



## Technical Note

## Effect of drying–wetting cycles on leaching behavior of cement solidified lead-contaminated soil



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## HIGHLIGHTS

- Effect of wetting–drying cycles on leaching behavior.
- Wetting–drying cycles accelerated lead leached in solidified specimens.
- Increase of cement addition resisted the corrosion of solution.
- Leached lead concentration increased with acidity of solution.
- pH of leachate decreased with wetting–drying cycles.

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## ABSTRACT

Lead contaminated soil was treated by different concentration of ordinary Portland cement (OPC). Solidified cylindrical samples were dried at 40 °C in oven for 48 h subsequent to 24 h of immersing in different solution for one drying–wetting. 10 cycles were conducted on specimens. The changes in mass loss of specimens, as well as leaching concentration and pH of filtered leachates were studied after each cycle. Results indicated that drying–wetting cycles could accelerate the leaching and deterioration of solidified specimens. The cumulative leached lead with acetic acid (pH = 2.88) in this study was 109, 83 and 71 mg respectively for solidified specimens of cement-to-dry soil (C/Sd) ratios 0.2, 0.3 and 0.4, compared to 37, 30, and 25 mg for a semi-dynamic leaching test. With the increase of cycle times, the cumulative mass loss of specimens increased linearly, but pH of filtered leachates decreased. The leachability and deterioration of solidified specimens increased with acidity of solution. Increases of C/Sd clearly reduced the leachability and deterioration behavior.

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## 1. Introduction

Remediation methods for heavy metals-contaminated soil include solidification/stabilization (S/S), chemical washing, electro-dynamics, bioremediation, etc. S/S is a relatively mature technology that is speedy, economical and convenient (Shi and Spence, 2004; Al-Tabbaa and Perera, 2005). Given these advantage, S/S is widely utilized in the remediation engineering of heavy metals-contaminated soil. The US Environmental Protection Agency (EPA) considers S/S as the best technology for handling toxic and hazardous waste (Gougar et al., 1996). S/S technology fixes harmful pollutants in soil or transforms them into inertial forms through physical or chemical methods to prevent their migration and diffusion in the

environment. Inorganic materials such as cement and lime were extensively utilized in the past based on cost and technical considerations (EPA, 2009). The stabilization mechanism of cement-treated contaminated soil is demonstrated in the hydration process in which heavy metals react with hydration products through absorption, ion exchange, valence bond coordination, and other means; heavy metals ultimately remain on the surface of the hydrated silicate colloid in the form of hydroxide or a complex (Malviya and Chaudhary, 2006; Chen et al., 2009). However, uncertainties over long term durability and previously cheap landfill disposal costs resulted in limited use in many countries. There is a need to characterise treated material and assess components containment and release, to improve S/S confidence (John et al., 2011).

So feasibility assessments of S/S materials are vital and are often undertaken after 28 d of curing (Bulut et al., 2009), with particular emphasis on the physical properties and durability of solidified specimens (Fleri and Whetstone, 2007). Various studies have

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investigated the leaching properties of Pb encapsulated in cement matrices. For example, several types of leaching tests were used to investigate the leaching behavior of Pb from cement treated waste materials (Li et al., 2001); semi-dynamic leaching test was used to investigate the leaching mechanism of cementitious materials treated Pb contaminated soils (Moon and Dermatas, 2006). In field, components in solidified materials become altered with increasing durations of hydration, and both the chemical and physical properties with environmental factors control their releases. These properties include the pH, Eh, porosity, permeability and tortuosity of the solidified samples, speciation and alterations in speciation of components, availability (leachable fraction) of components for release (Sloot et al., 2005), as well as acid rain, drying–wetting cycles and other climatic conditions (Du et al., 2012). Many properties were considered about leaching behavior of heavy metals in solidified materials (Bone et al., 2004; Xue et al., 2013a). However, long-term effectiveness and chemical durability of S/S treated materials are still not well understood (Bone et al., 2004). The laboratory leaching data can simulate the behavior of waste forms under ideal, static or worst case field condition, but the actual situation in field was not fully considered. This paper sets out to evaluate drying–wetting cycles dependent chemical leaching of lead from solidified clay, to assess changes in leaching behavior with increasing drying–wetting cycles and establish long-term chemical performance.

