Lead leachability in stabilized/solidified soil samples evaluated with different leaching tests

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Abstract

Leaching tests and model calculations were performed to investigate the immobilization mechanisms of Pb and compare different leaching protocols. Stabilization/solidification (S/S) treatments reduced Pb concentrations in the toxicity characteristic leaching procedure (TCLP) leachate from 5.9 mg/L for untreated soil to less than 0.7 mg/L. The results of eight different leaching protocols show that: (1) the main factor controlling the Pb concentration in the leachate is the final pH; (2) the final pH is a function of the leachant acidity; and (3) for a given final pH, the type of leachant has a relatively minor effect on leachability. The diffuse layer adsorption model, aqueous and precipitation reactions were employed in the MINTEQA2 program to describe the Pb leaching behavior. Both leaching tests and model simulations indicate that the Pb leaching behavior can be divided into three stages based on the leachate pH: a high alkalinity leaching stage at pH > 12, where Pb formed soluble hydroxide anion complexes and leached out; a neutral to alkaline immobilization stage in the pH range of 6–12, which was characterized by low Pb leachability caused by adsorption and precipitation; and an acid leaching stage with pH < 6, where the acid neutralizing capacity (ANC) of the S/S materials was totally consumed and therefore free Pb-ion leached out.
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1. Introduction

Stabilization/solidification (S/S) technology has been widely applied to immobilize heavy metals in contaminated soils, sediments, and sludge with additives such as cement, lime, and fly ash [1]. Quantifying the environmental impact of stabilized/solidified materials in real environmental scenarios is crucial for selecting proper disposal and reuse alternatives and for certification of immobilization technologies. The performance of S/S-treated wastes is generally measured in terms of leaching tests. Although numerous leaching tests are available to evaluate the S/S treatment, no single test can describe the complex leaching behavior of the treated materials.

The toxicity characteristic leaching procedure is the most commonly used regulatory protocol. However, it may under-estimate the leachability of some redox sensitive elements, such as As, since redox reactions may happen during the extraction [2]. The multiple extraction procedure (MEP), the availability test (NEN 7341), and sequential chemical extraction are also applied to a wide range of materials for different purposes, which creates confusion in how the results are to be interpreted and which extraction test should be used in determining the leachability. An approach to harmonize different leaching tests was proposed by van der Sloot [3]. However, the interpretation of different protocols is dependent on an accurate understanding of leaching mechanisms. This requires validation of the consistency of results between different types of test methods and different types of wastes.

Pb is the most common contaminant in the environment and has chronic toxicity. Pb contamination has been found in 604 out of 1221 superfund sites on the National Priorities List (NPL). There have been intensive studies about Pb immobilization mechanisms in S/S-treated wastes. In a review of heavy metal immobilization in ettringite and the calcium

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silicate hydrate (C-S-H) matrix of Portland cement, Gougar et al. [4] reported that Pb could replace Ca^{2+} in ettringite, but not in the C-S-H structure where Pb is immobilized by precipitation as hydroxide and carbonate. Pb stabilization in cement-treated materials is attributed to fast precipitation of lead compounds at the surface of colloidal materials during cement hydration [5,6]. This Pb precipitation layer acts as a diffusional barrier to water [7]. When the concentration is below the solubility of lead oxides, Pb is directly linked to C-S-H [8]. Previous studies show that leachate pH is the major factor in controlling Pb leachability [3,6,9–11]. Low Pb concentrations are observed in the neutral and basic pH range. Pb concentrations increase when pH changes to an extremely low or high value. This amphoteric behavior is the consequence of solubilization phenomenon at the solid–liquid interface [11–13].

Modeling of leaching behavior can improve the understanding of the leaching mechanisms and prediction of the long-term leachability. Pb solubility in groundwater and cement pore water was predicted by a modified MINTEQ2 database [14]. A surface complexation model was used to simulate Pb leaching behavior with an assumption that besides the principal sorbent of hydrous ferric oxide, other sorbent minerals were also responsible for the adsorption [15]. In this study, Pb-contaminated soil was treated with four binders and Pb leachability in the solid samples was evaluated with eight extraction tests. The diffuse layer model (DLM) was employed to describe the Pb leaching behavior.

2. Materials and methods

2.1. Sample preparation

Pb-contaminated soil samples were collected from the Central Steel (CS) site in Newark, New Jersey. The 12-acre site is an abandoned drum reconditioning recycling facility with several large metal buildings on the lot. The samples were sieved with a No. 4 sieve (4.75 mm opening size) to remove the coarse material at the site. The sieved samples were air dried and stored in capped containers to maintain the moisture constant.

S/S treatment was performed by mixing soil samples with 10% cement (weight of cement/weight of dry soil) (10%C), 25% cement (25%C), 10% lime (10%L), and a mixture of 20% flyash and 5% lime (FL), respectively. The solid mixtures were compacted at optimum water content according to the ASTM D 1557-91 standard. The compacted specimens were stored in sealed sample bags and cured at room temperature for 28 days. After the samples were tested for unconfined compressive strength, the solids were pulverized to pass through No. 40 sieve (0.425 mm opening size) and used in batch extraction tests. Small particles could ensure that a faster equilibrium is reached [9,16] and minimize the encapsulation effect by which the heavy metals are physically entrapped in a monolithic solid.

Total metal contents in the samples were determined by digesting 1.00 g of solid using 1:1 HNO_3, concentrated HNO_3, and 30% H_2O_2 repeatedly on a hot plate [17]. After cooling, the digested samples were diluted to 100 mL with deionized (DI) water for analysis of total metal content by furnace atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) emission spectrometry.

2.2. Leaching tests

Eight leaching methods were used to evaluate the leaching potential of lead in untreated and treated sludge samples as follows.

