Evaluating the applicability of a modified toxicity characteristic leaching procedure (TCLP) for the classification of cementitious wastes containing lead and cadmium

Cheryl E. Halim [a], Rose Amal [a,*], Donia Beydoun [a],
Jason A. Scott [a], Gary Low [b]

[a] *Centre for Particle and Catalyst Technologies, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia*
[b] *New South Wales Environment Protection Authority, Analytical and Environmental Chemistry Section, Lidcombe, NSW 2141, Australia*

Abstract

Having the toxicity characteristic leaching procedure (TCLP) as a starting point, this study examined the effect of the various leaching parameters on the leaching of Pb and Cd from cementitious wastes. Using modified TCLP procedures, the parameters investigated were the acid concentration, leaching duration, particle size of the crushed waste, liquid to solid ratio, and the acid type. The main finding was that the final leachate pH controls the leachability of metals due to its influence on their solubility. The high alkalinity of cementitious waste buffers the leachate at a pH where most metals become insoluble. The TCLP was found to result in an unrealistic condition for cementitious wastes due to the high resultant leachate pH.
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1. Introduction

Leaching tests are used in many applications, ranging from the classification of industrial wastes for disposal in landfills to assess the stability of solid wastes for their beneficial reuse [1]. Failure to pass a leaching test requires the waste to be treated where the contaminants in

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* Corresponding author. Tel.: +61-2-9385-4361; fax: +61-2-9385-5966.
E-mail address: r.amal@unsw.edu.au (R. Amal).

the waste are immobilised by stabilisation/solidification procedures prior to its disposal. Cement stabilisation is one example of such treatment. For regulatory purposes, the leaching procedure used in New South Wales, Australia, is based on the US Environmental Protection Agency toxicity characteristic leaching procedure (TCLP), and is described in the Australian Standards AS 4439.1-1997, AS 4439.2-1997, and AS 4439.3-1997 [2–4]. The TCLP was designed to simulate the leaching of heavy metals and organics from industrial wastes co-disposed in a municipal landfill. The US EPA TCLP specifies two leaching fluids: 0.1 M acetic acid at pH 2.88 and an acetate buffer solution at pH 4.92. In addition to these leachants, water and tetraborate buffer at pH 9.2 are also used in the Australian Standard AS 4439.3-1997. Water is used if the waste is to be disposed in a landfill undisturbed on the site or without any confinement while the tetraborate buffer leachant was chosen to simulate the leaching conditions for non-putrescible materials [4]. The US EPA TCLP specifies a maximum particle size of 9.5 mm whereas the Australian Standard specifies a maximum particle size of 2.4 mm.

There are limitations of using the TCLP for simulating the leaching of contaminants in landfills. These limitations have resulted in legal challenges concerning the failure of the US EPA to provide adequate justification for specifying the TCLP for the classification of several industrial wastes [5]. The TCLP was developed to represent the worst-case scenario for managing waste in co-disposal landfills. In the proceedings of Columbia Falls Aluminum vs. US EPA, it was highlighted that the TCLP did not consider the high alkalinity of wastes, low liquid to solid ratios, and disposal of waste to monofill systems [5,6]. It was argued that mineral processing and utility wastes are not usually disposed into municipal landfills and therefore should not be subjected to acidic leaching conditions [6]. The use of the acetic acid leaching fluid would overestimate the extent of leaching when compared to the relatively neutral to alkaline leachates in monofills, and incorrect classification of wastes would lead to unnecessary treatment. The use of the TCLP for classifying monolithic wastes, such as those produced from the mineral processing industries, may also lead to overestimation of contaminants due to the particle size reduction step required in the TCLP. This results in a larger surface area exposure of the waste to the leaching fluid than that would realistically be experienced [6].

In addition, Hooper et al. [1] found that the TCLP also underestimates the concentrations of elements that form oxyanions (Sb, As, Mo, Se, V), particularly at high pH values, because they are unlikely to complex with the acetate ions that are present in the TCLP leaching fluid compared to the organic compounds in real municipal landfill leachate.

The leaching of heavy metals from cementitious waste has been investigated in many studies [7–19]. The main finding from these studies has been that cementitious wastes have a high acid neutralising capacity (ANC) which tends to quickly neutralise the acidity of the TCLP leaching fluid (acetic acid). The resultant high equilibrium leachate pH in turn leads to precipitation of many of the metals. Also, in a co-disposed environment, the pH of landfill leachate typically lies between 5 and 8, depending on the age of the landfill. The dynamics of a leaching process depends on the properties of both the substrate that the waste is presented in and the leaching fluid itself. Hence, the TCLP may not be truly reflective of the disposal environment and the hazards of wastes can be overlooked with materials being incorrectly disposed of in municipal landfills.

Investigations on metal ion leaching from cementitious wastes have looked at the effects of different leaching parameters, such as pH, particle size, leaching duration, and liquid to solid ratio [11,13–15,17,20–26]. When investigating the different leaching parameters, the pH of the leaching fluid as the leaching process proceeded has rarely been measured or controlled. This is despite suggestions that pH is the most important factor to be observed during the leaching process as it influences the speciation and solubility of metals in the system [27–30].

The aims of this paper are to investigate the effects of several leaching parameters on the leachability of lead and cadmium from cementitious wastes, track the pH changes during leaching, and correlate these with the changes in the leached metal concentration. The leaching parameters to be investigated include the final pH of leachate, leaching duration, particle size, liquid to solid ratio and the type of leaching fluid. As an outcome of these studies, the applicability of the testing procedure as described in AS 4439.3-1997 will be assessed.

