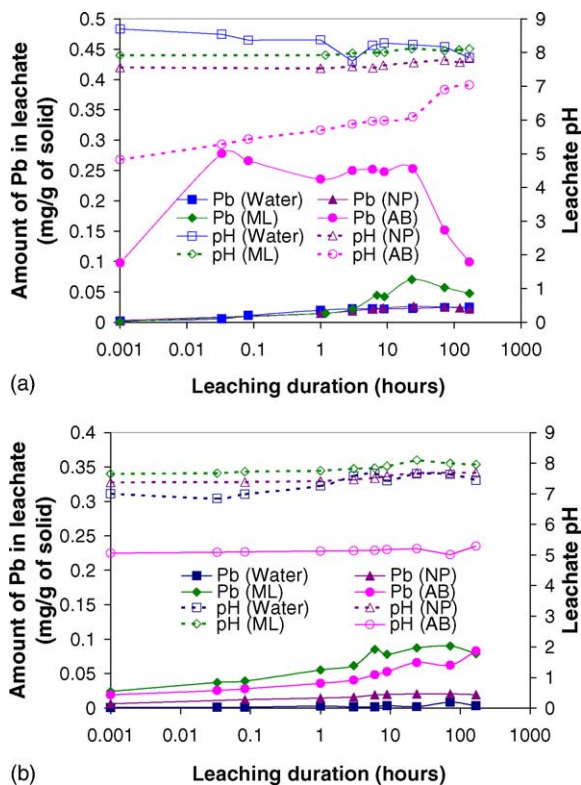


Fig. 6. Pb in leachate as a function of leaching duration for non-stabilized urban soil (12 mg Pb/g) and non-stabilized industrial soil (3.2 mg Pb/g). Leaching fluids: distilled water (water); non-putrescible waste landfill leachate (NP); municipal landfill leachate (ML); acetate buffer (AB). Samples were tumbled at 30 rpm with L/S ratio of 20.

ganic matter such as humic acid while Daughney and Fein [25] found that lead complexed with 2,4,6-trichlorophenolate and pentachlorophenolate in ground water.

Apart from the acetate buffer, the Pb and pH profiles of the industrial soil (Fig. 6(b)) were similar to the urban soil. Comparable amounts of Pb leached from both soils despite the higher total Pb concentration in the urban soil and may be due to solubility limitations in the leachate. The difference in the Pb profile for the acetate buffer may derive from the original form of Pb in the soil samples. To illustrate this, a comparison of the solubility of PbCO_3 and Pb adsorbed on hydrous iron oxide is presented in Fig. 7, as predicted by the geochemical modeling package, PHREEQC. Thermodynamic data used in the model was taken from the Lawrence Livermore National Library Database [31] and adsorption data from Dzombak and Morel [32]. Within the urban soil, Pb exists primarily as PbCO_3 whereas Pb was assumed to be adsorbed on the Fe-rich particles in the industrial soil. The solubility of Pb with pH for PbCO_3 precipitate compared to its adsorption on hydrous ferric oxide (Fig. 7) indicates that between pH 3.7 and 5.0, the desorption of Pb from ferric oxide is thermodynamically more favorable. Despite this, the initial release of Pb from the urban soil was greater, suggesting that adsorption may not be the only mechanism of Pb containment in the industrial soil.

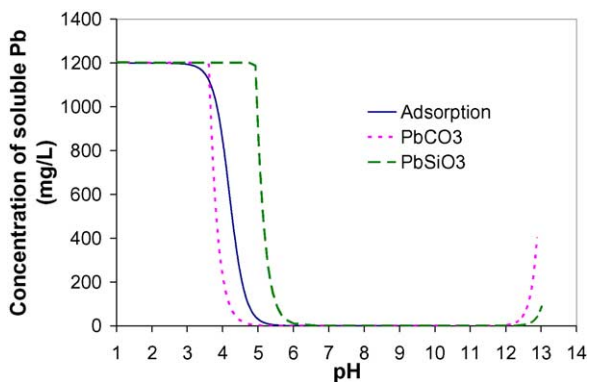


Fig. 7. Concentrations of soluble Pb obtained from geochemical modeling package PHREEQC for Pb ions adsorbed on hydrous ferric oxides (total number of sites of 0.1 mol, specific surface area 600 m²/g), PbCO₃ precipitate (solubility constant $K_{sp} = 10^{-13.54}$), and PbSiO₃ (neutralisation constant $K_n = 10^{5.67}$) precipitate [31].

