

Factors Affecting the Leaching Behaviors of Magnesium Phosphate Cement-Stabilized/Solidified Pb-Contaminated Soil, Part II: Dosage and Curing Age

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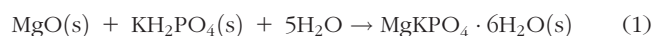
Magnesium phosphate cement (MPC) is frequently used to dispose synthetically spiked Pb contaminated soils by means of stabilization/solidification (S/S) technology. Leaching behaviors of heavy metal represent the most important parameters for MPC-treated metal-contaminated soil. Little information is available for the effectiveness evaluation and leaching mechanism investigation of MPC treatment. Moreover, various factors in the S/S process would affect its effectiveness, especially leaching behaviors. Part I presented the effect of original Pb concentration in soil and water-to-cement ratio on leaching behaviors of MPC treated synthetically spiked Pb contaminated soil, and this part investigated the effect of dosage and curing age on leaching behaviors of MPC treated waste. Leaching behaviors were investigated via toxicity characteristic leaching procedure (TCLP) and semi-dynamic leaching test about different MPC dosage and curing age. Results showed that both the MPC dosage and curing age would change the leaching behaviors of MPC treated synthetically spiked Pb contaminated soil. The TCLP leaching concentration of Pb decreased with the increasing MPC dosage and curing age. The calculated effective diffusion coefficients and leachability index indicated that the MPC treated Pb contaminated soil could be used for utilization after S/S treatment. The controlling leaching mechanism of Pb appeared to be diffusion for S/S products with different MPC dosage and curing age. © 2017 American Institute of Chemical Engineers Environ Prog, 00: 000–000, 2017

Keywords: stabilization/solidification, leaching, water-to-solid ratio, magnesium phosphate cement

INTRODUCTION

Stabilization/solidification (S/S) technology is widely used for remediation of synthetically spiked Pb contaminated soil [1–3], and cement is the most common used binder in S/S treatment for its relative convenience and economic advantages [4,5]. Meanwhile, cement production is not only a waste of energy but also harmful to the environment as the

large amounts of greenhouse gas released during cement production [6]. Besides, cement treated waste would be threatened by strength and durability problems when exposed to aggressive environment. As a result, it is necessary to find new environmentally friendly materials to substitute for cement. Juenger *et al.* [6] presented four promising binders to substitute for cement. Among numbers of prosperous alternatives, magnesium phosphate cement (MPC) is a promising candidate and has been investigated a lot for its effectiveness and strength [7–12]. MPC is mainly composed of dead burnt magnesia, whose annual production of the world is beyond 14 million tons [13]. Experimental studies were conducted to research the dipotassium hydrogen phosphate about the influencing properties of MPC [14,15]. Recycling of dead burnt magnesia is a resource-saving and environmental friendly strategy. Compared to OPC production, the main component of MPC (hard-burnt MgO) could eliminate greenhouse gas emission during its production, and a specific comparison of energy, greenhouse emission and raw material of MgO and PC was presented in a previous work [16]. During the MPC treated S/S process, an acid–base reaction between magnesium oxide and potassium dihydrogen phosphate develops in the presence of water, and the main reaction product is hexahydrated magnesium potassium phosphate or k-struvite, which constitutes a crystalline matrix that can host different wastes [17]. Main reaction of MPC is listed as follows:



Different amounts of water in the paste will generate different types of minerals. The k-struvite will be converted into cattite $[(\text{Mg}_3(\text{PO}_4)_2 \cdot 22\text{H}_2\text{O})]$ [18] in the presence of water, which is more stable and will finally be converted into $(\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})$ [19]. Bobierrite has also been observed in magnesium potassium phosphate cements [20].

Generally, great numbers of S/S waste were disposed in landfill while its long-term environmental risk assessment stay unclear, which does harm to environment besides wasting resource. MPC S/S treated synthetically spiked Pb

Table 1. Physical and chemical properties of hard burned MgO.

| Grade number | MgO/% ≥ | SiO ₂ /% ≤ | CaO/% ≤ | Fe ₂ O ₃ /% ≤ | Al ₂ O ₃ /% ≤ | Grain size (mm) ≤ |
|--------------|------------|--------------------------|------------|--|--|----------------------|
| MS-95 | 95 | 2.0 | 1.6 | 1.0 | 1.0 | 0.075 |

Table 2. The basic physical–mechanical properties of 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) |

contaminated soil is prosperous for utilization for its high strength and effectiveness. Leachability, strength, and permeability are important parameters to evaluate the utilization performance of target materials, among which leachability is the most important. Leachability assessment, including TCLP, and semidynamic leaching tests, is not only the key of effectiveness assessment for S/S treatment, but also crucial parameter for long-term leaching prediction of contaminant in S/S matrix.