(1) Toxicity characteristic leaching procedure. According to the U.S. EPA protocol [18], two types of extraction solution were used. A 0.1 M acetic acid solution with a pH of 2.88 was used to extract S/S-treated samples due to the high alkalinity of the wastes. An extraction solution comprised of 0.1 M acetic acid and 0.0643 M NaOH with a pH of 4.93 was used for untreated soil. The waste samples were extracted at a liquid to solid (L/S) ratio of 20 in capped polypropylene bottles on a rotary tumbler at 30 rpm for 18 h. After the extraction, the final pH of the leachate was measured and the liquid was separated from the solids by filtration through a 0.45 μm glass fiber filter.

(2) General acid neutralizing capacity test (GANC). This test was modified from Isenburg and Moore [19]. Eleven single batch extractions were performed in parallel. The amount of acetic acid in the extraction system varied from 0 to 4 eq/kg of solids in increments of 0.4 eq/kg. After 48 h tumbling at a L/S ratio of 20, the equilibrium pH and soluble Pb concentration were measured.

(3) Extended TCLP (Ext TCLP). This test was developed based on the TCLP and GANC tests to assess heavy metal leachability over a wide pH range. Ten identical suspensions of TCLP leachant and solid sample at a L/S ratio of 20 were prepared in 10 bottles. Different amounts of HCl or NaOH solution were added to the bottles so that the final pH values were distributed between 3.5 and 12.5 after 18 h of mixing. The other extraction procedures were the same as the TCLP.

(4) DI water extraction. This method simulates scenarios where a waste is in contact with an acid solution having a low buffering capacity such as rainwater. The extraction procedure was the same as TCLP except that DI water was used as leachant. An extended DI water extraction test was also performed over an equilibrium pH range between 3 and 12.

(5) Multiple extraction procedure (MEP) [20]. This test simulates leaching conditions that occur when a waste undergoes repetitive acid rain leaching in an improperly designed sanitary landfill. In the first step, waste samples were extracted according to the EP Tox where the solids were extracted with acetic acid solution at a L/S ratio of

16 for 24 h [21]. The suspension pH was controlled at 5 by addition of 0.5N acetic acid during the extraction. The residual solids after the EP Tox extraction were re-extracted nine times consecutively using synthetic acid rainwater which is a dilute H_2SO_4 and HNO_3 solution (H_2SO_4:HNO_3 = 3:2) with a pH of 3. Each extraction step was performed at a L/S ratio of 20 for 24 h. The final leachate pH and Pb concentrations were measured for each extraction.

(6) Availability test NEN 7341 [22]. The availability for leaching is determined by two consecutive extractions of a finely ground material at a L/S ratio of 50. If the solution is alkaline or neutral, 1 M HNO_3 is added to keep the pH at 7 during the first 3 h of mixing. If the pH of the solution is less than 7, no acid is added. After separation, the solid phase is extracted for another 3 h at pH 4. Finally, the two extraction solutions are combined together for analysis and the acid neutralizing capacity (ANC) is calculated based on the amount of the acid added during the extraction.

(7) Sequential chemical extraction. According to Tessier's method [23], Pb can be classified into the following five operationally defined fractions in soils:

F1-exchangeable: The sample was extracted for 5 h with 0.5 M $MgCl_2$ at pH 7.0 and a L/S ratio of 8.

F2-bound to carbonates: The residual from F1 was extracted with 1 M NaAc at pH 5 and a L/S ratio of 8 for 5 h.

F3-bound to iron and manganese oxides: The residual from F2 was extracted with 0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HAc for 6 h at 96 °C. The initial pH was 2.0 and the L/S ratio was 20.

F4-bound to organic matter: The residual from F3 was extracted with 30% H_2O_2 for 6 h at 85 °C, then extracted with 3.2 M NH_4Ac in 20% (v/v) HNO_3 with continuous agitation for 30 min.

F5-residual: This fraction was calculated from the difference between the total Pb content and the first four fractions.

(8) Infiltration test. Infiltration leaching is simulated with a flow-through leaching system to enable the prediction of heavy metal release in the field. A S/S specimen with 2 cm height and 5 cm diameter was placed in a confined chamber. During the experiment, a 0.014 M acetic acid solution at pH 3.45 was passed through the specimen under constant hydraulic head conditions. The infiltrate leachate was collected regularly to measure the volume of the leachate, solution pH, and heavy metal concentrations.

2.3. Surface complexation modeling

The adsorption diffuse layer model (DLM) was employed to describe the leachability of Pb and to determine the predominant Pb forms in untreated and treated soil samples in the pH range of 3–12. The computer program MINTEQA2 [24]

was used to simulate adsorption, precipitation and aqueous reactions.

In the modeling simulation, FeOOH was assumed to be the adsorbent in the soil. Since iron has a variety of forms in soil and their adsorption capacities are different [25], the total effective adsorption site concentration in the soils was determined to be 1 mM by fitting the Ext TCLP result with FITEQL32 [26], a computer program that combines a nonlinear least squares fitting routine with chemical equilibrium and adsorption models. All the aqueous and adsorption reactions with the associated constants used in FITEQL32 were the same as those in MINTEQA2 database. The only optimizing parameter in FITEQL32 was the total surface site concentration. The indicating parameter of goodness-of-fit by FITEQL, WSOS/DF, was 3.38. A WSOS/DF value within the range of 0.1–20 is considered to be a reasonably good fit [26].

3. Results and discussion

3.1. Lead leachability

The total acid digestion results listed in Table 1 indicate that the untreated soil sample contained 172.6 g/kg of iron and 3.8 g/kg of lead. The chemical composition of the sample treated with 10% cement (10%C) is also presented in Table 1. The treated sample contained high calcium (55.4 g/kg) and magnesium (4.4 g/kg). Lead and iron contents decreased to 3.6 and 168.8 g/kg, respectively, because of the dilution by cement. Cement treatment increased the pH from 7.8 for the untreated soil to 11.7. The water content decreased from 8% in untreated soil to 5% in the 10%C sample because of the consumption of water by cementitious reactions and evaporation loss during the mixing of cement with the soil.

