Investigation of the leaching behavior of lead in stabilized/solidified waste using a two-year semi-dynamic leaching test

Qiang Xue [c, *], Ping Wang [a], Jiang-Shan Li [a], Ting-Ting Zhang [a], Shan-Yong Wang [b]

[a] State Key Laboratory of Geomechanics and Geotechnical Engineering, Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, Wuhan, 430071, China
[b] ARC Centre of Excellence for Geotechnical Science and Engineering, The University of Newcastle Callaghan, NSW, 2308, Australia
[c] Institute of Rock and Soil Mechanics, Chinese Academy of Sciences, 430071, Bayi Road, Wuchang District, Wuhan, Hubei Province, China

HIGHLIGHTS

- Leaching mechanisms during different periods turned out to be diffusion.
- The effective diffusivity of Pb has time-dependence.
- Successive leaching behavior were investigated under different occasions.
- S/S materials keep stable in weak acid or weak alkaline environment for two years.

ARTICLE INFO

ABSTRACT

Long-term leaching behavior of contaminant from stabilization/solidification (S/S) treated waste stays unclear. For the purpose of studying long-term leaching behavior and leaching mechanism of lead from cement stabilized soil under different pH environment, semi-dynamic leaching test was extended to two years to investigate leaching behaviors of S/S treated lead contaminated soil. Effectiveness of S/S treatment in different scenarios was evaluated by leachability index (LX) and effective diffusion coefficient (D_e). In addition, the long-term leaching mechanism was investigated at different leaching periods. Results showed that no significant difference was observed among the values of the cumulative release of Pb, D_e and LX in weakly alkaline and weakly acidic environment (pH value varied from 5.00 to 10.00), and all the controlling leaching mechanisms of the samples immersed in weakly alkaline and weakly acidic environments turned out to be diffusion. Strong acid environment would significantly affect the leaching behavior and leaching mechanism of lead from S/S monolith. The two-year variation of D_e appeared to be time dependent, and D_e values increased after the 210th day in weakly alkaline and weakly acidic environment.

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1. Introduction

Stabilization/solidification (S/S) technology is the best available technology for 57 regulated hazardous wastes and the most commonly applied technology in the past few years (US EPA, 2004; Shi and Spence, 2004). However, the fatal flaw of this technology is the hazardous waste remaining in the S/S monolith, and the future environmental risk caused by waste leaching is difficult to evaluate. The question asked in conjunction with S/S treatment is not so much "if the environment causes contaminants to be released from a stabilized material" but "in what form and what speed" does this occur (Hinsenveld, 1992). Furthermore, large amount of S/S treated waste that was dumped into sanitary landfills is a waste of resources, and recycling of S/S materials may become an important method for the disposal of S/S waste. The bottleneck problem for recycling of S/S materials involves quantifying long-term leaching behavior of hazardous waste and predicting the long-term environment risk.

The leachability of the S/S treated waste has always been evaluated by the toxicity characteristic leaching procedure (TCLP) (US EPA, 1992) and semi-dynamic leaching tests (ANS 16.1, 1986; NEN 7345, 1993). The TCLP can only provide a single leaching result at

a specific time point after S/S treatment, which is usually conducted after short-term curing. Previous studies have failed to investigate the continuous leaching behaviors of waste from a S/S monolith. Although a few studies have assessed the leachability of S/S waste using TCLP after 5, 16 and 17 years of S/S treatment (Antemir et al., 2010; Al-Tabbaa and Boes, 2002; Wang et al., 2014), leaching result were only obtained from a single time point, and TCLP has been previously criticized (Kosson et al., 2002). Semi-dynamic leaching tests have been employed to provide much more information regarding the successive leaching behaviors of S/S waste and the leaching mechanism of waste. Unlike the flow-through dynamic leaching test, the semi-dynamic leaching test is a flow-around test where the leachate is replaced periodically to simulate leaching behavior of a S/S monolith with low permeability. However, most current studies using semi-dynamic leaching tests last less than 90 days (Guo et al., 2013; Moon and Dermatas, 2007; Song et al., 2013; Dermatas, 2004). A few studies have been correlated to long-term investigation of S/S treatments. Previous study of Wang et al. (2016) investigated leaching behaviors of lead under different pH conditions for 90 days. Liu et al. (2013) conducted a leaching test that lasted for 123 days to assess the leaching behaviors of phenol under different simulated situations. The Russian national analogue of the ISO testing standard (ISO, 1982) was performed by Ojovan et al. (2011) to evaluate the leaching rate of ^{137}Cs. However, the effectiveness and leaching mechanism were not evaluated. Jin et al. (2016) validated the 3-year effectiveness of S/S treated highly contaminant land with MgO based binders, which involved an evaluation at a specific time point after the S/S treatment. In general, all of the previously mentioned studies have not provided effective insight into the leaching behaviors and leaching mechanism of S/S waste during the entire process over a long period of time. As noted in previous studies, developing and evolving of crack in the S/S monolith would greatly change the leaching behaviors of waste components (Pabalan et al., 2009; Drace et al., 2012) and material integration does not last forever, which would affect the long-term leaching behaviors of waste. Besides, chemical reactions, such as sulphate erosions, carbonation and chloride attacks, would also affect long-term leaching behaviors of cementitious materials (Drace et al., 2012). Although problems with respect to long-term effectiveness of S/S treatment have been previously mentioned (Conner, 1990; Borns, 1997; Glasser, 1997; Loxham et al., 1997), satisfactory interpretations and direct evidence of the long-term performance of waste leaching from a S/S monolith both in experiment and in the field are lacking.

