



The effect of long-term freeze-thaw cycles on the stabilization of lead in compound solidified/stabilized lead-contaminated soil

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Abstract

The solidification/stabilization (S/S) method is a common technique for the remediation of soils polluted by heavy metal. This study, thus, evaluated the long-term effectiveness, in term of the stabilization of lead in the solidified/stabilized soils, under freeze-thaw cycles, which are important physical processes that lead to material weathering. Three types of compound binders were obtained by mixing the three most commonly used binders (cement, quicklime, and fly ash) in varying proportions for the remediation of lead-contaminated soils. The leachability, chemical forms, and microstructure characteristics of the solidified/stabilized samples after various numbers freeze-thaw cycles (i.e., 0, 30, 90, and 180 times) were examined by utilizing the toxicity characteristic leaching procedure (TCLP) test, chemical speciation analysis, and scanning electron microscopy (SEM). The results showed that the long-term freeze-thaw cycles lead to decreased leachate pH and increased lead concentration in the leachate. The larger the total mix quantities of cement and quicklime, the lower the concentration of lead was presented in the leachate, however, indicating that cement and quicklime are more effective in immobilizing lead ions than fly ash. Chemical speciation analysis revealed that the long-term freeze-thaw cycles did, however, reduce the content of carbonate-bound form lead while the quantity of the ion-exchange forms. SEM further confirmed the observed leaching characteristics and chemical speciation characteristics. In addition, it indicated that, at the same number of freeze-thaw cycles, high initial lead concentrations substantially delayed the hydration process of cement in solidified lead-contaminated soil.

Keywords Lead-contaminated soil · Solidification/stabilization · Long-term freeze-thaw cycle · Leachability · Chemical form · Microstructure

Introduction

Due to mismanagement of industrial and mining activities, excessive use of agricultural chemicals, improper disposal of

sewage sludge and waste, lead-contaminated soil has become a very serious world environmental problem. As early as 1992, the U.S. Environmental Protection Agency (U.S.EPA) listed lead (Pb) as one of the six most dangerous heavy metal pollutants (Cameron 1992). This is because lead's non-biodegradability, toxicity, persistence and bioaccumulation in the food chain and ecosystem are the main threat to human and ecological health. In fact, metallic lead in the soil environment can be rapidly transformed into active lead species, which increase the mobility of lead in the surrounding environment (e.g., water, soil, and plant), thus posing a risk to the ecological system (Cao et al. 2003; Hardison et al. 2004; Lin 1996; Migliorini et al. 2004). Therefore, in order to reduce the migration and transformation of lead in the lead-contaminated soil, it is very necessary to remediate the lead-contaminated soil.

Solidification/stabilization(S/S) is a commonly used heavy metal pollution remediation technology that involves mixing contaminated soils with binders to lower the leachability of

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contaminants and to reduce the migration and transformation of heavy metals in the soil (Chen et al. 2011; Du et al. 2014a; Du et al. 2014c; Du et al. 2012a; Du et al. 2012b). High-alkali cementitious materials, such as Portland Cement (PC), quicklime and fly ash, are among the more commonly used binders in S/S technology, as they are both convenient and cost-effective (Du et al. 2014b). Previous studies have shown, however, that while some properties of contaminated soils can be improved in the short term through remediation with S/S technology, heavy metal pollutants that are immobilized in alkaline-based-binder solidified soil might be activated in more easily leached forms after long-term exposure to harsh environment such as repeated freeze-thaw cycles, sulphate attacks, carbonation, acid rain infiltration, and dry-wet alternation, etc. (Du et al. 2012a; Ram and Mastro 2014; Xu et al. 2018; Zha et al. 2012). In China, seasonally frozen ground is widespread, regions without frozen soil at any time year only account for 1.1% of the country's land area, according to research by Xia (1984). In fact, it is not only China, but seasonally frozen ground is spread all over the world, such as the European portion of Russia (Roman and Ze 2010), and southern Western Siberia (Romanov and Khvostov 2015). It can be seen that how the freeze-thaw cycles experienced by seasonal frozen soil will affect the long-term stability of solidified/stabilized heavy metal contaminated soil is a worldwide problem to be solved.