3.1.1. TCLP and DI water extraction

The TCLP Pb concentration was 5.9 mg/L of leachate for untreated soil, which was higher than the regulatory limit of 5 mg/L for hazardous waste (Table 2). The four S/S treatments, 10%C, 25%C, 10%L, and FL, reduced the TCLP concentration to less than 0.7 mg/L, which was well below the TCLP limit. The effectiveness of the S/S treatment was in the order 25%C > FL > 10%L > 10%C > untreated based on the TCLP results. In contrast to the high TCLP leachability, DI water only extracted 9 µg/L Pb from untreated soil (Table 2). However, Pb leachability in the S/S-treated samples was higher than that of untreated soil as determined with DI

Table 1
Physical and chemical properties of untreated and treated (10%C) CS samples

	pH	Water content (wt.%)	Total metal content (g/kg) (wet)					
			Pb	As	Ca	Fe	Mg	Mn
Untreated	7.8	8	3.8	0.014	7.7	172.6	2.1	2.0
10%C	11.7	5	3.6	0.011	55.4	168.8	4.4	1.9

Table 2
Unconfined compressive strength and leaching results determined with TCLP, DI water extraction and NEN 7341

	Untreated	10%C	25%C	10%L	FL
Strength (psi)	27	114	657	59	77
TCLP					
pH	5.17	5.68	11.32	11.68	7.21
Pb (µg/L)	5900	699	2	43	8
DI					
pH	7.68	12.01	12.55	12.43	10.83
Pb (µg/L)	9	101	96	1024	28
NEN 7341					
Availability (mg/kg)	137.6	784.0	315.6	1428.1	304.1
ANC (mol/kg)	0.51	2.12	5.11	3.95	2.84

water extraction, ranging from 28 µg/L for FL to 1024 µg/L for the 10%L sample. According to the DI water extraction, the sequence of treatment efficiency was changed to untreated > FL > 25%C > 10%C > 10%L. This lack of agreement between the Pb leachability determined with TCLP and DI water extraction suggested that the leaching results could only be interpreted under their own experimental conditions.

3.1.2. Infiltration test

The infiltration test was a dynamic leaching test that simulated a field where natural water or groundwater was constantly renewed and the waste alkalinity was progressively removed. The infiltration leachate Pb concentration was plotted as a function of pH as shown in Fig. 1. It was obvious that Pb leachability was dependent on the leachate pH which continuously decreased as the result of increasing cumulative leachant acidity. Both S/S-treated samples and untreated soil have a similar "U" shape concentration versus pH curve, which represents the amphoteric property of Pb solubility over a wide pH range. This observation is in agreement with previously reported results [3,6, 9–13]. Based on the equilibrium leachate pH, the S/S-treated material underwent three leaching stages when it contacted water: first, the high alkalinity leaching stage occurred at pH > 12, where highly alkaline
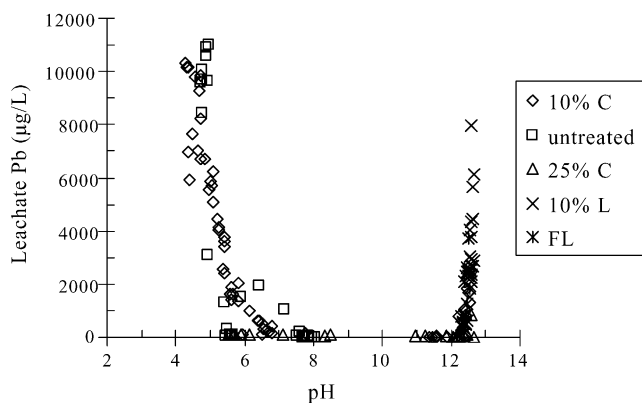

Fig. 1. Infiltration leachate concentration results for untreated and S/S-treated samples.

materials in the treated solids increased the equilibrium pH to an extremely high level and lead was released as soluble hydroxide anion complexes. The second stage was the neutral to alkaline immobilization stage where pH was in the range of 6–12, which was characterized with low lead leachability, due to adsorption and precipitation. The third phase was defined as the acid leaching stage, where the acid neutralizing capacity of the S/S materials was totally consumed and free metal ions were leached out.

The TCLP pH was 5.17 for untreated soil (Table 2), which was in the acid leaching stage (Fig. 1). The pH of the DI water extraction was 7.68, which was in the neutral to alkaline immobilization stage. The difference of Pb leachability determined with these two leaching tests, 5.9 mg/L with TCLP and 9 µg/L with DI, could be explained by the two different stages the methods led to. For the treated materials, the leachate pH with DI was much higher than that of the TCLP, and could be higher than 12 or in the high alkalinity leaching stage (Table 2). So these two batch tests could result in Pb leaching behavior in different leaching stages. TCLP is the regulatory test to classify hazardous materials, but it may fail to predict Pb release under highly alkaline conditions. The high final pH situations are often found when natural groundwater with low acidity contacts S/S-treated materials at a low L/S ratio. Therefore, DI water extraction should be performed in order to simulate the scenarios where low pH buffer leachant reacts with high alkalinity materials.

In order to evaluate the S/S treatment with the infiltration test, detailed results were plotted in Fig. 2 for untreated soil and the 25%C sample. The results in Fig. 2A show that the initial leachate pH of untreated soil was around 7.7 and remained constant until a cumulative leachate volume to sample weight ratio (v/w) of 5, corresponding to 0.05 eq H^+/kg of cumulative leachant acidity. Then, pH began decreasing to about 5.7 and remained unchanged through v/w of 18. During this pH drop, the Pb concentration reached a small peak of 1.9 mg/L at v/w of 6.4, and then reduced to less than 30 µg/L at v/w of 10. The concurrence of the Pb concentration peak and pH drop was due to the release of leachable Pb in the pH range between 7.7 and 5.7. Similar leaching behavior was also observed by Catalan et al. [27]. The Pb concentration was low in the v/w range of 10–20 because most of the readily leachable Pb at pH 5.7 had been released (Fig. 1). When the pH decreased to approximately 5.5 at v/w of 20 (acidity = 0.22 eq H^+/kg), the Pb concentration began to increase exponentially. The leachate Pb concentration reached a maximum of about 11.0 mg/L at v/w of 69.