Once there is a proper understanding of the controlling leaching mechanism of contaminant release from S/S waste, the leaching behaviors can be predicted using a geochemical and transport model (Hinsenveld, 1992). Numerous calculations have been performed to predict the long-term leaching behaviors of heavy metals, and the diffusion model is the most popular model (Crack, 1975). Most existing diffusion theories usually model long-term leaching behaviors of waste through some parameters calculated from short-term tests (Godbee et al., 1980; Batchelor, 1990). A partial fixation model (i.e., diffusion model in conjunction with absorption Côté, 1986) or dissolution (Côté et al., 1987) has been established to predict the long-term metals release from a S/S monolith under different environment conditions. In general, the previously mentioned model may be effective and fit the short-term leaching data well but the accuracy of these models for long-term predictions remains unclear.

In particular, the effective diffusion coefficient in previously mentioned models is always taken as constant, but the effective diffusion coefficient would change when the S/S materials degraded and micro-cracks appeared in the S/S monolith. Typically, D_e has been considered time dependent. However, a diffusion model with a time-dependent D_e has not been previously reported (Huang et al., 2003).

Furthermore, acid rain is a common phenomenon in many countries and can be quite severe in some cities, such as Nan Jing, where the rain pH has been as low as 2.89 (Nanjing EPA, 2012). Moreover, once the S/S waste is recycled in the environment, different types of liquid will surround it including acid rain with different pH values or alkaline leachates. Therefore, deeper insight into the long-term leaching behaviors under different pH conditions is required.

Therefore, to obtain a better understanding of the long-term leaching behaviors, leaching mechanism and effectiveness of S/S waste, lead was chosen as the target contaminant in the S/S monolith. Semi-dynamic leaching test was extended to two years to investigate the difference in the long-term leaching behaviors of cement stabilized/solidified Pb contaminated soil in different environment. The leaching mechanisms were validated by two-year leaching data. In particular, a time-dependent D_e was evaluated to gain insight into the variation in the constant D_e used in diffusion models.

2. Materials and methods

The materials used in this study as well as the preparation of an artificially contaminated soil and S/S specimen have been documented in a previous study (Wang et al., 2016; Li et al., 2014, 2015). Except for the extended semi-dynamic leaching test, measurement of leachate pH and lead concentration were performed according to the protocols in the same previous study.

2.1. Materials

2.1.1. Preparation of artificially contaminated soil

Most of the materials used in this paper and the preparation are similar to the previous publication (Wang et al., 2016). Due to its easy accessibility and relatively low cost, silty clay prepared from a subway construction site in Wuhan was used to prepare the simulated contaminated soil. The basic properties of soil are presented in Table 1, and these properties were obtained through the "Standard for soil test method" in China. The light compaction experiment was used to acquire the maximum dry density and optimum moisture content. Portland cement was used to immobilize the lead contaminated soil due to its wider application in S/S technology and its low cost and effectiveness (Spence and Shi, 2004).

A 2 mm sieve was used to eliminate the large soil particles, and the fine screening soil were collected for experiment. A certain amount of the dry soil was weighed, and the amount of $Pb(NO_3)_2$ required to ensure that the lead concentration in this artificial contaminated soil kept 5000 mg/kg was calculated before the preparation of lead contaminated soil. The reason for choosing $Pb(NO_3)_2$ was because nitrate ions would not affect cement hydration (Cuisinier et al., 2011). Then, the amount of deionized water required ensuring that the moisture of the weighed contaminated soil kept at optimum moisture content 19.5%, was calculated. Lastly, the calculated $Pb(NO_3)_2$ and water was mixed in a container to yield a solution containing $Pb(NO_3)_2$, and the solution was evenly added to the prepared soil. The Pb-contaminated soil was evenly mixed and cured for 10 days to ensure that the reaction between $Pb(NO_3)_2$ and the clay reached equilibrium.