2. Experimental procedure

2.1. Materials

Cementitious wastes containing Pb and Cd were prepared by mixing ordinary portland cement (OPC) supplied by Australian Cement with lead nitrate ($Pb(NO_3)_2$) or cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$) solutions. Leaching fluids were prepared using either analytical grade acetic acid or nitric acid. Different acid concentrations were prepared by dilution with deionised water.

2.2. Preparation of cementitious waste

The cementitious wastes prepared contained 2.4% Pb and 1.3% Cd by weight. The metal salts ($Pb(NO_3)_2$ or $Cd(NO_3)_2 \cdot 4H_2O$) were dissolved in deionised water and blended with the OPC. The water to cement ratios used were 0.38 and 0.44 for Pb and Cd, respectively. The mixtures were mechanically stirred using a mechanical stirrer for 15 min and left to cure for 28 days. The cured mixtures were crushed using three consecutive crushers (jaw crusher, cone crusher, and roller crusher) and passed through 9.5 and 2.4 mm mesh size sieves.

2.3. Leaching experiments

The batch leaching experiments were conducted in accordance with AS 4439.3-1997 [4]. A preweighed amount of crushed cementitious waste was mixed with a preweighed volume of leaching fluid in a high density polyethylene (HDPE) bottle to give a desired L/S ratio. The bottles were tumbled at a speed of 30 rpm for a set leaching duration. After tumbling, the liquid was vacuum filtered through a 0.8 μm pore size membrane filter. The pH of the recovered liquid (leachate) was measured and recorded, after which the samples were preserved at a pH less than 2 by the addition of nitric acid. The preserved samples

Table 1
Composition of cementitious wastes containing Pb and Cd analysed by XRF

Element	Cement composition (mg/g of waste)	
	Cement containing Pb	Cement containing Cd
Pb	23	0.0
Cd	0.0	13
Al	16	15
C	15	20
Ca	340	340
Fe	23	22
K	6.6	7.5
Mg	10	10
Na	4.5	2.2
Si	74	73
S	8.8	8.4
Th	0.9	0.9
Ti	0.6	0.6

were analysed for heavy metal ions (Pb or Cd), Ca, and Si using an Optima 3000 inductively coupled plasma-atomic emission spectroscope (ICP-AES). Each set of the experiment was performed at least in duplicates. On average, the results have an error of less than 10%.

In Sections 3.1 and 3.5, the leaching fluids studied were acetic acid at concentrations ranging between 0.1 and 5.7 M and nitric acid at concentrations ranging between 0.16 and 1.6 M while in other sections 0.1 or 0.6 M acetic acid was used as indicated. In Section 3.3, three particle size ranges were investigated: less than 2.4 mm, between 2.4 and 9.5 mm, and larger than 9.5 mm while in all other sections particles of less than 2.4 mm were used. For Section 3.2, the investigations of the leaching duration involved tumbling the waste for between 0 h and 7 days. A fresh sample was prepared for each leaching duration. The 0 h measurement corresponded to the case where the leachant and the cementitious waste were briefly agitated (~5 s of shaking) before being filtered. In other sections, the samples were tumbled for 18 h. In Section 3.4, the liquid to solid (L/S) ratios investigated were 10:1, 20:1, 40:1, and 60:1. A liquid to solid ratio of 20:1 was used for other sections.

2.4. X-ray fluorescence analysis

The chemical composition of the cementitious wastes used was obtained using X-ray fluorescence (XRF) analysis (shown in Table 1).

3. Results and discussion

3.1. Effect of leachate pH

In this section, the relationship between the leachate pH and the extent of metal ion leaching is examined. The term leachate pH here refers to the pH of the leachate measured
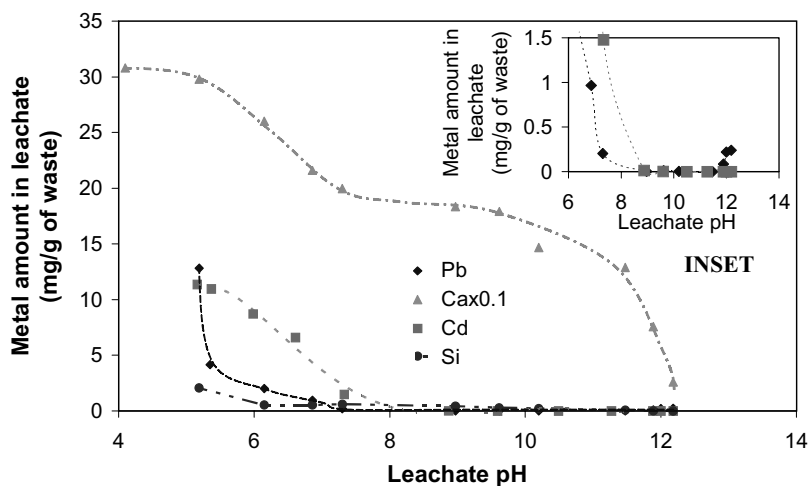
Fig. 1. The leachability of metal ions as a function of the leachate pH after 18 h of tumbling at 30 rpm. Initial Pb, Cd, Ca, and Si concentrations in cement were 23, 13, 340, and 75 mg/g of waste, respectively. The leaching fluids used were acetic acid at concentrations between 0.1 and 5.7 M at L/S 20. The inset shows more clearly the amounts of Pb and Cd at pH >6. Ca concentration was multiplied by 0.1.