## 2. Materials and methods

### 2.1. Soil

The clay utilized in the tests is silty clay obtained from a subway excavation site in Wuhan City. The physico-mechanical properties of the clay are shown in Table 1, which was obtained according to the “Standard for soil test method” of China. Light Proctor compaction method was used for the compaction test.

### 2.2. Pb-contaminated soil preparation

The clay was dried, ground and then sieved through a 2 mm screen. The sieved clay was used for the tests. Given the inertness of nitrate in cement hydration (Cuisinier et al., 2011), Pb(NO<sub>3</sub>)<sub>2</sub> solution was added to the clay until the Pb concentration in the soil reached 5000 mg kg<sup>-1</sup>. Deionized water was then added to the contaminated soil until the water content reached 19.5%. The Pb-contaminated soil was mixed evenly and braised for 10 d under standard curing conditions (20 °C ± 2 °C, 95% relative humidity) to allow Pb(NO<sub>3</sub>)<sub>2</sub> and the clay to reach equilibrium.

### 2.3. S/S treatment of Pb-contaminated soil

Ordinary Portland cement (OPC) was added to the lead-contaminated soil at cement-to-dry soil (C/Sd) of 0.2, 0.3 and 0.4. Mixing of these materials was conducted in a 10 L SPAR type mixer. The soils were homogenized for 15 min prior to the addition of distilled water. It was ensured that the ratio of addition of water to the binder and dry soil was 1:1. The mixture was cast into 40 mm × 80 mm plexiglass cylinder molds in three layers, with each layer compacted

by means of a vibrating table to yield good packing of the mixture. After the initial mixing, 1 d was allowed for setting before the solidified samples were demolded. A further 27 d were allowed for curing of the solidified specimens in a cabinet at a controlled condition (temperature = 25 ± 2 °C, relative humidity > 90%).

### 2.4. Test methods

The recommended method by Kamon et al. (1993) was adopted for drying–wetting cycles test, namely solidified cylindrical samples was dried under 40 °C in oven for 48 h subsequent to 24 h of immersing in different solution for one cycle. 10 Cycles were conducted on samples. The leaching solutions used in the tests were acetic acid (AA, pH 2.88), distilled water (DW, pH 6.80) and a mixture of dilute nitric and sulfuric acids (NSA, pH 5.00). Subsequent to completion of the 24 h extraction, lead concentration, pH tests were conducted on the filtered leachates according to the standard methods (APHA, 1992). An agilent 7700 inductively coupled plasma mass spectrometry (The MDL for Pb is 0.16 ppt) was used to determine Pb concentrations. The changes in mass loss of solidified cylindrical samples were measured by electronic balance before and after immersing in solution, and the cumulative mass loss was calculated by the following equation (*n* is the cycle times):

$$\rho_n = \frac{m_0 - m_n}{m_0} \times 100\%$$

where  $\rho_n$  (%) is the cumulative mass loss of sample after *n* cycles;  $m_0$  (g) is the mass of sample before drying–wetting cycles test and  $m_n$  (g) is the mass of sample after *n* cycles.

Three replicates were performed of each experiment, and the test results were obtained according to mean of three replicates.

## 3. Results and analysis

### 3.1. Leaching concentration

Leaching concentration of solidified specimens after drying–wetting cycles with AA as leaching solution was presented in Fig. 1a and b presented the results with DW, NSA as leaching solution. A typical observation was that the AA leachates contained 10,000 times more concentrations of leached lead as compared to both DW and NSA leachates. The leaching concentration of different solutions was in the order AA > NSA > DW. Increases of C/Sd ratios clearly reduced the leachability of solidified specimens. The leaching concentration of lead decreased rapidly with increased of cycle times in the initial phase, and then a slow reduction process was showed, but the leaching concentration of lead was still high, which might be attributed to the cracks formed. The cumulative fraction of lead leached followed a two-stage process, namely fast rising phase and slow rising to stabilization phase, which consisted with the results of semi-dynamic leaching tests (Moon et al., 2010).