Numerous papers have investigated the strength and micro structure of MPC treated synthetically spiked Pb contaminated soil [21–24]. The effect of heavy metals and water content on the strength of magnesium phosphate cements was presented by Buj *et al.* [20], and microstructure developing of magnesium potassium phosphate cement was showed in another paper [21]. Zhen *et al.* [24] studied the changes of hydration production during the S/S process of MPC, and several tests were performed to investigate the composition and microstructure change of MPC treated contaminated soil with different curing ages. Few researchers focused on leaching behaviors and leaching mechanism of metal from MPC solidified contaminated soil. TCLP was frequently used to evaluate the effectiveness of MPC [25–27]. While the widely spread leaching test TCLP can only be used to evaluate the leaching rate of S/S waste at a specific time and its limitations have been reported before [28,29]. Moreover, little useful information could be obtained from the TCLP to model the long-term leaching of waste from MPC-treated waste. Buj *et al.* [30] studied leaching behavior of magnesium phosphate cements containing high quantities of heavy metals with simple batch test (EN 12457-2), equilibrium leaching test, availability test (NEN 7371) and acid neutralization capacity test (ANC). All the leaching tests mentioned above were failing to evaluate effectiveness and leaching mechanism of metal from S/S treated waste. In order to evaluate effectiveness and elucidate the corresponding leaching mechanism, semidynamic leaching test [31] would be the best choice. Li *et al.* [14,15] compared the effectiveness of MPC and OPC solidified contaminated soil at the same dosage, and results showed that MPC was more effective to stabilize Pb contaminated soil at the same dosage. Zhen *et al.* [24] found that curing age would affect the composition and microstructure of MPC solidified synthetically spiked Pb contaminated soil, and the MPC dosage could be another effect to change its composition and microstructure, both of which would change the leaching behavior and leaching mechanism of MPC treated contaminated soil. Torras *et al.* [17] presented a study on the long-term leaching behavior of nickel containing wastes stabilized/solidified with magnesium potassium phosphate cements, and the leaching mechanism of potassium, total phosphorous, and magnesium were revealed in this paper. However, there is a lack of literature about the

leaching behaviors and mechanism of MPC treated synthetically spiked Pb contaminated soil. Besides, several factors during the application of S/S technology would affect leaching behaviors of MPC stabilized/solidified (S/S), such as original concentration of metal, waster-to-cement ratio, dosage and curing time. Each of these factors would change leaching behavior and mechanism of S/S treatment. As mentioned above, the curing age and MPC dosage would affect the mineral composition and micro structure of MPC treated contaminated soil, so as to change the leaching behavior and leaching mechanism of contaminant in the S/S products, which were the most important parameter to evaluate the long-term effectiveness of S/S treatment.

The aim of this paper was to investigate leaching behavior of MPC treated lead contaminated soil and elucidate the corresponding leaching mechanism of lead, and evaluated the effectiveness of S/S technology under different conditions. Both TCLP and ANS 16.1 were conducted to assess the effectiveness of MPC treatment, and the leaching mechanism under different occasions were also discussed based on the model developed by de Groot and van der Sloot [32] to offer information about long-term environmental risk evaluation of MPC treated synthetically spiked Pb contaminated soil. The revealed leaching mechanism of Pb in different scenarios of MPC treatment would be helpful to obtain knowledge about the leaching behavior and long-term modeling about Pb release from MPC treated Pb contaminated soils under different scenarios.