Much of the literature has reported on the effects of freeze-thaw cycles on the long-term stabilization of solidified/stabilized heavy metal contaminated soils, such as the work by Liu Jingjing et al. (Liu et al. 2020), which evaluated the long-term stability of zinc-contaminated soil treated with cement alkali residue under freeze-thaw cycles through a semi-dynamic leaching test, finding that freeze-thaw cycles increased the cumulative leaching rate of Zn^{2+} in solidified/stabilized zinc-contaminated soil samples. He, Lei et al. (He et al. 2021) reported that the leaching characteristics of Cd^{6+} in solidified/stabilized contaminated soil were related to the number of freeze thaw cycles and porosity. However, these studies mostly focused on the leaching characteristics of heavy metals in solidified/stabilized heavy metal contaminated soils subjected to freeze-thaw cycles, and there are few studies on the chemical forms of heavy metals. In fact, the mobility and toxicity of heavy metal elements depend to a large extent not only on their leaching properties but also on their chemical forms (Kot and Namiesnik 2000; Quevauviller et al. 1993; Quevauviller 1998).

Moreover, in general, scholars have only studied the effects of short-term freeze-thaw cycles (less than 15 times) on solidified/stabilized heavy metal contaminated soils, with no consideration of the effects of long-term freeze-thaw cycles. While 180 freeze-thaw cycles were considered in the current study, by way of example of lack in previous work, Lina Du et al. only studied. It studies the effect of freeze-thaw cycles on

the immobilization process of heavy metal lead in lead-contaminated soil with freeze-thaw cycles of 0, 1, 3, 6, and 9 times (Du et al. 2020). Ming-Li Wei et al. studied the effects of freeze-thaw cycles on the characteristics zinc- and lead-contaminated soil stabilized by the new KMP binder, in which the maximum number of freeze-thaw cycles is only 12 (Wei et al. 2015a). However, solidified/stabilized heavy metal contaminated soil in seasonally frozen soil areas is likely to undergo multiple freeze-thaw alternation states due to seasonal alternation. Under these conditions, the change trends of leaching characteristics and the variations in chemical forms of heavy metals have not yet been clarified. It is not known whether the number of freeze-thaw cycles will always affect the stability of solidified heavy metal contaminated soil, or if the freeze-thaw cycle reaches a certain number, continuing to increase the number of freeze-thaw cycles will not affect the stability of solidified heavy metal contaminated soil. For this reason, it is necessary to conduct an in-depth analysis and discussion of changes triggered by the environmental effects in solidified/stabilized heavy metal contaminated soil under conditions of long-term freeze-thaw cycles of at least 60 times. Consequently, the maximum number of freeze-thaw cycles set in this article is 180 times.

Portland cement (PC), quicklime and fly ash are all commonly used in soil S/S technology as binders (Galiano et al. 2011), and the current study, thus, aimed to systematically investigate the effects of long-term freeze-thaw cycles on stabilization of heavy metals in stabilized/solidified heavy metals-polluted soils treated with various proportions of these binders. A series of experiments, which included performing toxicity characteristic leaching procedure (TCLP) tests, and Tessier's sequential extraction procedures, were performed on soil samples subjected to freeze-thaw cycles for 0, 30, 90, and 180 times to investigate the effect of freeze-thaw cycles on leachability and the presence of various chemical forms of heavy metals in compound solidified/stabilized lead-contaminated soils, thus, evaluating the stabilization of lead in such soils.

Materials and methods

Materials

Samples of soil used in this work were taken from a construction site in the Jiangjin District, Chongqing, China, from depths of 0.5 to 1.5 m. This soil is reddish-brown in color. The collected soil samples were all air-dried in the laboratory for about two weeks before being sieved through a 16-mesh polyethylene screen (<1 mm) to remove various stones, branches, coarse materials, and other debris. Subsequently, the sieved soil samples were subjected to conventional soil tests in accordance with the Standards for Geotechnical Test

Methods (GB/T 50123-2019). The physical properties of the soil samples, thus, determined are shown in Table 1. According to the Engineering Classification Standard for Soil (GB/T 50145-2007), the soils were classified as fine-grained soils containing coarse grains, with a liquid-low limit. Since the liquid limit is less than 50, according to ASTM standards, the fine-grained soil part is clay. The main chemical components of the tested soils are as shown in Table 2, as determined by an X-ray fluorescence (XRF) technique.