after 18 h of tumbling. The effect of leachate pH on the amount of metals in the leachate (mg of metal ion/g of waste) is shown in Fig. 1. The leachate pH was varied by varying the initial concentration of the acetic acid leaching fluid between 0.1 and 5.7 M. An increase of the concentration of acid (from 0.1 to 1.0 M) resulted in a sharp decrease in the leachate pH from above 12 to approximately 4, and thereafter the pH stabilised at approximately 4 with a further increase in acid concentration. This observation can be mostly attributed to the neutralisation of the "free calcium", $Ca(OH)_2$, in the cement by the acid. It is this form of calcium that is highly responsible for alkalinity of the cement. The free calcium is present in the pores of the cement structure and does not significantly contribute to the overall strength of the cement [28]. The average amount of free calcium (reported as CaO) in the OPC is 0.23 kg CaO/kg cement [28]. Calcium in the form of silicate and aluminate hydrates form the backbone of the cement and is referred as the "bound calcium". This form of calcium has been reported to be approximately 0.40 kg CaO/kg cement [28].

It is clear from Fig. 1 that using a leaching fluid of a higher acid concentration (leachate pH <6) resulted in the release of both Ca and Si from the cement matrix. This finding indicates that under such conditions, the "bound calcium" had been attacked by the acid. Using a leaching fluid of a lower acid concentration (leachate pH 7.5–12), very little Si ions were detected in solution, indicating that acid had reacted mostly with the free calcium form (such as $Ca(OH)_2$). These results agree with the findings of Giampaolo et al. [31], Campbell and Krupka [32], and Glasser [27], who described the changes in pore fluid pH with time and the corresponding materials leached out from cement. Initially Na^+ and K^+ are leached out from the pore solution, followed by portlandite ($Ca(OH)_2$), and then the hydrated compounds [32].
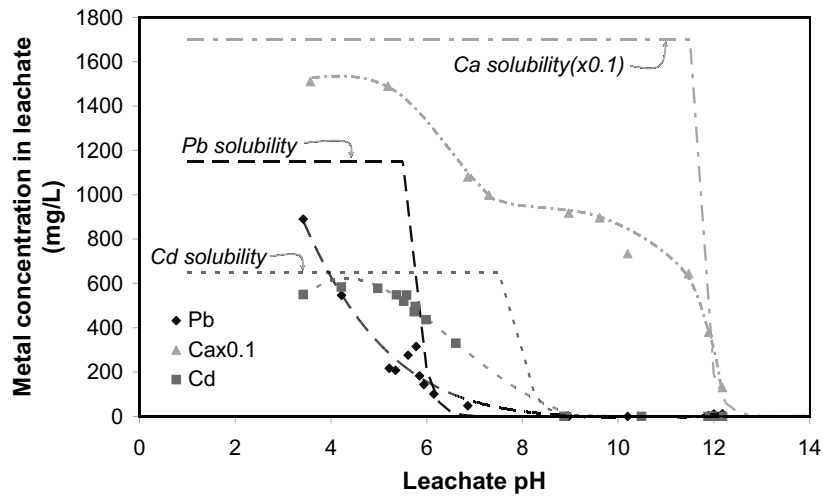
Fig. 2. Metal concentration as a function of leachate pH in comparison with the theoretical solubilities of Pb, Cd, and Ca as their hydroxides. The theoretical solubility curves were obtained using Pb, Cd, and Ca stability constants with maximum concentrations of Pb, Cd, and Ca of 23, 13 and 340 mg/g of waste, respectively. These are the maximum possible concentrations of metals that can leach out from the cementitious waste. They correspond to concentrations of 1200, 650, and 15,000 mg/l, respectively, at a liquid to solid ratio of 20:1. Ca concentration was multiplied by 0.1.

From Fig. 1, it is clearly shown that the leachate pH greatly influenced the amounts of Pb and Cd in the solution due to its effect on the solubility of these metal ions. The inset in Fig. 1 illustrates more clearly the concentrations of Pb and Cd at pH greater than 6. Cd decreased to an undetectable level above pH 9 due to the formation of its insoluble hydroxide whilst Pb was undetectable between pH 9 and 11, but was again detectable at pH 12 due to the formation of amphoteric Pb hydroxy complexes.

Fig. 2 shows the concentrations of Ca, Pb, and Cd in the leachate at different pH relative to the solubility profiles of their hydroxides. The theoretical solubilities were calculated using the solubility data given by Johnson et al. [33]. The figure shows that the solubilities of Ca and Cd at low pH (<6) compared well to those predicted from the calculations. However, at a higher pH range, the concentrations of Ca, Pb, and Cd in the leachate are lower than those predicted by the theoretical solubility profiles. For Ca ions, at pH values between 6 and 12, the Ca concentration in the leachate was lower than those predicted from the thermodynamic data. This can be attributed to the fact that in the cementitious wastes, Ca can exist as $Ca(OH)_2$, calcium silicate hydrate (C–S–H), ettringite, and other Ca compounds, while the theoretical profile was based on the solubility of $Ca(OH)_2$ only.

Fig. 2 also shows that the Pb concentration in the leachate for pH values less than 6 was also lower than the values predicted by the solubility diagram. This could be either due to the incorporation of Pb in the undissolved C–S–H matrix, as has been previously shown by Cheng [11] and Cocke [12], or the precipitation of Pb as Pb silicate compounds [21,34]. This shows that the silicate matrix has not completely dissolved. On the other hand, most of the Cd (600 mg/l) had leached out below pH 5. Cheng [11] suggested that Cd typically existed

as its hydroxide in cement. Some $Cd(OH)_2$ precipitate may be incorporated or adsorbed onto the C–S–H structure, resulting in a lower Cd concentration than the concentration predicted from the solubility of $Cd(OH)_2$ between pH 5.5 and 8. Microstructure analysis of Pb and Cd in the cementitious wastes using electron probe microanalysis confirmed that Pb ions were mainly found in the C–S–H matrix, while Cd mainly existed as $Cd(OH)_2$. A detailed analysis of these findings will be discussed elsewhere [35].