Phosphate stabilization (Fig. 8) significantly reduced the leachability of Pb by all leachates in both soil types. This is due to the formation of lead phosphate precipitates, which are more insoluble compared to other lead precipitates, agreeing with the findings of other researchers [9,10,12,13,33–35].

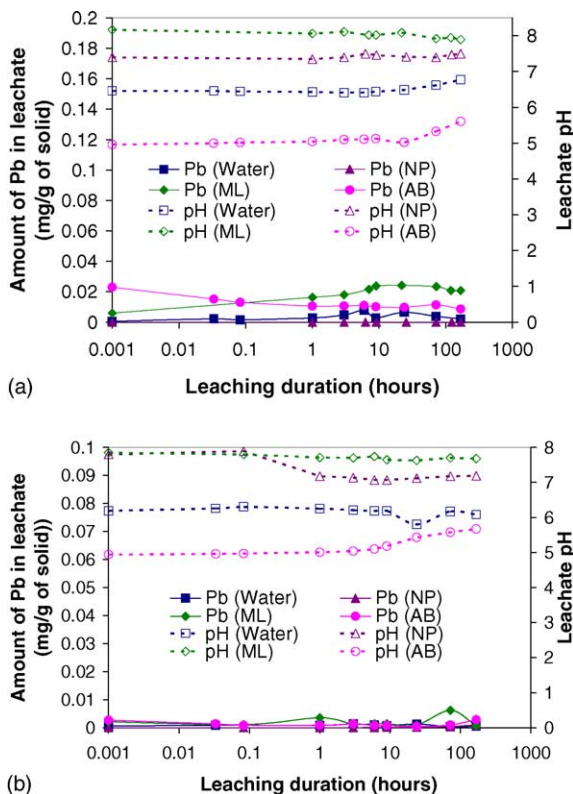


Fig. 8. Pb in leachate as a function of leaching duration for phosphate-stabilized urban soil (6.6 mg Pb/g) and phosphate-stabilized industrial soil (2.5 mg Pb/g). Leaching fluids: distilled water (water); non-putrescible waste landfill leachate (NP); municipal landfill leachate (ML); acetate buffer (AB). Samples were tumbled at 30 rpm with L/S ratio of 20.