MATERIALS AND METHODS

Preparation of MPC

The materials and methods used in this paper were as same as Part I. The MPC used in this test was obtained by mixing hard burned magnesium oxide with potassium dihydrogen phosphate powder at 50% weight [18], and the particle sizes of the mentioned materials were less than 75 μm. The analytical grade potassium dihydrogen phosphate was provided by Chinese Medicine Group Chemical Reagent. The hard burned magnesium oxide used in this paper was supplied by Haicheng Dongxu refractory material. The calcination temperature of the magnesium oxide was 1400°C, and its physical and chemical properties are shown in Table 1.

Preparation of Synthetically Spiked Pb Contaminated Soil

Due to its high accessibility and relatively low cost, Chinese clay was chosen for using in the simulated contaminated soil. The clay used in this paper was silty clay and obtained from a subway excavation site in Wuhan City. The basic physical–mechanical properties of clay, which were obtained according to the “Standard for soil test method” of China, were presented in Table 2.

The clay was dried, ground and sieved through a 2-mm screen. Specific amounts of $\text{Pb}(\text{NO}_3)_2$ and water were calculated and added to a certain quantity of prepared soil to ensure that the Pb concentration in this artificially contaminated soil reached 5000 mg/kg. $\text{Pb}(\text{NO}_3)_2$ was chosen because nitrate is inert for cement hydration [33]. Then, deionized water was added to the contaminated soil until the water content reached 19.5%. The Pb-contaminated soil was mixed evenly and braised for 10 days to ensure that the reaction between $\text{Pb}(\text{NO}_3)_2$ and clay reached equilibrium.

Specimen Preparation

To study the effects of MPC dosage and curing time on leaching behaviors of MPC-stabilized/solidified contaminated soil. Firstly, to prepare samples with different MPC dosage, the calculated MPC, deionized water and prepared artificially contaminated soil were mixed and stirred for 10 min to achieve homogenous mixture. Different amount of MPC were added into the mixture to make dosage of 30, 40, 50, 60, and 70% of dry weight of the mixture, which were labeled as MPC-D-30%, MPC-D-40%, MPC-D-50%, MPC-D-60%, and MPC-D-70%, respectively. The reason to choose these dosages was to ensure the effectiveness of S/S treatment for high Pb concentration contaminated soils and obtain the desired flowability to make the mixture easy to be molded. The W/S (water-to-solid ratio) was held at 0.50 to ensure the good mobility of the slurry. Then, the slurry was transferred into a $\Phi 50 \times 50$ mm cylindrical mold, and the mold was placed onto a vibrostand, whose frequency and amplitude were 48 Hz and 0.5 mm, respectively, to obtain satisfactory compaction. The prepared specimens were stored in sealed sample bags and cured under standard curing conditions ($20 \pm 2^\circ\text{C}$, 95% humidity) for 7 days.

When preparing specimens with different curing ages, the original Pb concentration in soil was 5000 mg/kg, and the MPC remained as 50% the weight of dry soil and the W/S was held at 0.50. These samples were also cured under the same conditions for 3, 7, 15, 28, and 56 days prior to the tests, which were labeled as MPC-C-3d, MPC-C-7d, MPC-C-15d, MPC-C-28d, and MPC-C-56d, respectively. The following curing methods before test was the same as mentioned above.

Test Methods

TCLP Test

Test methods and procedure were the same as Part I, which was presented as follows. The TCLP test was conducted in this paper to provide short-term validation of MPC treatments according to the USEPA protocol method 1311 [34]. Acetic acid solution (0.1M) with a pH of 2.88 was used to extract a control sample and MPC-treated samples. The samples were extracted at a liquid-to-solid (L/S) ratio of 20 ± 0.2 in capped polypropylene bottles in a rotary tumbler operating at 30 ± 0.5 rpm for 18 h. After the extraction, the final pH of the leachate was measured by a DZS-706 multiparameter analyzer immediately after the leachate was collected, and then, the leachate was separated from the solids by filtration through a $0.45\text{-}\mu\text{m}$ pore size membrane filter. Each test was conducted in triplicate, and the relative standard deviation values were below 5%. The concentration of Pb in the collected leachate was measured by an Agilent 7700 ICP-MS.