The ability of cementitious substrate in wastes to modify the pH of leaching fluid can have major implications on regulatory decisions based on leaching results. On contact with cementitious wastes, the leaching fluid reacts rapidly with the $Ca(OH)_2$ and changes the pH of the leaching fluid from an initial value of 5 to above 12. Taking the present regulatory limits for Pb and Cd as 5 and 1 mg/l, respectively [36], the final pH of the leachate of 12 would give a negligible concentration of Cd and 12 mg/l of Pb. In accordance with these results, the Cd-contaminated cementitious waste would comply with the regulatory limit whereas the Pb-contaminated cement would fail. To view in terms of real municipal landfill leachates, which have a pH range from 5 to 8, the use of TCLP or AS 4439.3-1997 would mean an underestimation of the amount of Pb and Cd that could leach out of the wastes if they were placed in a co-disposed landfill. As indicated by Fig. 1, in this pH range, Pb and Cd would be expected to be in the concentration ranges of 25–300 and 100–600 mg/l, respectively; all are higher than the TCLP threshold values. Thus, as suggested by Li et al. [15], under such circumstances the modified TCLP is not expected to correctly assess the potential hazards of cementitious wastes containing Pb and Cd for their disposal in municipal landfills.

3.2. Effect of leaching duration

Fig. 3 shows the metal concentrations in the leachate as a function of leaching duration using 0.1 M acetic acid as the leaching fluid. It was found that the amount of Pb in the leachate increased rapidly over the first 18 h of tumbling to 0.22 mg/g of waste and reached 0.3 mg/g of waste in 168 h (7 days). This confirmed the findings by Janusa et al. [14], which concluded that an increased contact time between leaching fluid and cementitious waste during the tumbling process increased the leaching of Pb from the waste until an equilibrium value was reached. Thus, since Pb concentration has not reached an equilibrium in 18 h, it is questionable whether the leaching duration used in the AS 4439.3-1997 leaching procedure is sufficient for this waste. The concentration of Cd, however, remained undetectable over the 7-day leaching period due to its low solubility at high pH.

3.3. Effect of particle size

In order to study the effect of particle size on leaching, the cementitious wastes were crushed and sorted into three size ranges, less than 2.4 mm, between 2.4 and 9.5 mm, and greater than 9.5 mm. As shown in Fig. 4, when 0.1 M acetic acid was used, the concentration of Cd in the leachate was undetectable while the concentration of Pb decreased with increasing particle size range. Cd was not detected as its hydroxide had already formed at pH 12, while for Pb, the concentration in the leachate (in the form of amphoteric hydroxide) decreased with increasing particle size due to the lower available surface area for leaching.
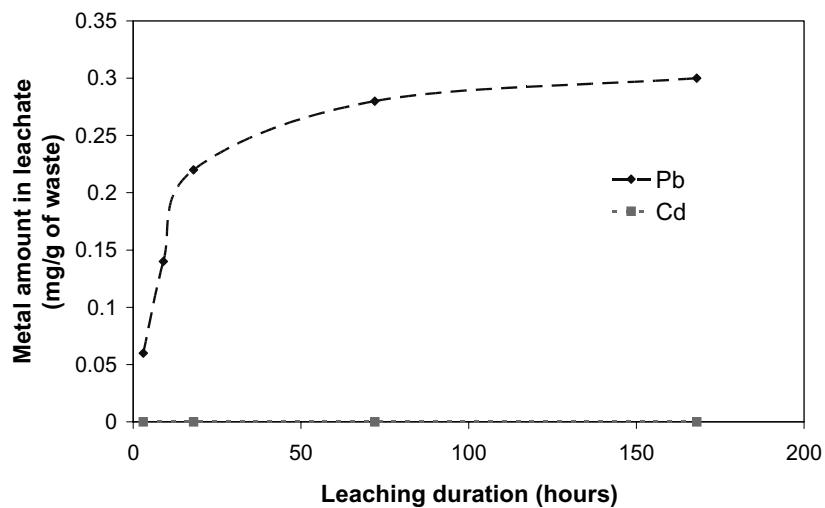
Fig. 3. The effect of leaching duration on the leachability of Pb and Cd from cementitious waste tumbled with 0.1 M acetic acid over 7 days. The pH of the leachate was constant for the duration of tumbling at approximately 12.4.
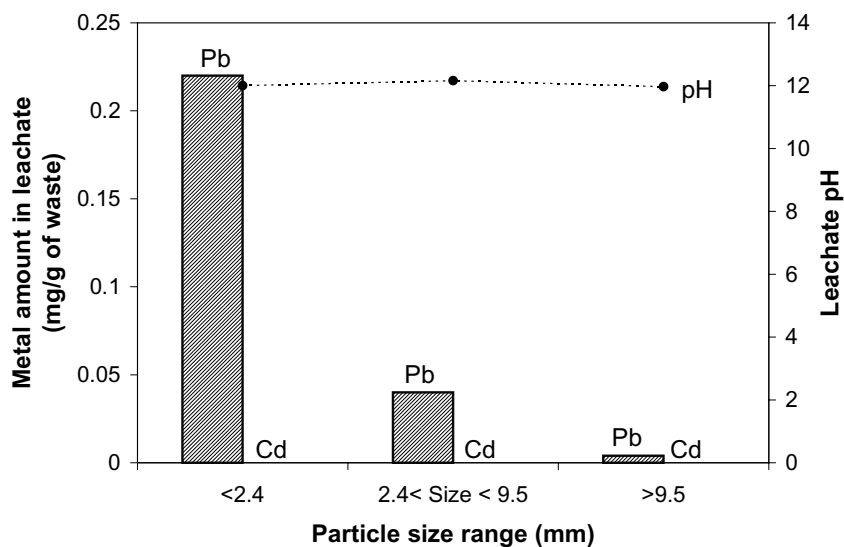