2.1.2. Sample preparation

The cement was bought from the China Huaxin Cement Co., Ltd. And the cement type was PO 42.5 N silicate cement, whose strength class was 42.5 and ordinary early strength indicated by N. More

Table 1
Basic physical-mechanical properties of the tested soil.

Water content	Natural density	Specific gravity	Void ratio	Liquid limit	Plastic limit	Optimum moisture content	Grain-size distribution			Maximum dry density
							Sand	Silt	Clay	
20.78%	1.89 (g/cm^3)	2.72	0.74	41.6%	21.8%	19.5%	3.45%	62.27%	34.28%	1.72 (g/cm^3)

specific properties of ordinary Portland cement could be found in a previous monograph (Rahman et al., 2014). Weighed a certain amount of cement (20% percent of dry soil) and added into Pb contaminated soil to perform S/S treatment. The mixture was stirred in a 10 L SPAR-type mixer. Firstly, cement was mixed with the contaminated soil for 15 min to prepare a homogenized mixture. Then, the calculated water was added into the mixture and stirred for an additional 10 min. At last, compact the mixture in a 40 mm × 80 mm mold for three layers to a target compaction degree of 98% (Xue et al., 2014), and the prepared specimens were placed in standard curing box for 7 days with temperature of 20 ± 2 °C and humidity of 95%.

2.2. Extended semi-dynamic leaching test

To investigate leaching behaviors and effectiveness of S/S treated Pb contaminated soil under different condition, the ANS 16.1 (1986) was modified by different kinds of leachant instead of distilled water and extended to two years. A series of leachant were prepared by adding different dosage of sodium hydroxide and acetic acid, whose pH values were 2.65, 3.65, 5.00, 7.00 and 10.00 (Wang et al., 2016). The leachate was collected and entirely replaced after 6 h, 1 d, 2 d, 3 d, 4 d, 5 d, 19 d, 47 d, 90 d, 150 d, 210 d, 270 d, 360 d, 450 d, 540 d, 630 d and 720 d, which is the extension of ANS 16.1 (1986). As documented in ANS 16.1 (1986), the replacement interval for the leachant was 2 h, 7 h, 1 d, 2 d, 3 d, 4 d, 5 d, 19 d, 47 d and 90 d, and the first replacement in this study occurred after 6 h because the replacement time for the first leachant (2 h) was not performed. According to ANS 16.1 (1986), leachate volume (V) to the specimen surface area (S) ratio (V/S) was maintained at 10 ± 0.2 cm, and loose particles on the specimen surface must be rinsed off through 30-s immersion in distilled water before test. DZS-706 multi-parameter analyzer was used to immediately measure leachate pH after collection of the leachate. Then filtered the leachate with a 0.45 μm pore-diameter membrane and acidized the leachate before analyzing Pb concentration with inductively coupled plasma mass spectrometer (ICP-MS 7700) (Agilent Technologies, Inc.). Triplicate samples and blanks were tested to control the accuracy and error.

3. Diffusion theory

Waste leaching from cementitious waste primarily involves a diffusion-controlled process (Dutré and Vandecasteele, 1996). According to the "Analysis of Results" section in ANS 16.1 (1986), when the cumulative fraction release of leachable species in a uniform, regularly shaped solid is below 20%, its diffusion controlled leaching behavior will approximate that of a semi-infinite medium. Therefore, under these mentioned assumptions the models could permit the calculation (Godbee and Joy, 1974) of an "effective diffusivity" using the following expression:

$$D_e = \pi \left[\frac{(a_n/A_0)}{(\Delta t)_n} \right]^2 \left(\frac{V}{S} \right)^2 T \tag{1}$$

where a_n is the contaminant loss (mg) during the particular leaching period with subscript n, A_o is the initial amount of contaminant that exists in the specimen (mg), V is the specimen volume (cm^3), S is the surface area of the specimen (cm^2), $(\triangle t)_n$ is the duration of the leaching period in seconds, and T is the time that elapsed to the middle of the leaching period n (sec). T can be determined using Eq. (2):

$$T = \left[1/2 \left(t_n^{1/2} + t_{n-1}^{1/2} \right) \right]^2 \tag{2}$$

where t_n is the total leaching time of the leaching period (n).