Semi-Dynamic Leaching Test

Acetic acid and sodium hydroxide were used to prepare a leachant with a pH value of 3.65, which was used to simulate aggressive conditions in the environment and to replace distilled water, as noted in ANS 16.1. The prepared samples were placed in a series of polyethylene crispers, and specific volumes of leachant were added to the crispers. The ratio of

the leachate volume (V) to the specimen's surface area (S) was maintained as 10 ± 0.2 cm. The renewal times were 2, 7, 1, 2, 3, 4, 5, 19, 47, and 90 days. According to ANS 16.1 [31], the loose particles at the specimen's surface were rinsed out via immersion in distilled water for 30 s prior to the test. The leachate pH was measured by a DZS-706 multiparameter analyzer immediately after the leachate was collected. The leachate was filtered by a $0.45\text{-}\mu\text{m}$ pore-size membrane filter before the concentration of Pb in the leachate was analyzed using an inductively coupled plasma mass spectrometer (ICP-MS 7700) made by Agilent Technologies. A number of blanks, replicates, and spiked samples were prepared with each batch of samples to control the accuracy and error.

Parameter Calculations

The ANS 16.1 semidynamic leaching test has standardized a Fick's-law-based mathematical diffusion model [31] for the evaluation of the leaching rate as a function of time. In addition, the effective diffusion coefficients D_e can be calculated as follows [35]:

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

where a_n is the contaminant loss (mg) during a particular leaching period denoted by the subscript n , A_0 is the initial amount of contaminant in the specimen (mg), V is the specimen volume (cm^3), S is the surface area of the specimen (cm^2), $(\Delta t)_n$ is the duration of the leaching period in seconds, and T is the time that elapsed to the middle of the leaching period n (s), where T can be determined as follows:

$$T = \left[1/2 \left(t_n^{1/2} + t_{n-1}^{1/2} \right) \right]^2 \quad (3)$$

in which t_n is the total leaching time of the leaching period n .

The leachability index (LX) is defined as follows [4]:

$$\text{LX} = (1/n) \sum_1^n [\log (\beta/D_e)] \quad (4)$$

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

The type of leaching mechanism that control the release of heavy metals can be determined based on the values of the slope of the logarithm of cumulative fraction release, $\log(B_t)$, vs. the logarithm of time, $\log(t)$, line [32]. If the diffusion is the dominant mechanism, the theory suggests the following relationship:

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

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 the 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 the product (kg/m^3).

EXPERIMENTAL RESULTS AND ANALYSES

TCLP and pH

The TCLP results and the corresponding leachate pH values were presented in Figure 1, which showed the Pb concentration and leachate pH as a function of MPC dosage and curing age in Figures 1a and 1b, respectively. As

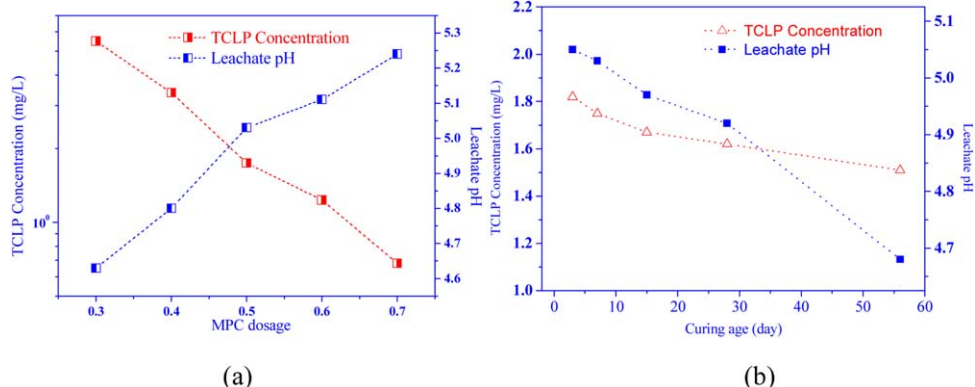


Figure 1. Pb concentration and pH of TCLP leachate under different conditions: (a) different MPC dosage and (b) different curing ages. [Color figure can be viewed at wileyonlinelibrary.com]