Fig. 4. The amount of Pb and Cd in the leachate as a function of particle size range when cementitious waste was tumbled with 0.1 M acetic acid (L/S 20) at 30 rpm for a leaching duration of 18 h (initial Pb and Cd concentrations were 23 and 13 mg/g of waste, respectively).
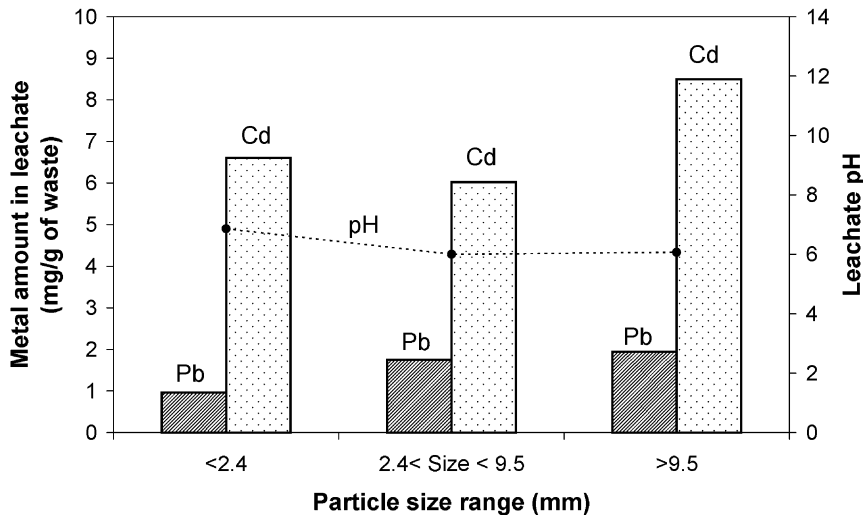
Fig. 5. The amount of Pb and Cd in the leachate as a function of particle size range when cementitious waste was tumbled with 0.6 M acetic acid (L/S 20) at 30 rpm for a leaching duration of 18 h (initial Pb and Cd concentrations are 23 and 13 mg/g of waste, respectively).

In order to clarify the behaviour of Cd leaching as a function of particle size, a higher acetic acid concentration (0.6 M) was used to obtain a system pH at which Cd would be soluble. The use of 0.6 M acetic acid as leaching fluid resulted in a final pH of between 6 and 7. These leaching results are presented in Fig. 5. The trends are as follows. The particles between 2.4 and 9.5 mm had a comparable amount of Cd being leached from particles with a size less than 2.4 mm. Both these size ranges exhibited lower leaching than particles of size greater than 9.5 mm. For the leaching of Pb, a slight increase was also observed as the particle size increased. These trends can be explained in terms of the different rates of alkalinity leached out from the different particle size. Smaller particles have a larger exposed surface area to the leaching fluid, leading to a faster rate of the leaching of the alkalinity, most of which is in the form of $Ca(OH)_2$, from the cement matrix. A faster rate of alkalinity leaching would lead to a faster increase in pH and hence an earlier onset of hydroxide precipitation. In other words, the small particles are more prone to hydroxide precipitation. On the other hand, due to a slower rate of alkalinity leaching and subsequently a slower pH increase, the larger particles were exposed to the acidic condition for a longer period of time. This is believed to have resulted in a higher amount of Pb and Cd in the leachate due to the higher solubility of metals at lower pH. The results agree with those obtained by Bishop [21] and Brown and Bishop [8], who found that the smaller particles of stabilised sludge containing Pb, Cd, and Cr in their experiments displayed a lower magnitude of metal leaching. They attributed this to the higher amount of alkalinity leaching experienced by the small particles which caused precipitation or adsorption of the released heavy metals. However, Bishop [21] found that the leachability of the smaller particles finally increased to be greater than that of the larger particles at a longer leaching duration. Such experiments were not carried out in our study.

The investigations into the effect of particle size again show that the leachate pH plays a dominant role in determining the leaching of metals from cementitious waste. For a constant pH, the smaller particles displayed a greater leachability, which was believed to be due to their larger specific surface area. However, it is postulated here that the smaller particles also exhibited a higher alkalinity-leaching rate, which led to a faster rate of increase in pH, resulting in a faster and greater extent of metal hydroxide precipitation. It is important to note that the leachate pH and the time taken to attain the equilibrium pH were not the same for the different size ranges studied, such that the true effect of particle size could not be measured.

When re-examining the significance of a controlled particle size as a standard requirement for a leaching procedure, the following conclusions are important:

1. The use of the TCLP for monolithic wastes, such as wastes from the mineral processing industries, might overestimate any contaminants leached out of the substrates. The overestimation is due to the unnecessary particle reduction step.
2. The leaching of metals from cementitious wastes in their monolithic form is underestimated. An uncrushed sample of cementitious waste gives a limited release of alkalinity compared to a crushed sample. This will in turn lead to a higher concentration of metals in the leachate due to a lower extent of hydroxide precipitation.