In particular, if the leaching amount of leachable species exceeds 20% prior to time t, the effective diffusivity can only be calculated from a shape specific solution of the mass transport equations (Anders et al., 1978; Nestor, 1980). When the cumulative fraction leached of the specific specie is larger than 20%, the effective diffusivity can be calculated using Eq. (3):

$$D_e = \frac{Gd^2}{t} \tag{3}$$

where G is a time factor for the cylinder and is dimensionless, d is the diameter of the cylinder (cm), and t is the elapsed leaching time since the beginning of the first leaching interval (s). More details regarding this calculation and specific information regarding the parameters can be found in ANS 16.1 (1986).

The leachability index (LX) was calculated from results of the semi-dynamic leaching test (ANS 16.1, 1986), which showed the mobility of the waste in S/S monolith According to (Environment Canada, 1991), the LX can be considered a performance criterion for the utilization and disposal of S/S treated waste. The S/S treatment is considered effective when the LX value of the specific waste is larger than 9, and the S/S product would be appropriate for "controlled utilization", such as road base, quarry rehabilitation and lagoon closure (Wang et al., 2016). When the LX value is between 8 and 9, the S/S treated waste could be disposed of in sanitary landfills. In addition, when the S/S wastes have an LX value less than 8, they cannot be disposed of. The LX is defined in Eq. (4):

$$LX = (1/n) \sum_{1}^{n} [\log(\beta/D_e)] \tag{4}$$

where $\beta = 1$ cm^2/s.

The type of leaching mechanism that controls the release of heavy metals can be determined based on the values of the slope of the logarithm of the cumulative release (log (B_t)) as a function of the logarithm of time (log(t)) (de Groot and van der Sloot, 1992). If diffusion is the dominant mechanism, the theory suggests the following relationship (de Groot and van der Sloot, 1992):

$$\log(B_t) = \frac{1}{2}\log(t) + \log \left[U_{\max} d \sqrt{\frac{D_e}{\pi}} \right] \tag{5}$$

where D_e is the effective diffusion coefficient (m^2/s) for component x (lead in this study), B_t is the cumulative maximum release of component x (mg/m^2), t is the contact time (s), $U_{\max}$ is the maximum leachable quantity (mg/kg), and d is the bulk density of S/S product (kg/m^3).

Based on previous model created by de Groot and van der Sloot (1992), leaching mechanisms of contaminant could be divided into three possible types through the slope mentioned above: diffusion, dissolution, and surface wash-off. The leaching mechanism could be defined as diffusion if the slope is 0.5 (de Groot and van der Sloot, 1992). If the slope is close to 1, then the leaching process is controlled by dissolution, which means that the dissolution of material from the surface proceeds faster than diffusion through the pore space of the soil matrix (de Groot and van der Sloot, 1992). During the dissolution process, the materials will not be depleted until the leaching experiment is complete (Dermatas, 2004). Finally, the leaching mechanism could be classified as surface wash-off if the slope is close to 0, which often occurs in the initial stage of leaching experiments when the soluble material in the soluble layer dissolves (Wang et al., 2016).

4. Results and analyses

4.1. Cumulative fraction of Pb leached (CFL) under different pH conditions

The CFL of tests under were calculated by Eq. (6) and presented in Fig. 1,

$$CFL = \frac{\sum\limits_{i}^{n} c_i \times V_i}{A_0} \times 100\% \tag{6}$$

where CFL is the cumulative fraction of Pb leached (%), c_i is the concentration of Pb in the leachate in the leaching period i (mg/L), V_i is the volume of the contact solution (L) and A_o is the initial amount of contaminant present in the specimen (mg).

The results from Fig. 1 demonstrate that there is a slight difference among the CFL under weakly acidic and weakly alkaline conditions in pH ranges of 5.00–10.00. However, the CFL substantially increased in the pH 3.65 leachant and significantly increased in the pH 2.65 leachant. It is important to note that the 720 d CFL was 48.64%, 0.11%, 1.1×10^{-2}%, 6.9×10^{-3}% and 1.0×10^{-2}% for the samples immersed in leachant with a pH of 2.65, 3.65, 5.00 6.86 and 10.00, respectively. Before elaborating on this phenomenon, it is important to note that chemical fixation of metals in cement can

occur via physical or chemical adsorption (Stegemann and Zhou, 2009), and during the precipitation of cementitious products, heavy metal ions can be sorbed onto their surfaces and enter the lattices to form a solid solution, altering their structure and solubility (Kitamaru et al., 2002). Therefore, their mobility is reduced. Cementitious products in the S/S monolith primarily consisted of calcium silicate hydrate (C-S-H) and calcium hydroxide. These observations may explain why the Pb concentration typically follows its hydroxide solubility in the leachant. The increased dissolution of hydration products in the leachate may result in a larger amount of lead released from S/S monolith. According to Drace et al. (2012), leaching of contaminant from cementitious materials could be owing to the sacrificial dissolution of cement substance. Similar observations were reported in previous studies (Sanchez et al., 2000; Kogbara et al., 2012). Moreover, a "U" shape was observed between the Pb concentration in the leachate and the leachate pH curve (Kogbara et al., 2012). Therefore, the CFL was the lowest in the pH 6.86 leachant, and a higher CFL was observed for the pH 5.00 and pH 10.00 environments.