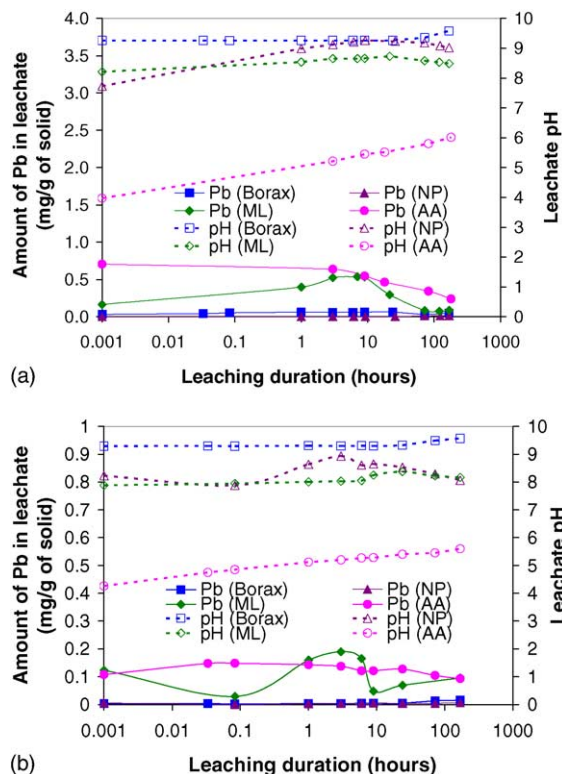


Fig. 9. Pb in leachate as a function of leaching duration for cement-stabilized urban soil (7.6 mg Pb/g) and cement-stabilized industrial soil (2.5 mg Pb/g). Leaching fluids: sodium tetraborate buffer (borax); non-putrescible waste landfill leachate (NP); municipal landfill leachate (ML); 0.1 M acetic acid (AA). Samples were tumbled at 30 rpm with L/S ratio of 20.

The similarities in leaching profiles for all leachates, despite the differences in pH, are due to the generally insoluble nature of the Pb–phosphate compounds over the range of final pH values obtained in this study. The slightly elevated release of Pb by the ML leachant may be due to the minor presence of organic complexation.

Even with stabilization of the soils with cement, solubilization, complexation, and reprecipitation of Pb by the acetic acid and ML leachants was evident (Fig. 9). Treatment with acetic acid resulted in Pb solubilization followed by precipitation as lead hydroxide or lead silicate. Similar processes have been observed for the leaching of Pb from Pb-spiked cementitious waste [36]. Organics in the ML leachate again initially complexed with Pb followed by domination of the kinetically slower hydroxide precipitation reaction. Similarly, Pagenkoph and Whitworth [37] have observed that metals which form the most stable complexes will preferentially precipitate, despite initial complexation. Fig. 9 also shows borax to have the same releasing capability of Pb as the NP leachate. This is in line with AS 4439.3-1997 which specifies borax to be representative of the leaching of non-putrescible wastes. The similar Pb levels obtained by the borax and NP systems are due to the low organic content of the NP leachate and the buffering capacity of the borax leachant.

Despite the lower pH attained by the cement-stabilized industrial soil upon leaching with acetic acid (Fig. 9(b)), less Pb was released than for the cement-stabilized urban soil (Fig. 9(a)). This effect may be explained by the different modes of Pb speciation in the two soils. PbCO_3 precipitate in urban soil is soluble at the highly alkaline conditions ($\text{pH} > 12$) introduced by the cement (Fig. 7). Addition of cement to the soil matrix may lead to partial (local) dissolution of the PbCO_3 with the dissolved Pb then available for incorporation into the cement by formation of silicate minerals, as suggested by Halim et al. [7]. The potential for lead silicate formation is shown in Fig. 7, demonstrating a lower Pb silicate solubility above pH 12.

The EPMA study of the non-stabilized industrial soil (Fig. 4) suggested Pb was primarily associated with Fe-rich particles of the soil. Under the alkaline conditions introduced by the addition of cement, Pb desorption of Fe-rich particles is limited, as demonstrated in Fig. 7, with any release likely to derive from the Pb in the loose black particles. The desorption from Pb from Fe-rich particles occurs to a lesser extent than the dissolution of lead silicate formed in the cement-stabilized urban soil, leading to lower amounts of Pb leached from the industrial soil.

3.3. Comparison of the stabilization methods

Fig. 10(a) and (b) illustrate the percentage amounts of Pb in the leachate as a function of leachate pH for the non-stabilized, cement-stabilized, and phosphate-stabilized urban and industrial soils, respectively, as well as a Pb profile leached from Pb-spiked cementitious waste. Descriptions of the preparation and investigation of the Pb-spiked cementitious waste are provided elsewhere [23,36]. It is immediately apparent that phosphate stabilization provided the greatest reduction in Pb leaching from both soils over the pH range studied, possibly due to the formation of stable Pb phosphate precipitates. Work by Wang et al. [5] showed a greater than 87% reduction in the TCLP extractable concentrations of Pb from soil upon the addition of CaH_2PO_4 while similar findings on the use of phosphate stabilization have been observed by many other researchers [5,9,10,13,38,39].