Therefore, the decision of whether or not to include a particle size reduction step in a leaching test is important, and should be linked to the final disposal procedure. It is clear, however, that waste particles of smaller sizes would ensure that a faster equilibration is reached.

3.4. Effect of liquid to solid ratio

The effect of liquid to solid ratio (L/S) on the leachability of metal using 0.1 M acetic acid is shown in Fig. 6. The results show that the leachate pH remained approximately constant at 12.1 as the L/S ratio was increased from 10:1 to 20:1. Further increases in the L/S ratio resulted in a decrease in the leachate pH.

Fig. 6 indicates that Cd was again negligible because of $Cd(OH)_2$ precipitation at high pH. For Pb, its concentration increased as the L/S ratio was raised from 10:1 to 20:1. A further increase of L/S ratio caused a sharp decrease in Pb concentration, falling eventually to an undetectable level at L/S ratio of 60:1. Pb existed as the Pb-hydroxy complexes under relatively highly alkaline conditions when the L/S is less than 20:1. Higher Pb concentration at L/S 20:1 can be attributed to the exposure of the waste to higher absolute level of acidity, thereby leading to a faster release of Pb during the leaching period. As the L/S ratio was further increased, the concentration of Pb decreased because the pH decreased to values where Pb was less soluble. Therefore, at L/S ratios of 10:1 and 20:1 the leachate pH was dominated by the alkalinity of the waste, but as the L/S ratio increased beyond this, the acidic leaching fluid began to exert an influence on the system.

A leaching fluid with relatively higher acid concentration (0.6 M) was used to examine the effect of liquid to solid ratio on the leachability of Cd and Pb from cementitious wastes. As shown in Fig. 7, depending on the L/S ratio, the pH of the 0.6 M acetic acid leaching fluid could change from an alkaline to an acidic condition. Under these conditions, it can
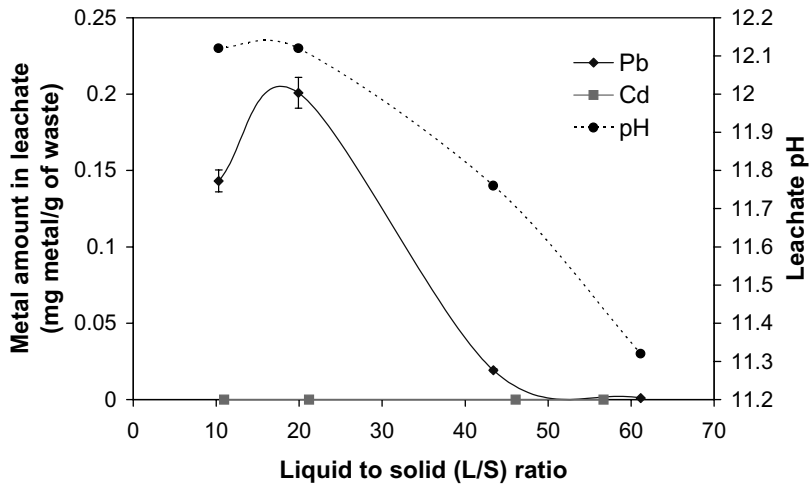
Fig. 6. The amount of Pb and Cd leached out as a function of liquid to solid ratio (L/S) using 0.1 M acetic acid as the leaching fluid, tumbled at a speed of 30 rpm for 18 h (initial Pb and Cd concentrations were 23 and 13 mg/g of waste, respectively).

be seen that the concentrations of both Pb and Cd increased with increasing L/S until a ratio of 40:1 was reached. After that, both the pH and the metal concentrations remained approximately constant. These increased concentrations of Pb and Cd with increasing L/S ratio were caused by both the decrease in pH and the higher amount of acid. The change
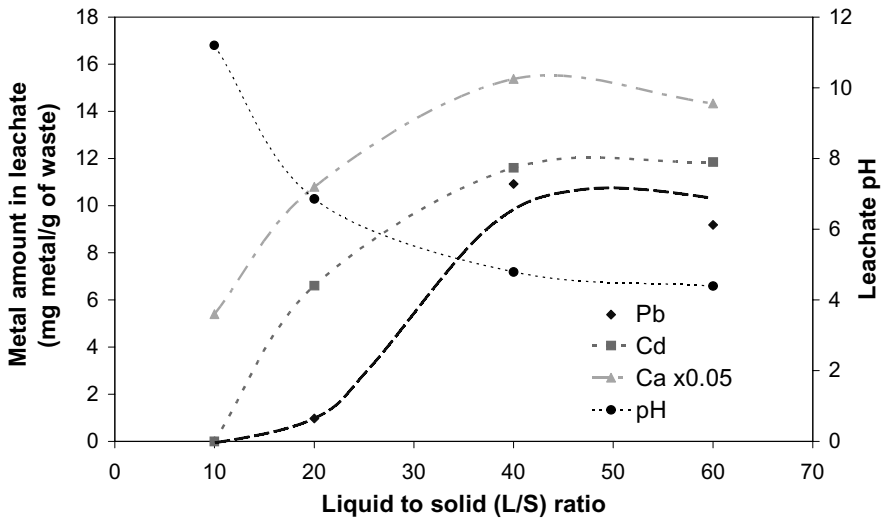