Pb²⁺ was selected as the contaminating ion for this study. In view of the high solubility of nitrate (high cation mobility) and its minimal interference with the S/S process (Cuisinier et al. 2011; Hill and Daugherty 1996), analytical-grade Pb(NO₃)₂ was used as the necessary heavy metal contaminant based on its quality indicators (Manufacturer: Sinopharm Group Reagent Co., Ltd.).

Three binder types, cement, quicklime, and fly ash, were selected to remediate the lead-contaminated soils in the this research. The cement selected was ordinary Portland cement (OPC325, Tangshan Hongye Cement Co., Ltd.); the main component of the quicklime was calcium oxide (analytical grade); while the fly ash was obtained from the Chongqing Power Plant (secondary). As the combined SiO₂, Al₂O₃, and Fe₂O₃ contents in the fly ash exceeded 70%, the fly ash used would be classified as Class F according to GB/T 1596-2017. All three binders were passed through a 0.075-mm nylon sieve to create uniformity and the underlying chemical compositions of the cement, quicklime, and fly ash were obtained by using XRF testing, as shown in Table 3.

Specimen preparation

Studies have shown that the initial concentration of heavy metal ions would affect the leaching ion concentration of solidified heavy metal contaminated soil (Fusheng et al. 2019). In this study, in order to eliminate the interference of the initial heavy metal concentration on the experimental results, lead content in the contaminated soil was set to 0.5, 1, or 1.5% by weight of the dry soil. To obtain artificially lead-contaminated soils, pre-determined qualities of Pb(NO₃)₂ were dissolved in deionized water, and the resulting solutions were added individually in portions of the uncontaminated soil and thoroughly stirred with a magnetic stirrer for about 10 min. Finally, each mixture was sealed and cured in a humidity box (22°C, relative humidity 95%) for three months.

Three types of compound binders were employed based on varying the proportions of cement, lime, and fly ash to treat these lead-contaminated soils. The contents of cement and quicklime in the compound binders were either 2.5 or 5% by weight of dry soil, while those for fly ash were 0, 2.5, or 5%. For each contaminated soil samples with a different initial lead content, the required quality of compound binder was added, and the mixture was mixed for 10 min with AM-CG108 dough mixer (Manufacturer: North America Electric (Zhuhai) Co., Ltd.). Subsequently, all fresh mixtures were moulded into cylindrical specimens of size Φ 39.1 mm × h 80 mm. Specimens were sealed and cured for 30 days in a humidity box (22°C, relative humidity 95%) for subsequent tests. The density and moisture contents of specimens were controlled at 95% of the maximum dry density (1.84 g/cm³) and optimal moisture content (19.5%) of the uncontaminated soil, respectively. This article sets three initial lead concentrations, three binder ratios, and four freeze-thaw cycle levels. The same initial lead concentration, the same binder ratio and the same number of freeze-thaw cycles correspond to the same set of samples, and each set of samples has three parallel samples. Thus, a total of 108 samples were prepared, as shown in Table 4.

Testing methods and instruments

Freeze-thaw cycle test

After the 30-day curing period, specimens were put into an alternating high- and low-temperature test chamber (TC401, Chongqing Taisite Test Instrument Co. Ltd.) to undergo freezing and thawing. The specimens were subjected to four levels in number of freeze-thaw cycles (0, 30, 90, 180 times). According to the slow freezing method in the GB/T 50082-2009 standard, the freezing time of the specimen in each freeze-thaw cycle is not less than 4 hours, so the temperature change diagram of a freeze-thaw cycle is shown in the Fig. 1 below. As shown in Fig. 1, one freeze-thaw cycle, which consisted of a constant temperature of -10°C for freezing for 11 h followed by a constant temperature of 20°C for thawing for another 11 h, was completed in one day.