Fig. 10(a) also indicates the percentage of Pb leached out from the cement-stabilized urban soil at all pH values is comparable to that of the Pb-spiked cementitious waste. This suggests the binding mechanism of Pb in these two systems is similar, supporting prior discussion on the dissolution of PbCO_3 particles in the soil, followed by redistribution and precipitation of the Pb as an alternate species throughout the cement matrix. Cement stabilization also alters Pb release with pH for the industrial soil (Fig. 10(b)), however the resulting profile does not correspond to the cementitious waste profile. Again, cement addition may alter Pb speciation in the industrial soil, but not to the same extent as the urban soil. This could be due to different Pb species originally present within the two soils.

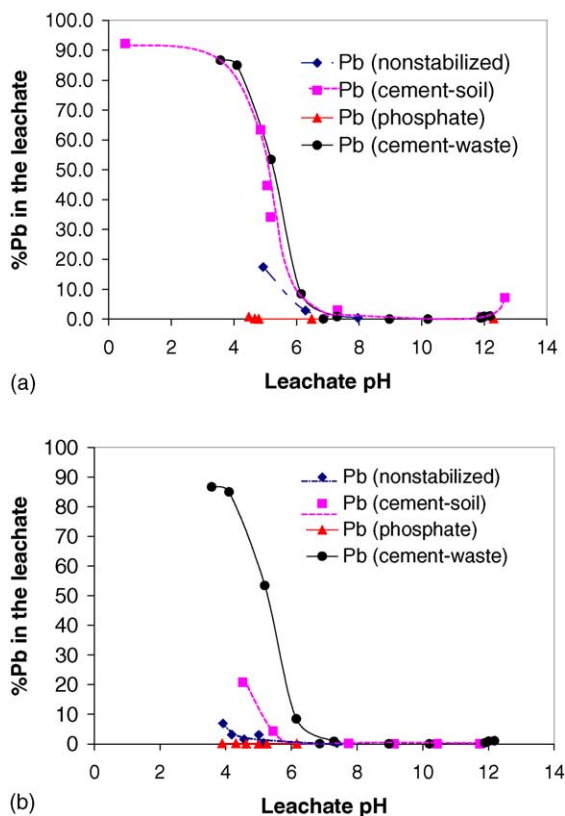


Fig. 10. Percentage of Pb leached as a function of leachate pH for (a) urban soil and (b) industrial soil. The non-stabilized (nonstabilized), cement-stabilized (cement-soil) and phosphate stabilized (phosphate) urban soils contained 12, 7.6, and 6.6 mg Pb/g solid, respectively. The non-stabilized, cement-stabilized and phosphate stabilized industrial soils contained 3.2, 2.5, and 2.5 mg Pb/g of solid, respectively. The cementitious waste (cement-waste) contained 23 mg Pb/g solid. Leaching fluids: acetic acid (0.05–0.6 M); distilled water; NaOH (0.1 M). Samples tumbled at 30 rpm for 18 h with L/S ratio of 20.

Two potential reasons exist for the observed increase in Pb leaching at acidic pH values for the cement-stabilized soils. Firstly, in order to attain similar leachate pH values for cement-stabilized and non-stabilized soils, a higher acid concentration is necessary to counter the alkalinity provided by the cement. The higher acid concentration may lead to greater destruction of the waste matrix and a greater release of Pb [35]. Secondly, as discussed earlier, cement addition may lead to the formation of lead species (e.g. lead silicate) that display greater solubilities at lower pH values.