Fig. 7. The amount of Pb, Cd, and Ca leached out as a function of liquid to solid ratio (L/S) using 0.6 M acetic acid as the leaching fluid, tumbled at a speed of 30 rpm for 18 h (initial Pb, Cd, and Ca concentrations were 23, 13, and 340 mg/g of waste, respectively). Ca concentration was multiplied by 0.05.
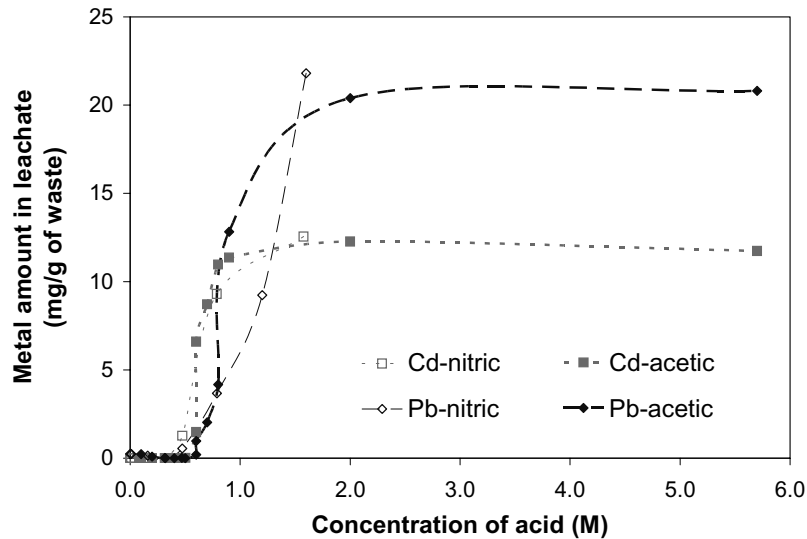
Fig. 8. The amount of Pb and Cd in the leachate as a function of nitric and acetic acid concentrations. The cementitious wastes containing 24 mg Pb/g of waste and 13 mg Cd/g of waste (concentrations of Pb and Cd, were 23 and 13 mg/g of waste, respectively) were tumbled with 0.16–1.6 M nitric acid or 0.1–5.7 M acetic acid (L/S 20) at 30 rpm for 18 h.

in pH governed the solubility of the metal ions, and higher amount of acid increased the destruction of the cement structure as shown by the corresponding increase of Ca.

3.5. Effect of leaching fluid

Nitric acid and acetic acid were compared for their effects on the leaching of Cd and Pb from cementitious wastes. Fig. 8 shows the concentrations of Pb and Cd in the leachate while Fig. 9 shows the concentrations of Ca and Si in the leachate as a function of acid concentration. From the results given in Fig. 8, it can be seen that the amount of Cd in the leachate was comparable at different acid concentrations for the two acids. For Pb, however, differences were observed and a rational explanation can be given for these differences by closely examining the release of Ca and Si from the cementitious waste.

As can be seen from Fig. 9, at acid concentrations less than 1.0 M, the amount of Ca was comparable for both acids. A further increase of acid concentration above 1.0 M led to a higher Ca concentration leached out by the nitric acid than that by the acetic acid. It is postulated that for acid concentrations above 1.0 M, the nitric acid could disintegrate the calcium silicate hydrate (C–S–H) matrix in cementitious waste more effectively. This could be further seen by the increase in the amount of Si to plateaus of 60 and 5 mg/g of waste, respectively, when the concentrations of nitric acid and acetic acid were greater than 1.0 M. In addition, the presence of a gel (identified as silica gel) was observed from the nitric acid leaching, but not so from the acetic acid leaching.
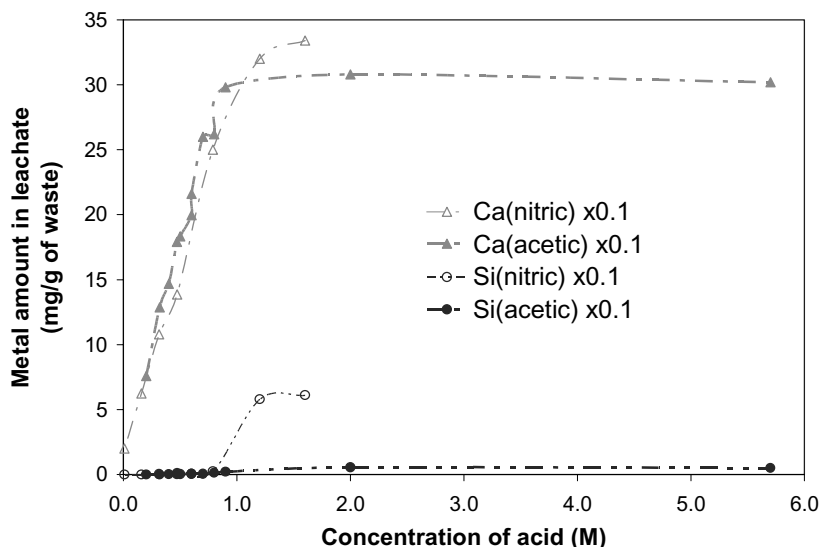
Fig. 9. The amount of Ca and Si in the leachate as a function of nitric and acetic acid concentrations. The cementitious wastes containing Pb and Cd (concentrations Ca and Si are 340 and 75 mg/g of waste, respectively) were tumbled with 0.16–1.6 M nitric acid or 0.1–5.7 M acetic acid (L/S 20) at 30 rpm for 18 h. Ca and Si concentrations were multiplied by 0.1.