demonstrated in Figure 1a, the Pb concentration in TCLP leachate decreased with the increasing MPC dosage. As MPC dosage of S/S samples increased from 30 to 70%, Pb concentration in the leachate dropped from 5.50 to 0.68 mg/L, signifying that MPC dosage would significantly affect the effectiveness of S/S treatment. The concentration limit of Pb was 5 mg/kg in TCLP regulatory, and that was to say the MPC treatment was effective when the MPC dosage was larger than 40%. The more amount of MPC in the S/S system, the more hydration products will be present, and the higher pH the system will be as more alkaline hydration produced in the process. Besides, hydration products, such as exhydrated magnesium potassium phosphate or k-struvite, will stabilize/solidify free Pb ions in the pore solution much more effectively, leading to the decline of TCLP concentration. Comparison to the variation of Pb concentration, the change of leachate pH behaved oppositely. The leachate pH decreased with increasing MPC dosage, although all of tested pH values were much higher than the original pH value of 2.88. This phenomenon could be attributed to two reasons: firstly, a lot of alkaline components would exist in the system as MPC dosage increased, and the proceeding of MPC hydration would form a lot of alkaline hydration products and increase the acid neutralization capacity of MPC system as MPC dosage increased [24]; secondly, the reaction of MPC hydration would consume H⁺ in the environment, so the unreacted matrix would consume the H⁺ in the leachate instead of the H⁺ produced by its own, which would also increase the leachate pH as MPC dosage increased. Some more specific information about the mentioned reaction of MPC could be found in previous works [20,24,30].

Figure 1b showed the variation of TCLP concentration and leachate pH as a function of curing age. As expected, the leaching concentration of Pb in leachate was declining with the prolonging of curing age. Due to the aging process, more and more hydration products, namely MgKPO₄·6H₂O, will be in the samples, increasing the effectiveness of MPC. In addition, the development of hydration will decrease the transportation of Pb in the matrix. As a result, the leaching concentration of Pb was dropping as curing age prolonged. Especially, the change of leachate pH along with curing age behaved the same way with TCLP concentration in leachate. As the curing age increased from 3 to 56 days, most of hydration reaction of MPC completed. Compared with sample with shorter curing age, and the hydration products of sample with longer curing age are more resistant to acidic conditions. Consequently, more alkaline hydration products will leach out under short curing age, which could be the reason why leachate pH decreased with increasing curing periods.

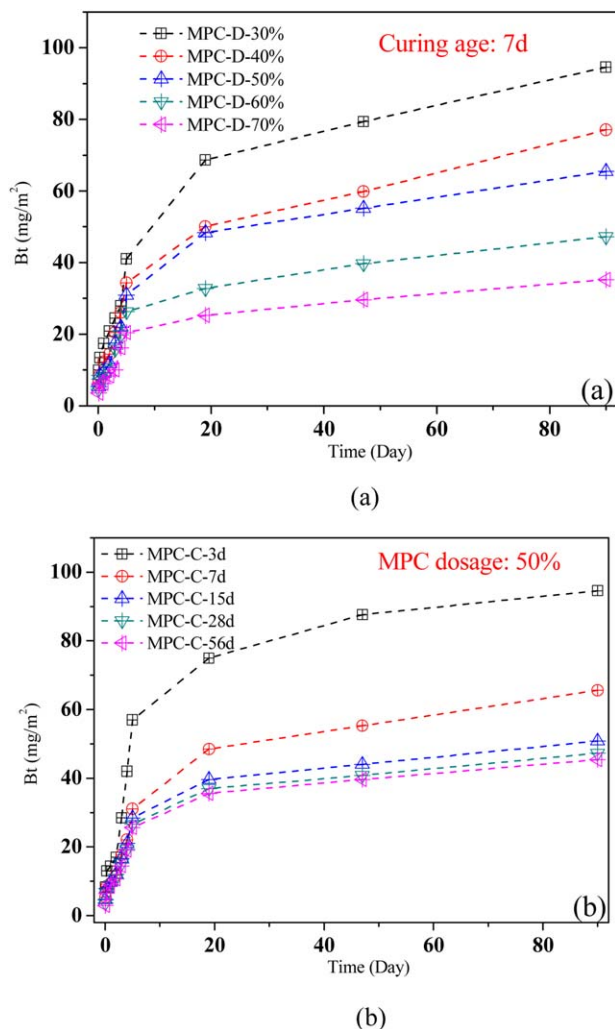


Figure 2. The cumulative fraction leached of Pb (B_t) with different parameters: (a) different MPC dosage and (b) different curing ages. [Color figure can be viewed at wileyonlinelibrary.com]

Cumulative Release of Pb (B_t)