Moreover, the 'new' lead species may be susceptible to factors other than increased solubility that can lead to its elevated release. This is illustrated in Fig. 11(a) and (b), which show the leaching of Pb from the stabilized and non-stabilized soils in the presence of ML leachate. In previous work by Halim et al. [22], the organics in ML leachate (Table 4) have been found to possess a high propensity for complexing with heavy metals. It is apparent that, particularly for the urban soil, cement stabilization leads to the formation of Pb species that are more vulnerable to complexation than their original state. This is shown

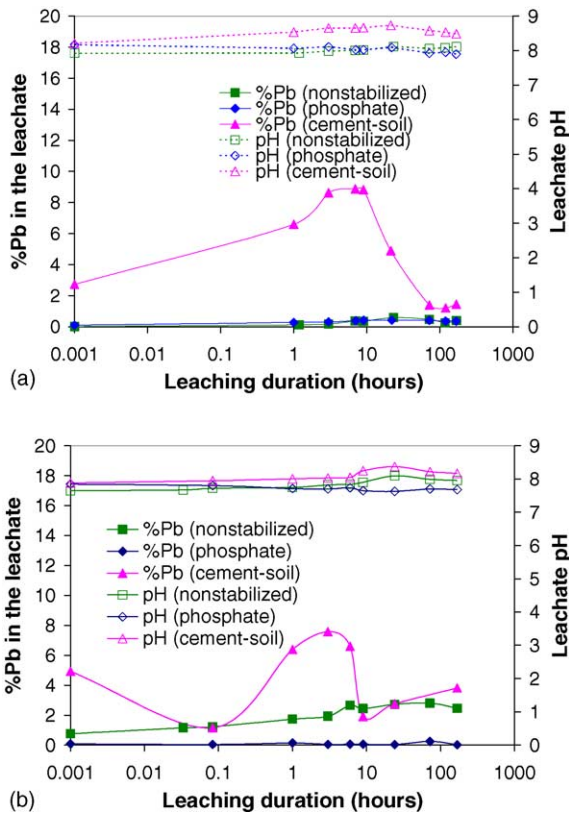


Fig. 11. Percentage of Pb leached as a function of leaching duration for (a) urban and (b) industrial soil. The non-stabilized (nonstabilized), cement-stabilized (cement-soil) and phosphate stabilized (phosphate) urban soils contained 12, 7.6, and 6.6 mg Pb/g solid, respectively. The non-stabilized, cement-stabilized and phosphate stabilized industrial soils contained 3.2, 2.5, and 2.5 mg Pb/g of solid, respectively. Samples tumbled with municipal landfill (ML) leachate at L/S ratio of 20 for 7 days.

by the elevated release of Pb in the cement-stabilized soil, despite similar leachate pH values between the stabilization techniques. Comparison of the NP leaching profiles for the two soil types (not shown), showed cement stabilization decreased Pb release. The NP leachate has previously been found to possess a lower capacity for organic complexation [22]. This work indicates that consideration of the waste characteristics and final disposal environment is crucial for assessing the suitability of cement as a tool for stabilizing wastes.

3.4. Implications of results on the applicability of the TCLP leaching fluids and the development of a leaching procedure

Comparison of lead release by the leachants with the TCLP threshold value (5 mg/L) of Pb [21] illustrates the suitability of the stabilization techniques for these wastes. In the instance of the non-stabilized urban soil (Fig. 12(a)), the acetate buffer significantly overestimates Pb release by the ML leachate as well as exceeding the TCLP threshold. The consequence of this outcome is incorrect classification of the waste