The release of Si and the observation of the formation of silica gel are both supportive of the C–S–H destruction in the cementitious wastes. This destruction is further indicated by a greater release of Ca into the leachate when nitric acid was used as a leaching fluid. These observations can be explained by the greater dissociation of nitric acid when compared to acetic acid and thereby resulting a higher H^+ concentration for the same initial acid concentration (upon exhaustion of the cement alkalinity). Measurements of the final leachate pH, as shown in Fig. 10, revealed that a lower final pH was in fact attained with nitric acid as the leaching fluid. Not only does the higher H^+ concentration support the postulation of the destruction of C–S–H, but it also explains the formation of silica gel [37].

The amounts of the Pb and Cd found in the leachate can be linked to the destruction of the C–S–H. For Pb, this can also be linked to its adsorption behaviour on the silica gel that subsequently formed. For Cd, the amount leached was found to be comparable in the two acids at different concentrations. This observation suggests that Cd exhibits the same mechanisms for leaching and precipitation for both leaching fluids. In Section 3.1 it was postulated that Cd is present as $Cd(OH)_2$ in the cementitious waste, either in adsorbed form or deposited in the pores of the cement. This provided the reason for the leachability of Cd to have closely followed the solubility of this $Cd(OH)_2$ as pH was varied. From the observations made in this section, it is postulated that the type of acid did not affect Cd leachability since Cd was not incorporated in the C–S–H matrix, and hence was not influenced by the collapse of the C–S–H. In supporting this postulation, no Cd was found on the silica gel formed during the nitric acid leaching experiments.
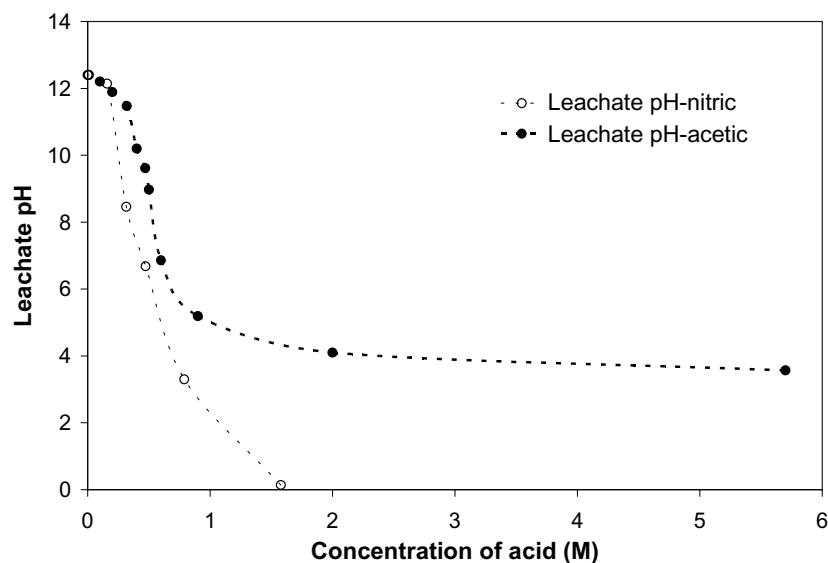
Fig. 10. The effect of acid concentration on the final leachate pH obtained from leaching experiments using cementitious waste tumbled with 0.16–1.6 M nitric acid or 0.1–5.7 M acetic acid (L/S 20) at 30 rpm for 18 h.

From the results of the Pb leaching between acid concentrations of 0.6 and 1.6 M, the Pb in the leachate was higher when using acetic acid as the leaching fluid. At an acid concentration of 1.6 M, the nitric acid leaching fluid led to a greater leaching of Pb. These results are discussed as follows.

The higher amount of Pb in the leachate using acetic acid between 0.6 and 1.6 M may be explained by its adsorption on the silica gel. In order to verify this postulation, a sample of the silica gel formed during a nitric acid experiment was collected and digested. The gel had a Pb content of 4.2% (w/w), which demonstrated the ability of Pb to adsorb onto the silica gel. Cheng [11] has also reported the adsorption of Pb onto the surface of silica during leaching. Hence, Pb adsorption on the silica gel may explain the lower Pb ion concentration detected in the leachate using the nitric acid. At an acid concentration of 1.6 M, the higher Pb concentration in the leachate for the nitric acid system is believed to be due to the high H^+ concentration (as shown in Fig. 10) which resulted in a greater C–S–H collapse compared to the acetic acid system.

In Section 3.1, it was shown that the leachate pH played an important role in determining the concentrations of Pb and Cd in the leachate by governing their solubility. In this section, we build on those findings to include the important role that the initial acid concentration plays in governing leaching.

4. Conclusion

The leachate pH was found to be a primary factor influencing the leachability of metals as it governs the solubility of the metal hydroxides. For Cd, the metal concentrations in

the leachate decreased with increasing leachate pH due to hydroxide precipitation. For Pb, however, due to its amphoteric nature, Pb concentration in the leachate increased for pH greater than 12. Variations in particle size, liquid to solid ratio, and the leaching duration on Pb and Cd leaching from cementitious wastes influenced the leachate pH. By studying the importance of acid type on leaching, it was also found that this does in fact affect the leaching of metals by controlling the concentration of H^+ in the system.

The modified TCLP was not found to simulate the release of heavy metals (Pb and Cd) from cementitious wastes if the wastes were placed in a municipal landfill due to the high alkalinity in the cementitious wastes which buffered the pH at an alkaline pH range. Any leaching test applied to a solidified/stabilised waste has to take the buffering capacity of the waste into account.

Acknowledgements

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