To compare the leaching concentration in this study to the result of a semi-dynamic test (Song et al., 2013), different solidified specimens (C/Sd = 0.2, 0.3, 0.4) were prepared and submitted to the semi-dynamic leaching test (acetic acid with pH of 2.88) for 30 d. The cumulative leached lead with acetic acid in this study was

**Table 1**  
Basic physico-mechanical properties of soil used in tests.

Water content (%)	Natural density (g cm <sup>-3</sup> )	Specific gravity	Void ratio	Liquid limit (%)	Plastic limit (%)	Optimum moisture content (%)	Grain-size distribution (%)			Maximum dry density (g cm <sup>-3</sup> )
							Sand	Silt	Clay	
20.8	1.89	2.72	0.74	41.6	21.8	19.5	3.4	62.3	34.3	1.72

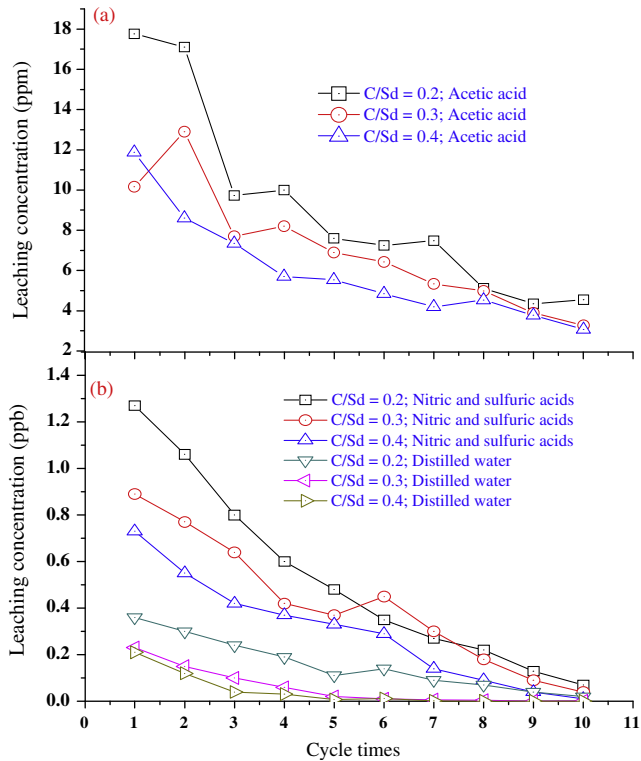


Fig. 1. Leaching concentration of solidified samples after drying-wetting cycles.

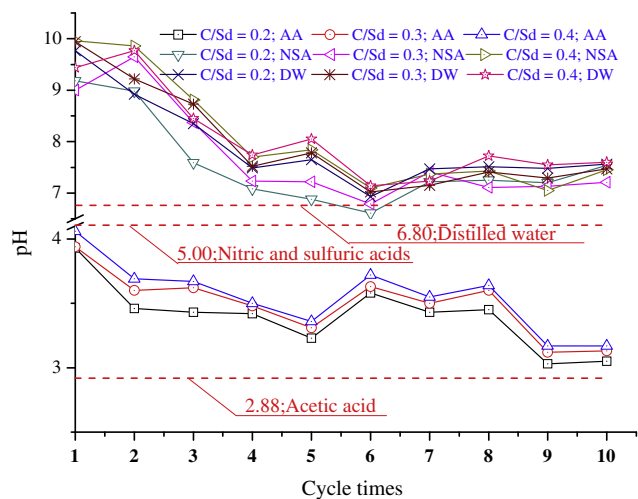


Fig. 2. pH of leachate for solidified specimens after drying-wetting cycles (AA: acetic acid; NSA: nitric and sulfuric acids; DW: distilled water).

109, 83 and 71 mg respectively for solidified specimens of C/Sd ratios 0.2, 0.3 and 0.4, but for semi-dynamic leach test, the cumulative leached lead was 37, 30, and 25 mg respectively. So drying-wetting cycles could accelerate the leaching of lead in solidified specimens and should be taken into account for the analysis of effectiveness of S/S treatment.