A high initial pH of 12.18 was observed in the infiltration leachate for the 25%C sample (Fig. 2B) and the two subsequent leachate pH values were even higher at 12.58 and 12.68, respectively. Then the pH decreased slowly to 11.43 during the experiment due to the excess calcium hydroxide in 25%C sample. The initial Pb concentration was 29 µg/L, and increased to a maximum of 834 µg/L with the occurrence of the highest leachate pH of 12.68 at a v/w ratio of 1.1. Then the Pb concentration decreased and remained lower

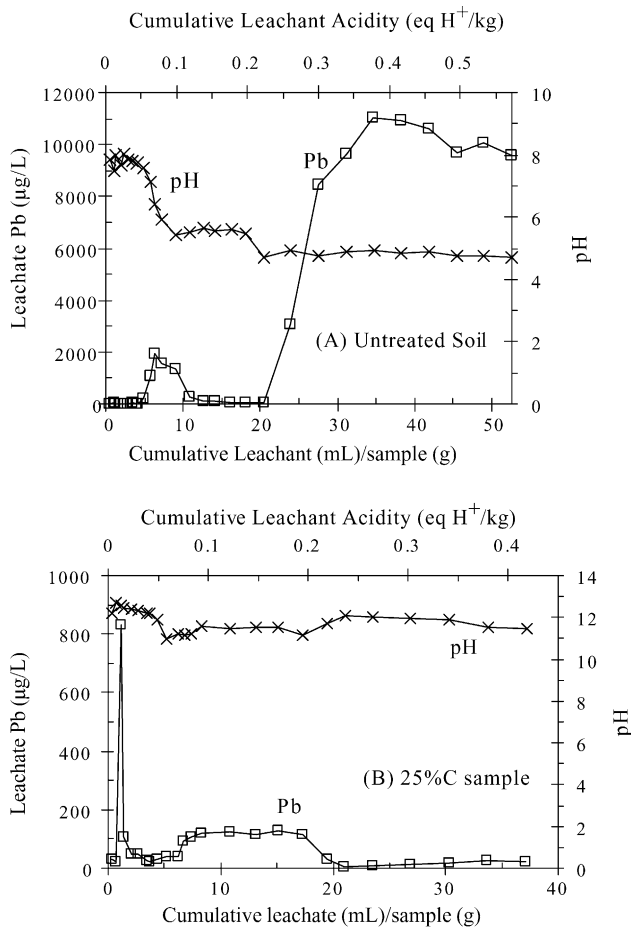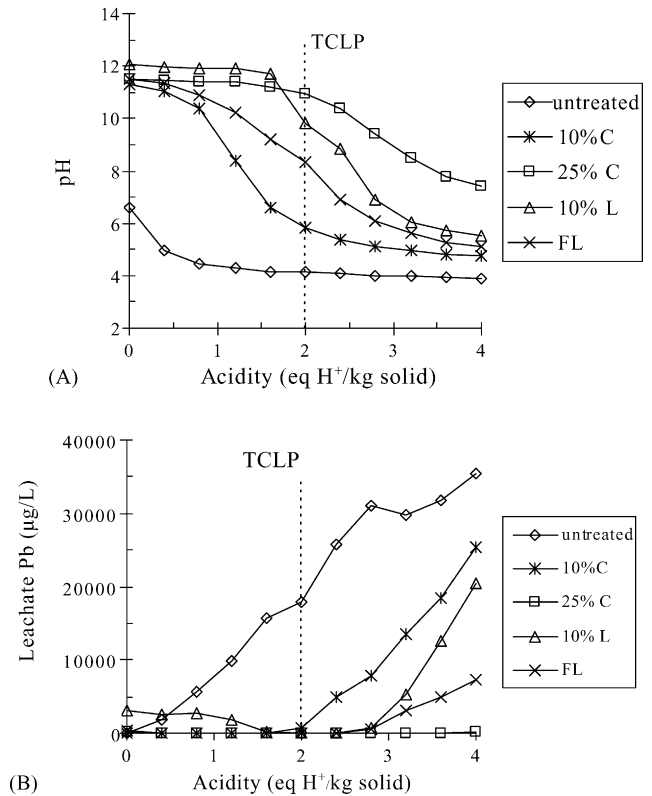Fig. 2. Infiltration results for untreated soil (A) and 25%C sample (B).

Fig. 3. The change of pH (A) and leachate Pb concentration (B) with increasing leachant acidity for untreated and treated samples determined with GANC.

than 130 μg/L thereafter. This initial sharp peak represented the high alkalinity leaching stage occurring with 25%C. The lag of this peak may be caused by slow dissolution kinetics in the heterogeneous infiltration test. When the v/w ratio was between 5 and 20, a temporary pH decrease occurred, which could be attributed to the micro-channeling effect.

3.1.3. GANC test

GANC was a single extraction test where an increasing amount of acetic acid was used to determine the ANC and the metal leachability [19]. The GANC results in Fig. 3A indicated that the untreated soil could not resist acid attack, and its pH decreased to less than 5 at a leachant acidity of 0.4 eq H$^+$/kg. The pH of S/S-treated samples began to decrease at an acidity of 0.4 eq H$^+$/kg for the 10%C and FL sample, 1.6 eq H$^+$/kg for the 10%L sample, and 2 eq H$^+$/kg for the 25%C sample. The leachate Pb concentrations of S/S-treated samples at acidity 2 eq H$^+$/kg were comparable for GANC and TCLP, since the equilibrium pH was in the immobilization stage with both tests. However, the GANC Pb concentration was 17.8 mg/L for untreated soil at acidity 2 eq H$^+$/kg, which was much higher than that in the TCLP leachate. This result was not surprising when the equilibrium pH of the two

tests was compared: 5.17 for TCLP and 4.14 for GANC. The higher pH in TCLP was the consequence of adding NaOH to the extraction solution to bring the leachant pH to 4.93 as specified in the protocol [18]. Based on Fig. 1 when leaching behavior was in the acid leaching stage at pH < 6, the leachability increased exponentially with decreasing pH. Pb was readily released once there was acid attack in untreated soil (Fig. 3B), and the leachate Pb concentration increased significantly with increasing leachant acidity. The S/S treatment increased the ANC of the solid materials so that the wastes could resist attack of higher acidity. At an acidity of about 2 eq H$^+$/kg, Pb was released from the 10%C sample, while the acidity value for Pb release was 2.8 eq H$^+$/kg for 10%L and FL, and higher than 4 eq H$^+$/kg for the 25%C sample.