4.2. Leachate pH

The results of the leachate pH are shown in Fig. 2 and indicate that the leachate pH are larger than that of the original leachant due to the high alkalinity of the S/S materials. In addition, the leachate pH became stable after 90 days for a similar replacement interval, except for the test with a leachant pH of 2.65. At the beginning of the leaching test, the leachate pH values were similar during the first five days due to frequent replacement of the leachant. As the immersion time of the samples increased and the buffering capacity of S/S material declined, the leachate pH increased as the experiment time increased. The stable pH was approximately 7.80, 10.70, 11.20 and 11.70 when the original pH of the leachant was 3.65, 5.00, 6.86 and 10.00, respectively. In particular, for the test with a leachant pH of 2.65, the leachate pH decreased from 90 d to 720 d due to a decrease in the buffering capacity of the S/S materials. Due to the extended length of the immersion time of the sample in strong acid, the alkaline matrix in the S/S material leached out, leading to a decrease in the neutralizing capacity of the acid solution. The pH is dominated by alkaline cement hydrate in the beginning stage of S/S treatment (Drace et al., 2012). Similar observations have been previously reported (Du et al., 2014). When immersed in a weakly acidic or weakly alkaline leachant, the
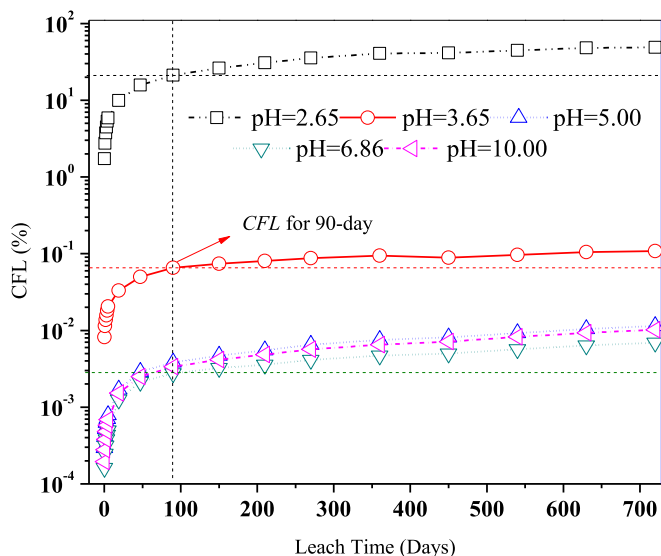

Fig. 1. CFL of Pb (%) from different tests under different pH conditions.
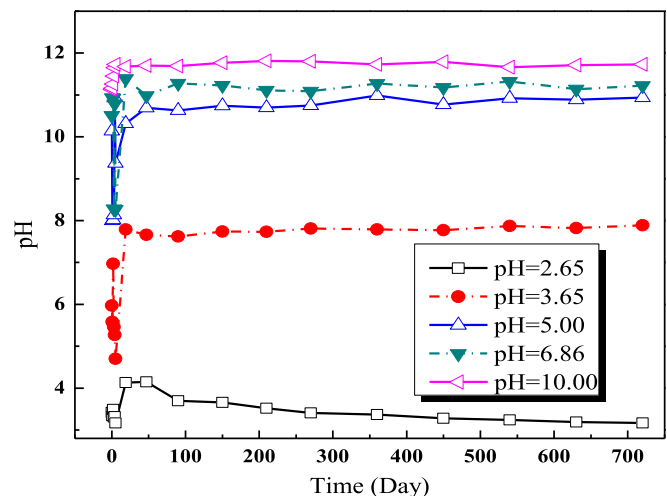

Fig. 2. Leachate pH during the semi-dynamic leaching tests.

leachate pH values were approximately 11.0 and 12.0, which is consistent with previous results (Du et al., 2014).