The cumulative fraction leached of Pb (B_t) were presented in Figure 2 as a function of different MPC dosage and curing age. The B_t values were 94.57, 77.07, 65.46, 47.22, and 35.24 mg/m² for the samples with different MPC dosage

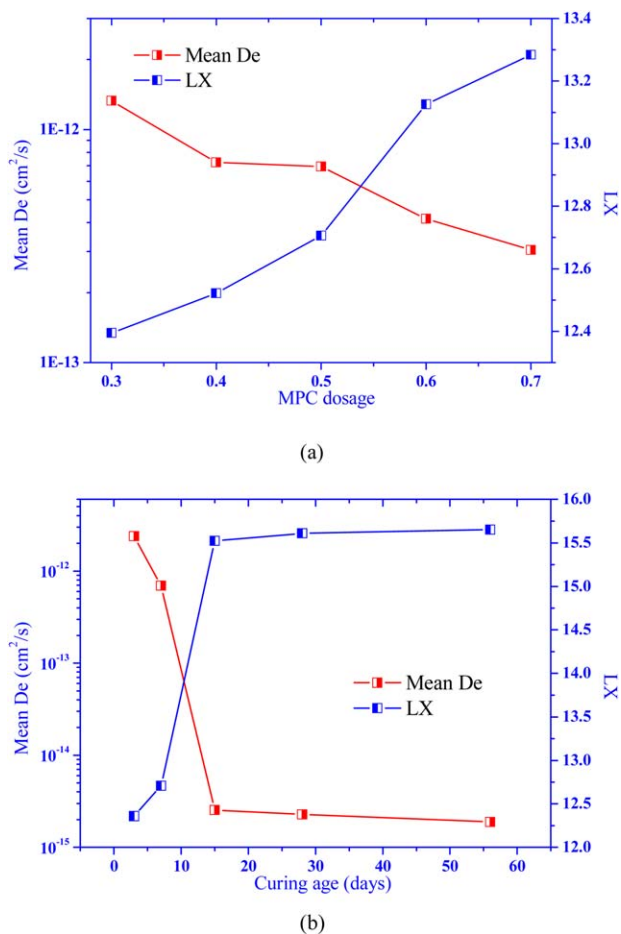


Figure 3. Mean D_e and LX values of different tests with different parameters: (a) different MPC dosage and (b) different curing ages. [Color figure can be viewed at wileyonlinelibrary.com]

of 30, 40, 50, 60, and 70%, respectively. It was vividly showed that the final cumulative release of Pb in the 90-day ANS 16.1 semidynamic leaching test decreased with the increasing MPC dosage. As the MPC dosage increased, the relative amount of lead in the sample would decrease since the concentration of Pb in the artificial contaminated soil was constant, leading to larger numbers of Pb leaching out from samples with lower MPC dosage. The more MPC existing in the system, the more alkaline hydration products the system would have. As waste in contaminated soil were stabilized through chemical binding, physical absorption and physical encapsulation [36]. Thus, the free metal ions in the matrix would be chemical stabilized and physical encapsulated, making Pb in the matrix hard to release when MPC dosage increased.

B_t values variation of samples under different curing age were presented in Figure 2b as function of time. The 90-day cumulative release of Pb were 94.60, 65.60, 50.81, 47.30, and 45.40 mg/kg for samples with curing age of 3, 7, 15, 28, and 56 days, respectively. As curing age prolonged, the leaching amount of lead in S/S samples turned to be declining. The hydration products changed with curing age, which change the leaching behaviors of lead. The proceeding of hydration reaction would generate increasing amount of hydration products, which would increase the effectiveness of S/S treatment of MPC. Moreover, the products would make the MPC treated Pb contaminated soil more compacted and decrease the pore in samples with during hydration process.

Hydration products in the beginning days ($MgHPO_4 \cdot 7H_2O$) was less stable than that with long-curing periods ($MgKPO_4 \cdot 6H_2O$) [24]. As a result, the longer curing age the MPC treated Pb contaminated soil was, the more stable chemical composition the solidified soil would be. Stable chemical property made the alkaline matrix hard to dissolve in acid leachant, leading to the Pb ions in S/S product difficult to release and decreasing the cumulative release of Pb.