In order to understand the relation of leachant acidity with long-term leaching potential, a simplified calculation was performed. The acidity of different types of water was assumed to be the following [28]:

Rainwater acidity = 100 μeq/L (5 mg/L as CaCO$_3$)
Landfill leachate acidity = 100 meq/L (5000 mg/L as CaCO$_3$)
Groundwater acidity = 1000 μeq/L (50 mg/L as CaCO$_3$)

It was assumed that average rainfall = 1.0 m/year, the leachate velocity = 1.0 m/year = 1.0 m^3/m^2 surface year if all

the rainfall penetrates the waste evenly rather than running off. Thus, the amount of acidity due to rainfall, landfill leachate, and groundwater can be calculated as 100, 100,000 and 1000 meq H^+/m^2 year, respectively. If the waste is 3 m thick with an average density of 1922 kg/m^3, the acidity contributed by rainfall, landfill leachate and groundwater would be 1.73E−5, 1.73E−2, and 1.73E−4 eq H^+/kg waste year, respectively. Therefore, the TCLP with acidity = 2 eq H^+/kg would represent the acidity added for about 114 years if the above three acidity contributors act together. However, in the flow-through system, readily soluble Ca and Mg components of the wastes will be washed out and cannot take part in the neutralizing reaction [27,29,30]. Thus, only one-third of the ANC determined from batch tests could be used for the neutralizing reaction in the flow-through system. This ratio was derived independently based on experimental data [29,30] and theoretical calculations [27]. If pH < 6 stands for the acid leaching stage where waste solids lose all their alkalinity, the acidity required to reach this pH value was <0.4, 2, 2.8, 3.2 and >4 eq H^+/kg for untreated, 10%C, FL, 10%L and 25%C, respectively (Fig. 3A). If the washout effect was considered and only one-third of the solid waste alkalinity was effective for neutralization, the time frame to resist the overall acid attack was estimated to be <8, 38, 54, 62, and >77 years for untreated, 10%C, FL, 10%L and 25%C, respectively. This simplified calculation showed that 25%C treatment can resist long-term acid attack and therefore is the best treatment for Pb immobilization.

3.1.4. Availability test

According to the NEN 7341 results presented in Table 2, the available Pb content was 137.6 mg/kg in untreated soil. If this amount of lead was dissolved in the TCLP extraction, the TCLP concentration would be as high as 6.9 mg/L which was in the same order of magnitude as the TCLP (5.9 mg/L). The Pb leachability determined with NEN 7341 for S/S-treated samples was much higher than that of the TCLP. No correlation was found between leaching results determined with TCLP and NEN 7341. The availability test indicated the amount of a particular component that might leach out from a material under extreme circumstances (such as in the very long-term, after disintegration of the material, full oxidation and loss of acid neutralization capacity) [22]. It can only measure the portion that was not bound in the silicate matrix and poorly soluble minerals [3]. Since the NEN 7341 leachate was the mixture of two solutions at pH 4 and 7, the result did not indicate what leaching stage the test represented and did not reveal solubility information.

It was interesting to note that based on the results of NEN 7341, S/S treatment increased the availability of Pb (Table 2). This might be explained by the operational procedure of the NEN 7341 protocol. The amount of available Pb was calculated on the basis of two consecutive extractions at pH 7 and 4. The S/S-treated materials consumed more acid than untreated soil. Since the 3 h leaching time may not be long

Table 3
Chemical forms of Pb in the treated and untreated samples

Chemical forms (%)	Untreated	10%C	25%C	10%L	FL
Exchangeable	0.01	0.02	0.11	0.40	0.01
Bound to carbonates	29.11	20.21	0.05	4.42	7.33
Bound to Fe–Mn oxides	57.16	56.00	52.00	62.42	36.42
Bound to organic matter	8.56	7.04	10.85	20.25	13.91
Residual	5.16	16.73	36.99	12.50	42.33

enough to reach equilibrium [31], the availability obtained would not be under steady state conditions.

In addition to the available Pb concentration, NEN 7341 can also be used to determine the ANC of the materials. The S/S treatment increased the ANC from 0.51 mol/kg in untreated soil to as high as 5.11 mol/kg in the 25%C sample (Table 2). NEN 7341 obtained slightly higher ANC values than the GANC test (Fig. 3), which could be attributed to the second extraction step of NEN 7341 with a more aggressive solution at pH 4.

3.1.5. Sequential extraction test

The sequential extraction results in Table 3 show that the amount of exchangeable Pb accounted for only 0.01% of the total Pb in the untreated soil. Most of the Pb in untreated soil was bound to carbonates (29%) and Fe–Mn oxides (57%). This suggested that Pb may be present as lead carbonate minerals, such as cerussite or hydrocerussite, or adsorbed on iron oxides which were abundant (172.6 g Fe/kg) in untreated soil (Table 1). Only 5% of the Pb was in the residual form that would be released only when the solid was completely dissolved. The S/S treatment decreased the amount of Pb associated with carbonates and increased the amount of residual Pb. It is most likely that lead carbonate minerals were transformed to more stable hydroxide precipitates under high pH condition with the excess hydroxide provided by cement. This result was in agreement with a previous study of Pb containing sludge stabilized with cement [32].