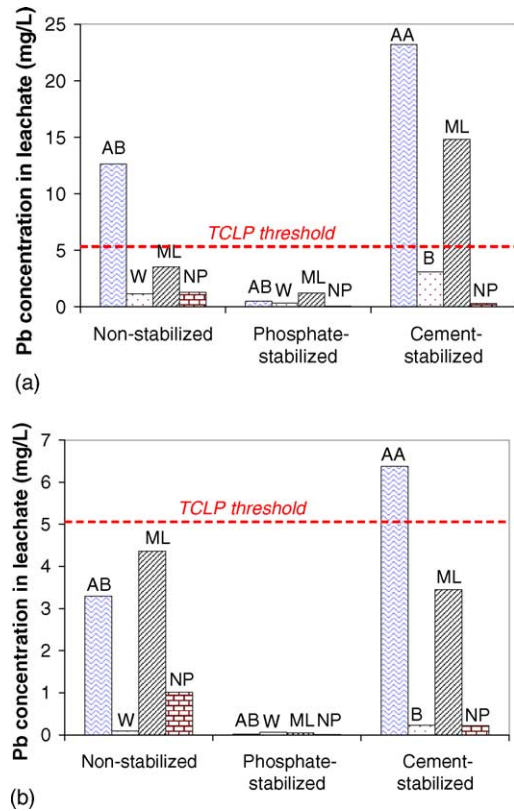


Fig. 12. Comparison of TCLP threshold with Pb concentration in leachate. Contaminated soils tumbled with leaching fluids at L/S ratio of 20:1 for 24 h. Leaching fluids: acetate buffer (AB); acetic acid (AA); water (W); borax (B); municipal landfill leachate (ML); non-putrescible waste landfill leachate (NP).

leading to unnecessary treatment of the soil. Water however, suitably estimated Pb release by the NP leachate. Phosphate stabilization of the urban soil reduced Pb release to well below the TCLP threshold for all leachants, while cement stabilization was detrimental, increasing the extent of Pb release by the ML leachate to be greater than the TCLP limit. Again the use of acetic acid overestimated the release of Pb, in relation to the ML leachate, from the stabilized waste while borax provided a reliable estimation of Pb leaching from NP leachate. Apart from the leaching of the cement-stabilized industrial soil by acetic acid, Pb release by all leachants for the stabilized and non-stabilized industrial soils did not exceed the TCLP threshold (Fig. 12(b)). It is also apparent that phosphate stabilization significantly reduced the leaching of Pb in all cases.

Problems with the use of a single value taken at a set time to estimate contaminant release and subsequently classify the waste are highlighted by this work. As discussed earlier, the mechanisms of contaminant release differ with leaching fluid, the state of the contaminant, its binding to the waste matrix, and the waste treatment procedure (if any). The choice of a single value for classification does not elucidate the impact of these factors and provides no information on the ability

of the selected test to mimic contaminant release by landfill leachate. Attempts to address this failing have been undertaken by workers such as Kosson et al. [40], who are developing an integrated testing framework aimed at providing a more reliable means of waste classification.

The choice of a time at which the representative sample for waste classification is taken is also critical. Wastes which pass a leaching test after 24 h may not pass the test over a longer time frame and vice versa. For example, after 24 h of leaching of the cement-stabilized urban soil by acetic acid the Pb concentration in the leachate exceeded the TCLP threshold. In comparison, due to further precipitation of the Pb as a hydroxide or silicate, after 7 days the Pb concentration had decreased to 0.09 mg/g (Fig. 9(a)), corresponding to 4.5 mg/L, a value below the TCLP threshold. Hence the use of a batch test which depends only on a single leaching result may not give an accurate estimation of long-term leaching of compounds from waste, especially as the time taken for equilibrium to be reached will differ depending on factors such as the waste type, particle size and the leaching fluid.

4. Conclusion

Electron probe microanalysis, XRD, and leaching results have been used to explain the leaching behavior of Pb from non-stabilized and stabilized soils. The results suggest that an appropriate leaching fluid is dependent on the nature of the metal (Pb) association with the soil as well as the properties of the leachant.

TCLP leachants were found to be poor fluids for assessment of the hazards of Pb-contaminated soil. Water was found to exhibit a potential for simulating the leaching of Pb from non-stabilized and phosphate-stabilized soils, while borax was suitable for the alkaline systems studied in this work. All synthetic leaching fluids failed to provide a useful estimation of the leaching of Pb from all soil samples for the municipal landfill leachate, as they did not account for the formation of stable Pb complexes. While the selection of leaching fluids depends largely on the form of Pb in the soil, it is important to realise that there is currently no universal leaching procedure that can assess the hazards of all soils. Aspects such as the effect of soil characteristics and heavy metal type require further consideration before any general conclusions can be drawn. Additionally, further research using other landfill leachates should be conducted to support these findings.

Of the stabilization methods considered, the buffered phosphate procedure enhanced immobilisation of the Pb while cement stabilization, in some instances, was detrimental to Pb suppression.

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