The Effectiveness of MPC

Although S/S technology has been applied to treat heavy metal contaminated soil widely for its economy and convenience, it is still hard to recycle of S/S waste back into environment as the uncertainty of its long-term effectiveness. Large numbers of S/S waste were disposed in landfill, which was definite a waste of resources. Consequently, utilization of S/S waste would be the most important problem that should be settled in future. At present, efforts have been done to evaluate the utilization of S/S waste. The leachability index calculated according to ANS 16.1 can be taken as the performance criteria for the utilization and disposal of S/S-treated waste [37]. According to Environment Canada [37], S/S products are appropriate for “controlled utilization” if the LX value of the specific waste is larger than 9. When the LX value is between 8 and 9, S/S-treated waste can be disposed of in sanitary landfills. In addition, if the S/S wastes have an LX value of lower than 8, they are not permitted for disposal. According to Nathwani and Phillips [38], diffusion coefficients generally range from 10^{-5} (very mobile) to 10^{-15} cm^2/s (immobile). Therefore, the effective diffusion coefficient was also listed to depict the mobility of Pb in S/S samples after MPC treatment.

The calculated effective diffusion coefficient and leachability index varied with different MPC dosage and different curing ages were presented in Figure 3. Results of the calculated parameters mentioned above were showed in Figure 3a as a function of MPC dosage, aiming to assess the effects of MPC dosage on the metal mobility and effectiveness of MPC treatment. As MPC dosage of samples varied from 30 to 70%, the mean effective diffusion coefficient D_e decreased from $1.33E-12$ to $3.04E-13$ cm^2/s , and the corresponding LX value ranged from 12.40 to 13.28. Upon addition of MPC, the mean D_e values was declining, demonstrating that the mobility of Pb in S/S samples was getting lower as MPC dosage increased. It's important to note that mobility of Pb after MPC treatment was also low even the dosage was 30%. The calculated LX values recorded in Figure 3a showed that the contaminated soil treated by MPC could be used for recycling as all the LX values were beyond 9, which was the threshold value for utilization in Environment Canada [37].

The effects of curing age on the effectiveness of the MPC treatment were vividly demonstrated in Figure 3b, which showed that the LX values increased with prolonging of during ages. Obviously, the variation of D_e values behaved in another way. The D_e values ranged from $2.39E-12$ to $1.88E-15$ cm^2/s as the curing age increased from 3 to 56 days, and the corresponding LX values increased from 12.36 to 15.65. In addition, the change of D_e or LX value was significant during the early stage, which could be concluded through the variation of D_e from 3 to 7 days, nearly a magnitude of order increased in this stage. That could be attributed to the fast hydration reaction of MPC at the beginning, and which would slow down as time passed as D_e values changed slightly for the samples carried larger than 15 days. Especially, all the MPC treatment could be utilized as all the LX values were larger than criteria for utilization.

Generally, the mobility of Pb ions in MPC product decrease with the increase of MPC dosage and curing age, this phenomenon could be owing to the following two reasons: Firstly, more alkaline hydrates would be appeared

Table 3. Slope values of different leaching mechanisms.

| Sample | Slope value | R^2 | Leaching mechanism |
|-----------|-------------|--------|--------------------|
| MPC-D-30% | 0.35 | 0.9555 | Diffusion |
| MPC-D-40% | 0.38 | 0.9636 | Diffusion |
| MPC-D-50% | 0.39 | 0.9404 | Diffusion |
| MPC-D-60% | 0.37 | 0.8810 | Diffusion |
| MPC-D-70% | 0.35 | 0.9247 | Diffusion |
| MPC-C-3d | 0.36 | 0.9041 | Diffusion |
| MPC-C-7d | 0.38 | 0.9404 | Diffusion |
| MPC-C-15d | 0.39 | 0.9534 | Diffusion |
| MPC-C-28d | 0.39 | 0.9546 | Diffusion |
| MPC-C-56d | 0.40 | 0.9507 | Diffusion |

during the S/S process when MPC dosage increased and curing time prolonged; Secondly, the booming hydration products of MPC would change the microstructure of MPC solidified body since the structure became more compact and crack in the inner space of solidified body decreased as morphology of MPC changed [24]. Pb ions in the solidified body would release slower if matrix solubility and pore volume in the S/S monolith decreased, which were the main reason why Pb mobility decreased with the increasing MPC dosage and curing time.