According to the total Pb content of 3.8 g/kg (Table 1) and the exchangeable Pb in untreated soil, the Pb concentration in the TCLP leachate would be 19 μg/L if only the exchangeable Pb were released in the TCLP test. The observed Pb concentration in the TCLP leachate was 5.9 mg/L for untreated soil (Table 2), suggesting the release of other Pb forms. In contrast to the slight increase of exchangeable Pb fraction, the TCLP leachability of Pb in S/S-treated samples decreased significantly (Table 2). The decreased Pb in the TCLP leachate was coincident with the increased solution pH to the neutral to alkaline immobilization stage. This result demonstrated that the Pb concentration in the TCLP leachate was controlled by the leachate pH rather than by the amount of exchangeable Pb.

The amount of exchangeable Pb in untreated soil (38 mg/kg) was much less than the available Pb (137.6 mg/kg, 3.62%) determined with NEN 7341, which was lower than the carbonate and Fe–Mn forms (Table 3). In S/S-treated sam-

ples, no correlation was found among TCLP, DI water extraction, NEN 7341, and the different Pb fractions. The principle of the sequential extraction test is that a series of increasingly more aggressive extraction solutions are applied successively. Ideally, only the metal from a particular matrix should be released and other forms of metal should remain in the solids. However, these assumptions may not be true in practical systems [32]. The sequential extraction was originally developed for sediment and its application for S/S-treated wastes needs further study.

3.1.6. MEP test

The multiple extraction procedure was designed to simulate the leaching that a waste would undergo with repetitive infiltration leaching of acid rain on an improperly designed sanitary landfill. MEP results in Fig. 4 show that 4.8 mg Pb/L on average was leached out each time in nine consecutive extractions in untreated soil. The equilibrium pH in each extraction was around 4. The Pb concentrations varied from 0.6 to 137 μg/L for treated samples. Thus, S/S treatment can resist multiple acid rain leaching based on MEP results. The "U" shape curve obtained from MEP (Fig. 4) was similar to that obtained from infiltration results (Fig. 1), which supported the supposition that the leaching stage was controlled only by the equilibrium leachate pH, regardless of leaching protocols.
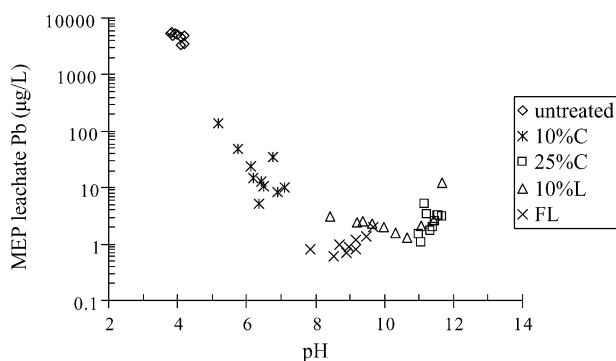

Fig. 4. Pb leaching behavior determined with the multiple extraction procedure for untreated and treated samples.

3.2. Mechanisms of Pb immobilization

Pb has been considered to be chemically stabilized in the S/S-treated matrix, with physical solidification playing a minor role [7]. Solubility was previously used to explain the amphoteric characteristic of lead leachability [11,14]. A surface complexation model was successfully employed to describe lead leaching behaviors in S/S-treated materials [15]. In this work, the mechanisms of Pb immobilization were studied with the diffuse layer model.

Surface parameters and equilibrium constants used in the DLM were from the standard database in the chemical equi-

Table 4
Reactions and parameters used in the model calculations

| Reactions		Equilibrium expressions	$\log K$
Surface and solution parameters			
Adsorbate (Pb) = 0.917 mM			
Adsorbent FeOOH = 13.69 g/L			
Total surface site (SOH) = 1 mM			
Ionic strength = 0.1 M			
Surface area = 600 m^2/g			
Surface complexation reactions			
$SOH + Pb^{2+} = SOPb^+ + H^+$	(1)	$K = \exp(F_{\psi_0}/RT)[SOPb^+][H^+]/[SOH][Pb^{2+}]$	4.65
$SOH + H^+ = SOH_2^+$	(2)	$K_{a1} = \exp(F_{\psi_0}/RT)[SOH_2^+]/[SOH][H^+]$	7.29
$SOH = SO^- + H^+$	(3)	$K_{a2} = \exp(-F_{\psi_0}/RT)[SO^-][H^+][SOH]$	−8.93
Aqueous reactions			
$Pb^{2+} + H_2O = PbOH^+ + H^+$	(4)		−7.597
$Pb^{2+} + 2H_2O = Pb(OH)_{2(aq)} + 2H^+$	(5)		−17.094
$Pb^{2+} + 3H_2O = Pb(OH)_3^- + 3H^+$	(6)		−28.091
$Pb^{2+} + 4H_2O = Pb(OH)_4^{2-} + 4H^+$	(7)		−39.699
$2Pb^{2+} + H_2O = Pb_2(OH)^{3+} + H^+$	(8)		−6.397
$3Pb^{2+} + 4H_2O = Pb_3(OH)_4^{2+} + 4H^+$	(9)		−23.888
$4Pb^{2+} + 4H_2O = Pb_4(OH)_4^{4+} + 4H^+$	(10)		−19.988
$Pb^{2+} + Ac^- = PbAc^-$	(11)		2.68
$Pb^{2+} + 2Ac^- = Pb(Ac)_2$	(12)		4.08
$Pb^{2+} + 2CO_3^{2-} = Pb(CO_3)_2^{2-}$	(13)		9.938
$Pb^{2+} + CO_3^{2-} = PbCO_{3(aq)}$	(14)		6.478
$Pb^{2+} + CO_3^{2-} + H^+ = PbHCO_3^+$	(15)		13.200
Precipitation reactions			
$Pb^{2+} + CO_3^{2-} = PbCO_{3(s)}$	(16)		13.130
$3Pb^{2+} + 2CO_3^{2-} + 2H_2O = Pb_3(CO_3)_2(OH)_{2(s)} + 2H^+$	(17)		18.771
$Pb^{2+} + 2H_2O = Pb(OH)_{2(s)} + 2H^+$	(18)		−8.150
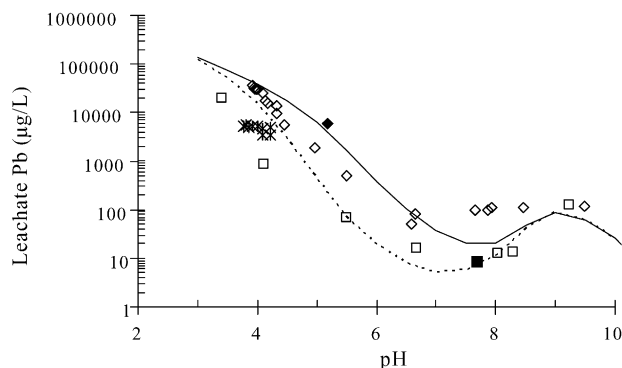
Fig. 5. Thermodynamic calculations and experimental lead leachability in untreated soil determined with TCLP (♦), DI (■), MEP (✳), Ext TCLP (◇), Ext DI (□), and infiltration (×). The solid (dashed) line is the model with (without) 0.1 M HAc.