Toxicity characteristic leaching procedure test

The leachability of lead in the specimens was measured using toxicity characteristic leaching procedure (TCLP), in

Table 1 Basic physical properties of uncontaminated soil

Physical property index	Liquid limit/%	Plastic limit/%	Plasticity index (I _p)	Optimum moisture content/%	Maximum dry density/g/cm ³
Soil sample	29	17	12	19.5	1.933

Table 2 Main chemical components of uncontaminated soil (expressed as oxides)

Chemical components	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	Na ₂ O	PbO
Contents (%)	58.83	23.65	13.43	1.46	1.02	1.09	0.25	0.13	ND

ND means not detected

accordance with U.S. EPA Method 1311 (USEPA 1992). The extraction solution used in this procedure was determined according to the pH value of the sample. Where the pH value of the sample is less than 5, a No. 1 extraction solution should be used; this is a mixed solution containing 5.7 mL of glacial acetic acid and 64.3 mL of 1 mol/L NaOH in 1 L deionized water. Otherwise, the No. 2 extraction solution is used; this is made by diluting 5.7 mL of glacial acetic acid with 1 L of deionized water (F-s Zha et al. 2013).

The sample that reaches the number of freeze-thaw cycles of the test design is taken out from the alternating high- and low-temperature test chamber, and about 25 g of the sample is removed from the sample for the TCLP test. Pass the broken 25-g sample through a 1-mm sieve and take a 5-g sample to measure its pH value. The measured pH values of the samples used in this experiment all exceeded 5, and thus the No. 2 extraction solution was used in all cases. A liquid-solid (L/S) ratio of 20 mL/g was adopted by adding 10 g of each crushed and sieved sample into 200 mL of No. 2 extraction solution, then decanting this into a 2 L polyethylene bottle. After 18 ± 2 h agitation on an inverted oscillating device, 20 mL leachate for all tests was extracted after filtering the mixtures through a 0.45 μm filter (Li et al. 2019). The pH values of the leachate were measured using a PHS-3E pH meter (Shanghai INESA Scientific Instrument Co., Ltd.), while the concentrations of lead were measured using a PerkinElmer inductively coupled plasma emission spectrometer (ICP-OES).

Chemical speciation analysis

To study the effect of freeze-thaw cycles on the chemical speciation of lead in solidified lead-contaminated soil, chemical speciation analysis for this study was carried out on solidified lead-contaminated soils with initial Pb contents of 1%, cement contents of 5%, and quicklime and fly ash contents of 2.5% (Pb1C5S2.5F2.5) for 0 times and 90 times freeze-thaw cycles. According to the “Geological Survey Standard of

China Geological Administration” (DD2005-03), the extractant and procedures adopted for this study were based on the Tessier sequential extraction correction method, which is modified itself based on the sequential extraction method proposed by Tessier et al. (Tessier et al. 1979) to further classify the oxidizable forms (organic state) of heavy metals into the weak organic form (humic acid combined form) and strong organic combined form (Wang et al. 2005).

Fractions of seven forms of lead were thus determined, a water-soluble form, an ion exchange form, a carbonate combined form, an iron-manganese oxidation form, a weak organic form, a strong organic form, and a residue form. The remaining samples from the TCLP test were sieved through a 100-mesh sieve, and then subjected to chemical speciation analysis. To perform the procedure, 2.5 g of the sieved sample were accurately weighed and placed into polypropylene plastic centrifuge tubes with stoppers. The procedures detailed below were then applied with relevant extractants:

- Fraction A—water-soluble form:* 25 mL of boiled and cooled deionized water with a pH of 7.0 was added to the weighed 2.5g sample, and then the mixture was shaken for 2 h at a temperature of 25±5°C;
- Fraction B—ion-exchange form:* 25 mL of 1 mol/L MgCl₂ with a pH of 7.0 was added to the residue obtained from procedure a); the mixture was then shaken for 2 h at a temperature of 25±5°C;
- Fraction C—carbonate combined form:* 25 mL of 1 mol/L NaAc with a pH 5.0 was added to the residue obtained from procedure b); the mixture was then shaken for 5 h at a temperature of 25±5°C;
- Fraction D—humic acid combined form:* 50 mL of 0.1 mol/L Na₄P₂O₇ and 0.25 mol/L HCl were added to the residue obtained from procedure c); the mixture was then shaken for 6 h at a temperature of 25 ± 5°C;
- Fraction E—iron manganese-oxide combined form:* 50 mL of 0.25 mol/L NH₂OH · HCl and 0.25 mol/L HCl