4.3. Long-term effectiveness evaluation

For comparison with the 90 day mean D_e and LX values, the calculated results of the two parameters are shown in Table 2. In Table 2, $D_e(90d)$ means that the effective diffusivity was calculated from the 90 day leaching data and $D_e(2Y)$ was calculated from the 2 year leaching data (i.e., LX(90d) and LX(2Y), respectively). The results indicated that there is no significant change between the 90 day and 720 d D_e values. Therefore, the leaching behavior of lead from the S/S material remained stable for two years. However, a decrease between $D_e(90d)$ and $D_e(2Y)$ was observed in the tests with leachant pH values of 2.65 and 3.65, and in the other three tests (leachant pH values of 5.00, 6.86 and 10.00), the opposite behavior was observed. The decrease in D_e under acid conditions was due to the large amount of lead being leached out, and the leachable amount of waste declined in the S/S monolith, resulting in a decrease in the leaching rate of lead. Moreover, the end of the hydration reaction and degradation of the S/S materials may have resulted in the slight increase in D_e increased over two years under weakly acidic and weakly alkaline conditions.

The LX value and D_e are frequently used to evaluate the effectiveness of a S/S treatment. Both low D_e and high LX values indicate the high mobility of metals in S/S monolith. The calculated mean D_e and LX values of the samples immersed in different pH leachant for two years are plotted in Fig. 3. According to Environment Canada (1991), the LX can be considered the performance criteria for the utilization and disposal of S/S treated waste. When the LX value is higher than 9, the S/S waste can be used for "controlled utilization". The two-year LX values indicated that the S/S waste can be used for "controlled utilization" in the environment with pH values of 3.65, 5.00, 6.86 and 10.00, which correspond to LX values of 13.79, 16.02, 16.44 and 16.11, respectively. The results demonstrated that the S/S samples used in this study can be disposed of in the landfill even under pH 2.65 conditions with a LX value of 8.58. Moreover, the D_e and LX values of the specimens that were immersed in weakly acidic or weakly alkaline environments (pH ranges from 5.00 to 10.00) were on the same order and changed very little. A slight difference in the S/S monolith leaching behavior was observed under the different environments with pH values ranging from 5.00 to 10.00. This phenomenon may be due to the S/S samples not being eroded by the surrounding liquid and the hydration products not dissolving when immersed in weakly acidic and weakly alkaline conditions. In addition, most of the Pb leached out of the S/S monolith into the leachate due to diffusion resulted in low D_e values that changed very little under such conditions.

4.4. Controlling leaching mechanism

Three types of mechanisms for metal leaching from the S/S samples (surface wash-off, diffusion and dissolution) can occur, and the controlling leaching mechanisms can be evaluated using the diffusion model developed by de Groot and van der Sloot (1992).

Table 2
Parameter comparison of the 90 day and 2 year test results.

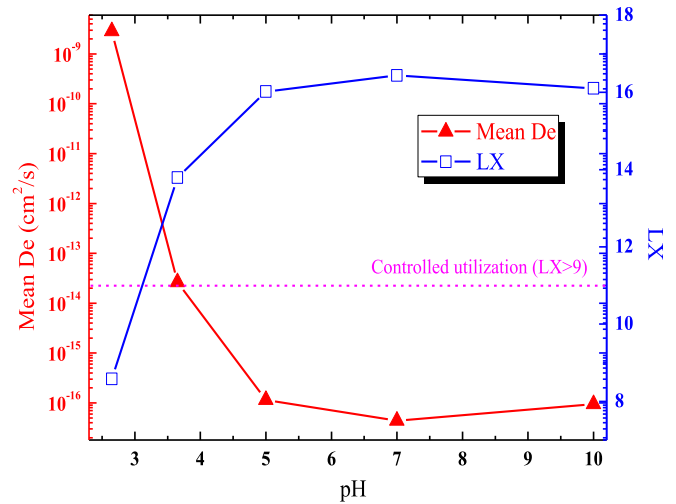| Slope	D_e (90d) (cm^2/s)	D_e (2Y) (cm^2/s)	LX (90d)	LX (2Y)
pH = 2.65	3.52E-9	2.86E-9	8.49	8.58
pH = 3.65	4.23E-14	2.64E-14	13.49	13.79
pH = 5.00	8.27E-17	1.15E-16	16.15	16.02
pH = 6.86	3.89E-17	4.37E-17	16.48	16.44
pH = 10.00	6.90E-17	9.46E-17	16.24	16.11

Fig. 3. Mean D_e and LX values from different tests (2 years).

The type of leaching mechanism that controls the release of Pb from the S/S product can be determined based on the values of the slope of the logarithm of the cumulative release (log (Bt)) as a function of the logarithm of time (log (t)) de Groot and van der Sloot (1992). The fitting curves that demonstrate leaching mechanisms in different leaching scenarios are shown in Fig. 4. The two year leaching mechanisms under weakly acidic or weakly alkaline environment primarily involved diffusion because all of the slopes were approximately 0.5. Except for the test with a leachant pH of 3.65, the other leaching tests exhibited a declining trend as the pH decreased, demonstrating the controlling leaching mechanism changed from diffusion to surface wash-off.