### 3.2. pH of leachate

The pore solution in the solidified samples typically has a pH value ranging from 12 to 13.5 (Fan et al., 2010). The pH of leachate changing with drying-wetting cycles was showed in Fig. 2. The pH of leachate was much higher than that of corresponding leaching

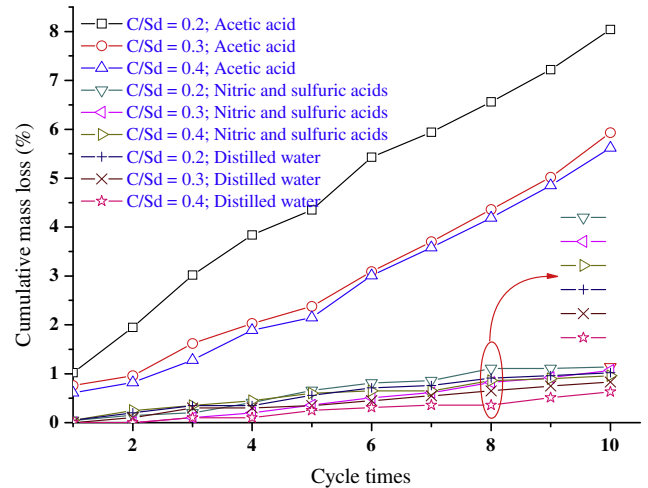


Fig. 3. Cumulative mass loss of solidified specimens after drying-wetting cycles.

solution. In the acid environment, physical and chemical reactions occur in the solidified specimens, which results in a reduction of the pH value of pore solution and an increase for leachate. The  $\text{Ca}(\text{OH})_2$  presented in the solidified specimens probably consumed the  $\text{H}^+$  in the leaching solution. As the monolithic solid remained in contact with the leaching solution for a longer period, the pH of the leachate was expected to continue to rise (Yin et al., 2006). The pH of leachate decreased with increase of drying-wetting cycles overall, but showed a slight increase after cycles 6, which was resulted from the cracks formed. Decreased pH of the leachate with drying-wetting cycles indicated that  $\text{Ca}(\text{OH})_2$  in the solidified specimens was consuming. When the reactions continued, the solidified specimens gradually lost its mechanical strength, resulting in cracking, mass loss, and eventually structural failure.

### 3.3. Cumulative mass loss

Based on visual observations described above, it was obvious that honeycomb voids were formed as conditioning continued, causing the mass change, which could be measured by an electronic scale with an accuracy of 0.01 g. Cumulative mass loss vs. drying-wetting cycle times for solidified specimens is shown in Fig. 3. It was observed that the cumulative mass loss of solidified specimens linearly increased with cycle times. For samples immersed in acetic acid, the cumulative mass loss increased fast and reached 8%, 6% and 6% for samples of C/Sd 0.2, 0.3 and 0.4 respectively. The cumulative mass loss for samples immersed in distilled water, nitric and sulfuric acids increased slowly and were generally less than 1%. So the corrosion of solidified specimens depended on the pH of leaching solution. In the acid environment, physical and chemical reactions between  $\text{H}^+$  and hydration products occur in the solidified specimens, which results in the dissolution of cement and spalling of soil particles (Fan et al., 2010). Increases of C/Sd ratios clearly reduced cumulative mass loss of specimens. Hydration products in solidified specimens filled the pores between soil particles and bonded them together. The more the hydration products are, the smaller the permeability of solidified specimens are, which can resist the corrosion of chemical solution (Xue et al., 2013b).

## 4. Conclusions

This study investigated the effect of drying-wetting cycles on leaching and hydraulic characteristics of cement treated lead contaminated clay. Soaking tests were conducted and mechanisms

determining test results were discussed. Following conclusions can be drawn:

- (1) It was observed that the acetic acid leachates contained 10,000 times more concentrations of leached lead as compared to both distilled water and sulfuric/nitric acid leachates. Increases of C/Sd ratios clearly reduced the leachability of lead from the solidified specimens. The drying–wetting cycles could accelerate the leaching of lead in solidified specimens. The cumulative leached lead with acetic acid in this study was 109, 83 and 71 mg respectively for solidified specimens of C/Sd ratios 0.2, 0.3 and 0.4, but for semi-dynamic leach test, the cumulative leached lead was 37, 30, and 25 mg respectively.
- (2) The pH of leachate was much higher than that of corresponding leaching solution and decreased with increase of drying–wetting cycles overall, but showed a slight increase after cycles 6, which was resulted from the cracks formed.
- (3) It was observed that the cumulative mass loss of solidified specimens linearly increased with cycle times. For samples immersed in acetic acid, the cumulative mass loss increased fast and reached 8.04%, 5.93% and 5.62% for specimens of C/Sd 0.2, 0.3 and 0.4 respectively. The degree of corrosion of solidified specimens depended on the pH of leaching solution. Increases of C/Sd ratios clearly reduced cumulative mass loss of specimens.

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