Table 3 Chemical composition of the binders used (expressed as oxides)

Chemical components	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	TiO ₂	Na ₂ O
Content (%)								
Cement	58.01	3.66	22.26	8.84	3.79	1.04	0.51	0.20
Quicklime	84.23	4.32	3.10	3.10	0.29	ND	ND	ND
Fly ash	1.73	3.68	39.65	21.42	9.17	ND	ND	2.62

ND means not detected

Table 4 Sample quantity statistics

Initial lead concentrations	Binder ratios	Level of freeze-thaw cycles	Total number of samples
0.5%	C5S5	0 times	108
1%	C2.5F5S5	30 times	
1.5%	C5F2.5S2.5	90 times	
		180 times	

Binder ratio labeled $C_jS_kF_m$ denotes the binder ratio with cement dosages of $j\%$, quicklime dosage of $k\%$, and fly ash dosage of $m\%$ by weight of the uncontaminated dry soil

were added to the residue obtained from procedure d); the mixture was then shaken for 6 h at a temperature of $25 \pm 5^\circ\text{C}$;

- f) *Fraction F—strong organic combined form*: 5 mL of 30% H_2O_2 and 3 mL of HNO_3 were added to the residue obtained from procedure f); the mixture was then shaken evenly and kept in this state for 1.5 h at a temperature of $83 \pm 3^\circ\text{C}$. Then, 3 mL of 30% H_2O_2 was added into the mix, which was agitated from time to time for a further 70 min; 2.5 mL of 3.2 mol/L of 30% NA_4Ac was added to this mix, which was diluted to 25 mL in volume and retained for 10 h.
- g) *Fraction G—residual form*: a complete $\text{HF}/\text{HClO}_4/\text{HCl}/\text{HNO}_3$ dissolution of the residual sample was performed.

After each procedure (a to f), the resulting mixtures were centrifuged at 4000 g for 20 min and the supernatants subject to ICP-OES analysis. Prior to beginning the next procedure, the residues were washed with deionized water, and these washed residues were centrifuged again and the washing solutions discarded. All samples were tested at least in duplicate to reduce risk of errors.

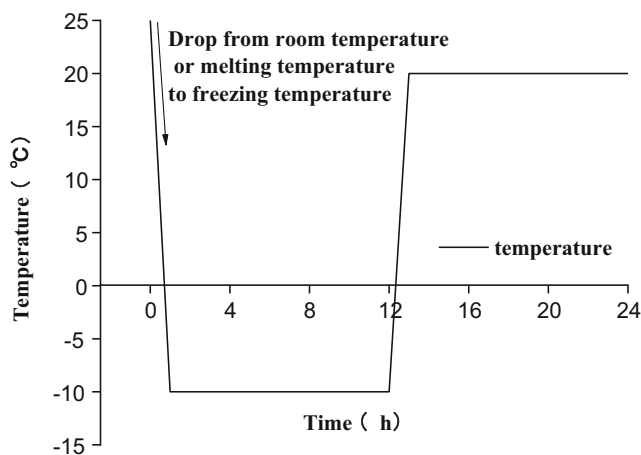


Fig. 1. Schematic diagram of temperature change in one freeze-thaw cycle

Microstructural observation

Repeated freezing and thawing will destroy the original cohesion between soil particles and the soil skeleton structure, which causes the soil particles to rearrange, thereby affecting the porosity of the soil (Rui et al. 2019). Studies by He Lei et al. (He et al. 2021) have shown that the leaching concentration of heavy metals is related to the porosity. Therefore, in order to further study the microscopic mechanism of freeze-thaw cycles affecting the leaching characteristics of solidified contaminated soil, the microstructures of the samples taken from the exposed surface after breaking off the samples used in the first two experiments were examined using a TM4000PlusII desktop scanning electron microscope. However, aiming to obtain a clearer image, the samples were first sprayed with gold for 30 s to enhance their conductivity.

The full experimental scheme for this study is shown in Table 5, where the nomenclature $\text{Pb}iC_jS_kF_m$ denotes a specimen with initial Pb content of $i\%$, a cement dosage of $j\%$, a quicklime dosage of $k\%$, and a fly ash dosage of $m\%$ by weight of uncontaminated dry soil.