Many flocculent deposits were observed in the leachate as the immersion time increased, and these deposits may influence the concentration detection for lead. In general, the two year leaching tests confirmed that the diffusion model fit well to the leaching results. Due to low solubility of the S/S alkaline matrix, the controlling leaching mechanism under weakly acidic or weakly alkaline conditions (pH: 5.00—10.00) appeared to be strictly diffusion based.

To compare the change in leaching mechanism as a function of time, the two year leaching data (i.e., 17 points for each test) were
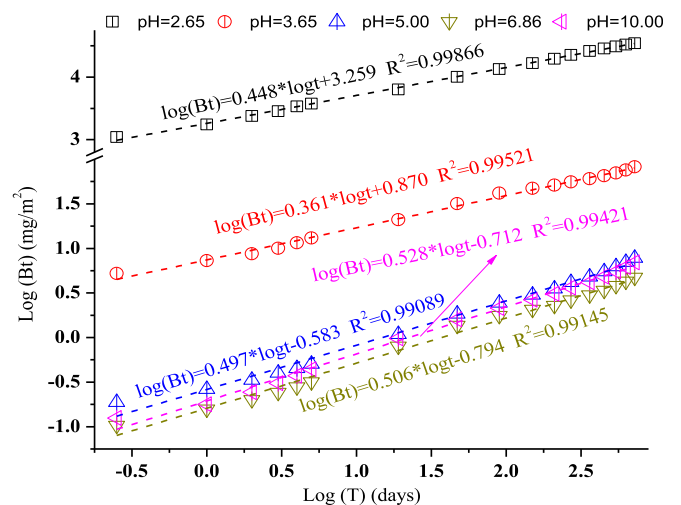

Fig. 4. Fitting curves for mechanism determination under different pH conditions.

fitted by three parts as follows: K_{0-2Y}, K_{90d} and K_{90d-2Y} represented the slope of the leaching data from two years (17 points), the first 90 days (9 points) and 90th day to 720th day (8 points). The slopes and goodness of fits (R^2) are shown in Table 3, and all of the slopes confirmed that diffusion was the leaching controlling mechanism of Pb release from the S/S monolith over the course of two years. In addition, the slope of the fitting curve from the 90 day data (K_{90d}), which comes from ANS 16.1 (1986), was similar to the slope of K_{0-2Y}. Therefore, the leaching behaviors of the S/S monolith remain stable for the first two years, and the diffusion model fitted well to the leaching data. Moreover, the two year CFL values from different leaching tests were fitted well on a log scale to the square root of the leach time ($R^2 > 0.99$). These values exhibited a better fit than the fitting goodness of the 90 day leaching results, demonstrating that the two year leaching results can be fitted better by the diffusion model than the 90 day results noted in the ANS 16.1 leaching test.

4.5. D_e variations during the two year leaching test

The diffusion model has been widely applied to predict the long-term leaching behaviors of waste in S/S monolith (Godbee et al., 1980; Côté et al., 1987; Nathwani and Phillips, 1978), and these models also fit well to the leaching data. However, nearly all of the models were based on the assumption that the effective diffusivity was constant and did not change over the long term. Unfortunately, a rapid increase in the D_e value was observed when micro-cracks occurred in the testing sample (Huang et al., 2003). Previous studies indicated that the effective diffusivity was time dependent, but there is a lack of literature regarding the time-dependent effects of the effective diffusivity.

Under different pH conditions, the two year variations and mean D_e values were calculated plotted in Fig. 5. The change in D_e under different pH conditions varied. D_e increased during the leaching process due to micro-cracks or degradation of the S/S materials. A similar phenomenon was observed in this study. D_e changed slightly in a weakly acidic or weakly alkaline environment. However, a significant increase was discovered in the leaching test with strong acid (pH 2.65), which was eight orders of magnitude larger than that in the pH 6.86 environment. Moreover, the time dependence of D_e was confirmed in the two year semi-dynamic leaching tests under different pH conditions, and the variation in D_e was depended on the environmental pH. For the sample immersed in the pH 2.65 leachant, the D_e of lead decreased after the 270th day, which may have contributed to the long-term erosion of the strong acid and the large amount of leachable lead released from the S/S monolith. Therefore, the lead in the S/S monolith was difficult to leach in the following periods, leading to a decrease in D_e. In contrast, in the other four tests with leachant pH values of 3.65, 5.00, 6.86 and 10.00, all of the D_e values reached the minimum value after approximately 210 days and started to increase in the subsequent days due to little S/S material being eroded in these leachant. Due to completion of the hydration reaction of S/S cement at approximately 210 days, the D_e decreased from the 90th day to the 210th day. At the same time, a large amount of calcium ions were released from the S/S monolith along with lead (Du et al.,
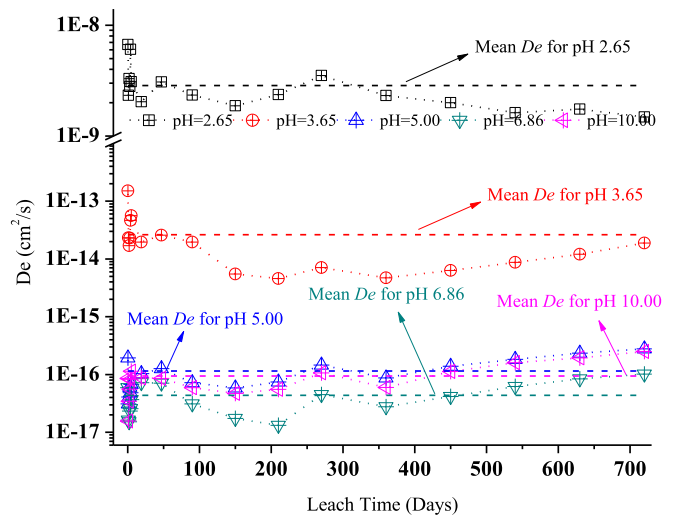