Fig. 6. Model prediction and Ext TCLP (◇) results of Pb distribution in untreated soil.

librium program MINTEQA2 (Table 4) [24]. Pb adsorption on the surface was described by Eq. (1) in Table 4:

$$SOH + Pb^{2+} = SOPb^+ + H^+ \quad \log k = 4.65$$
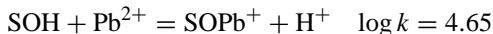
where "SOH" in the reactions denotes the surface hydroxyl sites and "SOPb$^+$" represents lead surface complexes. The surface complexation reactions and associated equilibrium constants as shown by Eqs. (1)–(3) in Table 4 are based on the work of Dzombak and Morel [33], and are included in MINTEQA2. Aqueous complex reactions of Pb with OH$^-$, acetate, and carbonate were considered in the calculations as shown by Eqs. (4)–(15). Precipitation reactions were also included in the model. Cerussite (PbCO$_3$(S)), hydrocerussite (Pb$_3$(CO$_3$)$_2$(OH)$_2$(S)) and Pb(OH)$_2$(S) were considered as possible lead precipitation products as shown by Eqs. (16)–(18) in Table 4. All reaction constants were from the MINTEQA2 standard database. According to the total Pb content in the soil (Table 1) and the L/S ratio of 20 used in the extraction, the total Pb concentration in the extended TCLP system was 0.917 mM. An ionic strength of 0.1 M was used in the calculations. The carbonate content in untreated soil was determined with the ASTM D4373-96 standard method to be 0.02 g as CaCO$_3$/g solid. The amount of carbonate in the TCLP solution was then calculated to be 0.01 M at a L/S ratio of 20.

The leachate Pb concentrations obtained with the Ext TCLP test for untreated soil were used to calibrate the DLM because the curve extended over a wide pH range (Fig. 5). The extended DI water extraction results were also used as a complementary restraint of the model. The DLM calculation fitted the untreated Pb concentrations well (Fig. 5). The model demonstrated that the Pb concentrations in the extended DI water extraction could be lower than that of the acetic acid leaching when pH < 8. Pb could form complexes with acetate according to Eqs. (11) and (12) in Table 4, which would compete with the adsorption reaction. When pH > 8, the same Pb concentrations were obtained for DI and TCLP extraction, since no Pb–Ac complex was formed. The model-calculated Pb distribution diagram in Fig. 6 showed that Pb was adsorbed
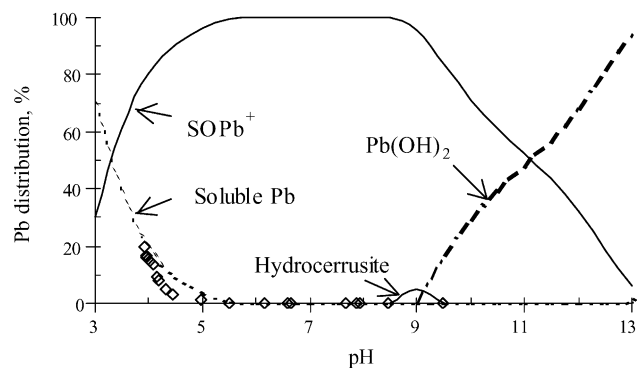
by forming a SOPb$^+$ surface complex in the pH range from 6 to 9. At pH 9, 4.8% Pb was precipitated as hydrocerussite. Pb(OH)$_2$ began to precipitate at pH 9 and became the predominant Pb species when pH > 11. From pH 12 to 13, 0.01–0.84% of total Pb could dissolve as Pb(OH)$_4^-$ which increased the soluble Pb concentration from 19 to 1596 μg/L. Greater than 0.2% Pb was dissolved when pH < 6 and the soluble Pb concentration increased significantly when pH decreased from 6 to 3. The model explained the observed three leaching stages well.

The DLM was used to predict the leachability of Pb in the 10%C sample. Based on the total Pb content in the 10%C sample (Table 1), the total lead concentration in the TCLP extraction system was 0.87 mM, and the calcium concentration was 67 mM. However, only 10 mM Ca was available even at the low pH of 4.29 in the Ext TCLP. This was because some calcium was associated with cementitious reaction products such as calcium silicate hydrate. So the available 10 mM Ca was input into the MINTEQA2 program as the total calcium. The carbonate concentration was 0.04 g as CaCO$_3$/g solid, which corresponds to 0.02 M in TCLP solution.