Table 5 Experimental scheme

Freeze-thaw strength	Freeze-thaw cycles (times)	Test program	Specimen label
-10~20°C	0, 30, 90, 180	Toxicity characteristic leaching procedure (TCLP) test	Pb0.5C5S5;
			Pb1.0C5S5;
			Pb1.5C5S5
0, 90	0, 90	Chemical speciation analysis	Pb0.5C2.5S5F5;
			Pb1.0C2.5S5F5;
			Pb1.5C2.5S5F5
			Pb0.5C5S2.5F2.5;
			Pb1.0C5S2.5F2.5;
0, 90	0, 90	Scanning electron microscopy (SEM)	Pb1.5C5S2.5F2.5
			Pb1.5C5S2.5F2.5

Results and discussion

Leachate pH

The change in pH value of the leachate of different samples under the action of various long-term freeze-thaw cycles is shown in Fig. 2.

The pH value of the extracts used in the study was initially about 2.88. However, after mixing and shaking with solidified samples, the pH values of the extracts can rise to between 5 and 6. The reason for this increase in pH value is that binders such as cement and quicklime contained in the solidified/stabilized lead-contaminated soil samples are alkaline. During their reactions with the acidic leaching solution, the alkaline matrices between the binders are decomposed, and free OH^- is released from the base, resulting in an increase in the OH^- content of the leaching solution and thus an increase in pH value. Studies (Nehdi and Tariq 2007) have also shown that $\text{Ca}(\text{OH})_2$ is dissolved from the soil pores and released into the extract early in the leaching process.

While the number of freeze-thaw cycles was still relatively small, at 30 times, Fig. 2 shows the pH value of the extracts of sample C5S2.5F2.5Pb1.5 and sample C5S5Pb0.5 having increased significantly. In the early stages of a freeze-thaw cycle, the hydration reaction of the binders has not completely occurred, due to the small number of freeze-thaw; thus, that portion of the binders that has not fully reacted will continue to react with the acidic leaching solution, and the base will be decomposed, permitting the free OH^- to escape from the base, which in turn causes the OH^- content in the leaching solution to increase and the pH value to rise. Part of the reason for the increase in pH value of the extract of sample C5S2.5F2.5Pb1.5 is due to the high concentration of lead ions in that sample, which creates a retarding effect on cement hydration, due to the rapid precipitation of lead hydroxide to form a continuous coating around the cement particles (Liu et al. 2019; Pan et al. 2019).

With increase in the number of freeze-thaw cycles, the pH value of the extracts is seen to decrease overall, however. This is because the freeze-thaw cycle process is accompanied by

various endothermic and exothermic processes that will affect the hydration reaction of the main components of cement, such as C_2S ($2\text{CaO}\cdot\text{SiO}_2$), C_3S ($3\text{CaO}\cdot\text{SiO}_2$), and C_3A ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), thereby affecting the generation of hydration products and hindering the formation of portlandite. This means that the acid buffering capacity of the solidified soil is reduced, and the pH of the leachate is, thus, also reduced.

As both cement and quicklime can generate alkaline hydration products through hydration and hydrolysis during the curing process, cement or quicklime added into lead-contaminated soil can effectively improve the buffering properties of the sample, however, fly ash alone has almost no hydraulic gel properties, and cannot solidify lead ions through hydration products produced by hydration and hydrolysis as seen with cement or quicklime. It also does not have the ability to solidify contaminants when used as a curing agent alone, creating an inability to increase the concentration of OH^- ions in solution through the replacement reaction of heavy metal ions under conditions of high heavy metal content (Thevenin and Pera 1999). As the concentration of heavy metal ions increases, the pH value of the leaching solution continues to decrease, if, and where fly ash is used instead of cement as a binder for lead-contaminated soil, the pH value of the leaching solution obtained from the sample will decrease in proportion to this increase in the amount of fly ash. This helps explain why the pH of the C2.5S5F5 sample is smaller than that of the C5S5 sample, and it is also consistent with the conclusion of Li et al (Li et al. 2001).