Leaching Mechanism

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 fraction release, namely, $\log(B_t)$, vs. the logarithm of time, namely, $\log(t)$, line [32]. The slope of the fitting curve would distinguish the controlling leaching mechanism of Pb leaching, namely 0.5 for diffusion, 0 for surface wash-off and 1 for dissolution [32].

Regression analyses of different semi-dynamic leaching tests were listed in Table 3, including the slope values, R^2 values of the fitting curves and the corresponding leaching mechanism. Generally, most of the R^2 indicated a highly linear correlation between $\log(B_t)$ and $\log(t)$. According to NEN 7345 (1995), the leaching mechanism of metal was found to be diffusion if the slope values were between 0.35 and 0.65. Slopes of all the samples with different MPC dosage were all between 0.35 and 0.65, indicating that all the controlling leaching mechanism of Pb appeared to be diffusion for all occasions. In another way, the addition of MPC did not change the leaching mechanism of Pb in S/S monolith, and diffusion turned out to be the main leaching mechanism for Pb in MPC treated contaminated soils. Similarly, slopes of the samples with different curing ages were between from 0.36 to 0.40, and the main mechanism controlling Pb releasing was diffusion. Although the slopes were increasing with curing ages, the variation of curing age did not change the controlling leaching mechanism.

Although the leaching mechanism of Pb turned out to be diffusion as the MPC dosage and curing age of S/S monolith changed, there also some variations among the slope values of fitting curves. As a result, there also could be some gaps between the actual leaching data and predicted data using diffusion model. The experiment time of semidynamic leaching test ANS 16.1 (90 days) was quite longer than any other test, but there still a lot of work should be done to investigate the long-term leaching mechanism of heavy metal form S/S monolith. Principally, long-term effectiveness of any binders used to stabilize/solidify heavy metal contaminated soil should be validated before putting into use, among which leaching behavior was the most important. Although leaching mechanism of Pb from MPC stabilized soil were

validated in different scenarios, there still many work to be done to assess the long-term environmental risk of MPC treated Pb contaminated soil.

CONCLUSIONS

MPC is a promising candidate to substitute for OPC in some areas for its environment-friendly and some cement-like properties, and it behaves better in S/S remediation of heavy metal contaminated soil. Numbers of efforts have been done to study its strength and microstructure evolution of MPC, and the leaching behavior and leaching mechanism stay unclear. In order to evaluate the effectiveness and long-term environmental risk of MPC S/S waste in different scenarios, leaching mechanism should be elucidated previously. This study investigated the effects of the MPC dosage and curing age on the leaching behaviors of MPC treated Pb-contaminated soils, and the effectiveness of MPC treatment and leaching mechanism of lead under different conditions were presented using the TCLP and semi-dynamic leaching tests. The main conclusions are as follows:

1. Based on the leaching results and TCLP regulatory for Pb concentration (5 mg/L) in leachate, MPC treatment was effective even after 3-day curing, but it could be considered effective only when MPC dosage was larger than 40%.
2. When the MPC dosage increased from 30 to 70%, the corresponding cumulative leaching amount of Pb decreased markedly from 94.57 to 35.24 mg/m², which could be attributed to the increasing alkaline hydration products as MPC dosage increased. As curing time prolonged from 3 to 56 days, morphology change of MPC hydrates would make the minerals more stable and inner pores volumes decreased, leaching to the cumulative release of Pb decreased from 94.60 to 45.40 mg/m².
3. The mobility of Pb in MPC treated contaminated soil kept a low level for all the samples with different MPC dosage and different curing age; all the S/S products could be used for utilization according to Environment Canada [37] for all the LX values were larger than 12. It is noteworthy that Pb concentration in the TCLP leachate beyond environment limit (5 mg/L), which was inconsistent with effectiveness evaluation by method developed by Canada. Further effectiveness evaluation of remediation technology should be done more specifically on different enquirements.
4. The main mechanism that controlled Pb leaching from MPC treated S/S samples appeared to be diffusion. The variation of curing age and MPC dosage did not change the leaching mechanism of Pb from S/S products. Diffusion model could be used for the long-term leaching prediction of Pb in MPC treated Pb contaminated soil.

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