The model and experimental results are presented in Fig. 7 for the 10%C sample. The DLM predicted the leaching behavior of lead reasonably well. When acetic acid was con-
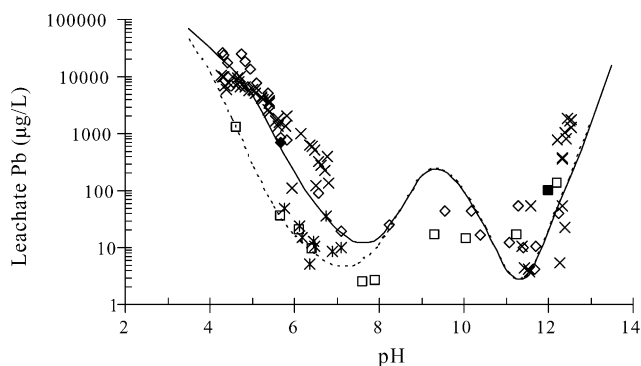

Fig. 7. Thermodynamic calculations and experimental lead leachability in the 10%C sample determined with TCLP (♦), DI (■), MEP (✳), Ext TCLP (◇), Ext DI (□), and infiltration (×). The solid (dashed) line is the model with (without) 0.1 M HAc.
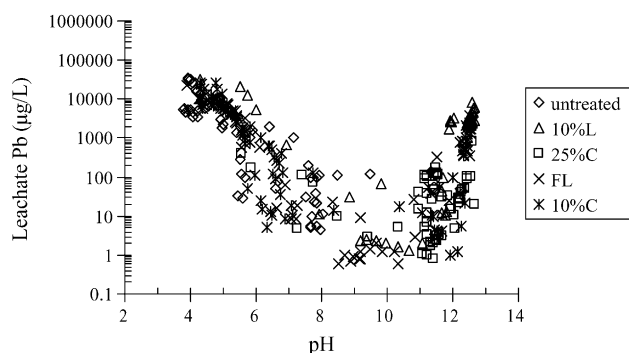
Fig. 8. Experimental lead leachability in S/S-treated and untreated samples determined with TCLP, DI, MEP, Ext TCLP and infiltration.

sidered in the calculation, the model predicted that 68.5 mg Pb/L would leach out at pH 3.5. The leachability dramatically decreased to 21 μg/L when the pH was increased to 7.5 due to the adsorption reaction. With the continued increase of pH and the existence of carbonate, Pb leachability increased to 89 μg/L at pH 9. Then the Pb concentration decreased to 1.5 μg/L at pH 11 owing to the precipitation of hydrocerussite and $Pb(OH)_2$. When pH > 11, Pb was released as lead hydroxide anion complexes. In the acetic acid leaching system, the Pb concentrations were higher than that of the DI water extraction when pH < 8 as explained above. The MEP results were distributed along the non-HAc modeling (dashed line) since synthetic acid rainwater instead of acetic acid was used in the MEP test. The infiltration results were also included in the figure and followed the same concentration versus pH curve defined by the model.

The model prediction and experimental results showed that Pb concentrations would be less than 250 μg/L when 6 < pH < 12, which was in the neutral to alkaline immobilization stage. For untreated soil, the TCLP was more aggressive than DI since the TCLP leachate pH was around 5 which was in the acid leaching stage. For S/S-treated samples, the model predicted an exponential increase of Pb concentration when pH > 12. Such a high leachate pH could be reached only when a leachant with low acidity such as DI water was mixed with treated solids. The final TCLP leachate pH was always lower than 12.

Pb leachability in untreated soil and S/S-treated samples as determined by various leaching tests is summarized in Fig. 8. Although the soil was treated by different binders and tested with different leaching protocols, the leachate Pb concentrations followed a similar concentration versus pH pattern. The experimental data and model calculations indicated that Pb leachability was mainly controlled by adsorption at pH < 9 and precipitation at pH > 9.

4. Conclusions

Pb immobilization mechanisms were studied with eight leaching tests and surface complexation modeling. Both un-

treated soil and S/S-treated samples with 10%C, 25%C, 10%L, and FL followed the same concentration versus pH profile determined with different equilibrium leaching tests. Model calculations showed that Pb leachability was controlled by adsorption and precipitation reactions.

All binders used in this study could immobilize Pb in the solid phase, and the treated wastes could pass the TCLP regulatory concentration of 5 mg/L. The best S/S treatment is 25%C since this sample resulted in the lowest TCLP leachate concentration and the highest strength among all wastes.

Based on the leachate pH, leaching behavior can be separated into three stages which are: high alkalinity leaching stage at pH > 12, neutral to alkaline immobilization stage in the pH range of 6–12, and acid leaching stage with pH < 6.

The Pb concentration in the leachate of each test is mainly controlled by the leachate pH. The final pH is inversely related to the acidity of the leachant. For the S/S waste with a moderate ANC in the range of 2–5 eq/kg, TCLP could underestimate the Pb leachability since the TCLP acidity is not sufficient to deplete the solid ANC. This resulted in a leachate pH at the neutral to alkaline immobilization stage. More aggressive leaching tests with higher acidity, such as extended TCLP, GNAC and the infiltration test could neutralize all the alkalinity in the S/S sample and lead to much higher leachability in the acid leaching stage. On the other hand, the DI water with no acidity resulted in higher Pb concentrations than TCLP for the S/S-treated solids since the leachate pH was at the high alkalinity leaching stage.

The TCLP, DI water extraction, extended TCLP, GNAC, MEP, and infiltration test are batch leaching tests and leaching results can be expressed as a function of pH. The similar leaching profiles determined with different extraction methods suggested that the type of leachant has a minor effect on Pb leachability compared with pH. These equilibrium tests resulted in comparable leachability based on their leachant acidity.

NEN 7341 and the sequential extraction test provide some information on heavy metal availability and distribution in various chemical forms. However, the results obtained with these two operationally determined tests have no correlation with other equilibrium leaching tests.

Among various leaching tests, TCLP and DI water extraction can be used to determine the leaching potential under high acidity (2 eq H^+/kg) and low pH buffering capacity, respectively. TCLP is the regulatory test used to classify hazardous materials. But it failed to evaluate Pb release under high alkalinity conditions which are often found when S/S-treated materials are in contact with natural rainwater or groundwater with low acidity. Therefore, DI water extraction is recommended along with the TCLP.

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