Fig. 5. Time dependence and mean value of D_e for two years.

2014), damaging the internal structure and enlarging the micropores in the sample. Therefore, the leaching rate of Pb increased slightly in the subsequent days.

In general, the two year leaching test results indicated that D_e was time dependent and the variation in D_e was related to the environmental pH. Except for the D_e values decreasing after the 90th day under strongly acidic (pH 2.65) conditions, the D_e values increased after the 210th day in an environment with pH values ranging from 3.65 to 10.00.

5. Conclusions

S/S technology provides a convenient and economical method for treating heavy metal contaminated soils. However, the long-term effectiveness of the S/S treatment may endanger the environment. More "real-time" leaching data both in the laboratory and in the field are needed to validate waste leaching from the S/S monolith over the long run. The two year semi-dynamic leaching tests under different pH conditions were conducted to investigate the long-term "real-time" leaching behaviors of lead in a S/S monolith. The results from these tests could provide information regarding the leaching amount of lead, leaching mechanism and effectiveness of S/S under different conditions.

The results of these leaching tests indicated that the cumulative fraction of Pb leached over two years changed very little under weakly acidic or weakly alkaline conditions (pH 5.00–10.00). However, strongly acidic conditions can significantly increase the leaching amount of Pb because C-S-H and calcium hydroxide dissolved under strongly acidic conditions (pH 2.65). Except for the sample immersed in the pH 2.65 leachant, the leachate pH of the tests with original leachant pH values of 3.65, 5.00 6.86 and 10.00 became stable in the last year for the same replacement of leachant. Due to a decline in the buffering capacity of the S/S materials, the leachate pH gradually decreased after the 90th day. The calculated D_e and LX values indicated that the S/S monolith could retain its

Table 3
Fitting results for the leaching mechanism determination.

Slope	K_{0-2Y}	R^2	Mechanism	K_{90d}	R^2	Mechanism	K_{90d-2Y}	R^2	Mechanism
pH = 2.65	0.44	0.9986	Diffusion	0.43	0.9961	Diffusion	0.47	0.9965	Diffusion
pH = 3.65	0.36	0.9952	Diffusion	0.37	0.9827	Diffusion	0.35	0.9801	Diffusion
pH = 5.00	0.50	0.9908	Diffusion	0.47	0.9691	Diffusion	0.60	0.9934	Diffusion
pH = 6.86	0.51	0.9914	Diffusion	0.50	0.9700	Diffusion	0.53	0.9814	Diffusion
pH = 10.00	0.53	0.9942	Diffusion	0.52	0.9789	Diffusion	0.61	0.9899	Diffusion

effectiveness for a long period of time under weakly acidic or weakly alkaline conditions. However, the S/S materials are not suitable for recycling in a strongly acidic environment (i.e., areas with frequent strong acid rain). The fitting curves of the cumulative leaching amount as a function of the leaching time on a log scale demonstrated that the predominant leaching mechanism of Pb release from the S/S monolith was diffusion under different pH conditions. In particular, the goodness of fit of the two year leaching data was better than that of the 90 day data, demonstrating that the diffusion model fitted well to the two year leaching behaviors. The two year variation in D_e was time dependent under all of the studied pH conditions, and further studies should be carried out to better understand the D_e variation. In addition, a diffusion model with variable D_e values should be established to obtain a more accurate prediction of waste leaching from the S/S monolith.

Acknowledgments

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