It can be seen from Fig. 2 that under the action of short-term freeze-thaw cycles (the number of freeze-thaw cycles is less than 30), the pH value of the leachate will increase. For example, sample Pb0.5%C5S5 (Fig. 2(a)) and sample Pb1.5%C5S2.5F2.5 (Fig. 2(c)), when the number of freeze-thaw cycles is less than 30, the pH value of their leachate has been increasing. However, for solidified lead-contaminated soil samples that have undergone long-term freeze-thaw cycles, when the number of freeze-thaw cycles reaches 180, the pH value of the leaching solution is reduced by about 2.04 to 6.58% compared with solidified lead-contaminated soil samples that have not undergone freeze-thaw cycles. When the

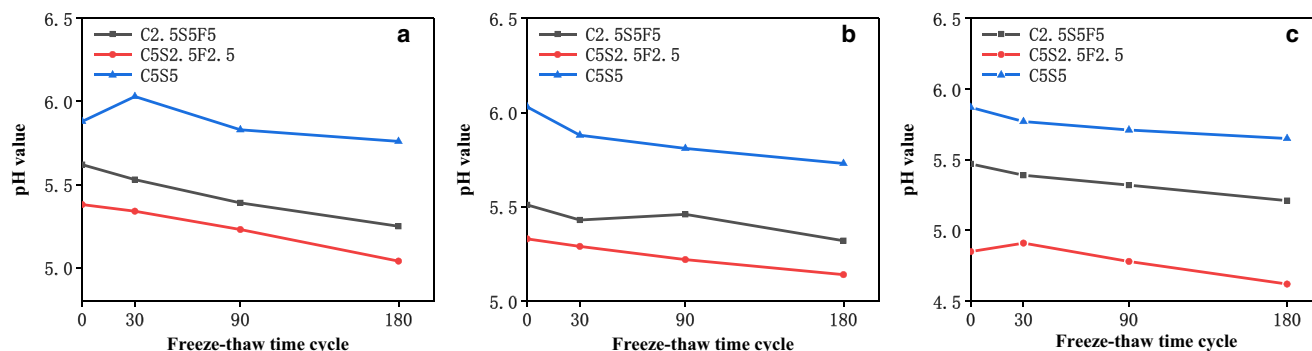


Fig. 2 Leachate pH as a function of the number of freeze-thaw cycles: (a) 0.5% Pb, (b) 1.0% Pb, and (c) 1.5% Pb

number of freeze-thaw cycles is less than 30, the increase in pH value of the leachate could be attributed to the cement hydration reaction that has not been completed at this time, which generated the silicate hydration product, thereby increasing the acid buffering capacity of the solidified soil leachate, resulting in the rise in leachate pH value. After the long-term freeze-thaw cycle, due to the large number of freeze-thaw cycles and the long freeze-thaw action time, the hydration reaction in the solidification/stabilization process has been completed, and no new hydration products would be produced. However, repeated freezing and thawing continued to destroy the structure of calcium silicate hydrate gel (C-S-H), calcium aluminate hydrate (C-A-H), $\text{Ca}(\text{OH})_2$, etc., so that the acid buffering capacity was reduced, which eventually leads to a continuous decrease in the pH of the extract.

Leaching Pb^{2+} concentration

The leaching test was performed on different solidified lead-contaminated soil samples after freeze-thaw cycles. The relationship between the concentration of Pb^{2+} in the leachate and the number of freeze-thaw cycles is shown in Fig. 3, which indicates that, at the same number of freeze-thaw cycles, Pb^{2+} concentration in leachate decreases with increasing cement content added to lead-contaminated soils. In the S/S process, there are three main mechanisms for the immobilization of pollutants (Du et al. 2010; Paria and Yuet 2006): a) chemical fixation of pollutants through the interaction between the hydration products of the binders and the pollutants, b) various binder hydration products physically adsorb pollutants on the surface, c) physical encapsulation of pollutants. So the reason for the decrease in lead ion concentration is probably because of the larger hydrated gel-like calcium silicate hydrate gel (C-S-H) and calcium aluminate hydrate (C-A-H) produced when cement meets water, generated by the hydration reaction of the various minerals in cement, such as C_2S ($2\text{CaO}\cdot\text{SiO}_2$), C_3S ($3\text{CaO}\cdot\text{SiO}_2$), and C_3A ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) (Fusheng et al. 2019; Kogbara 2014). The hydrated gel produced by these hydration reactions has both a large specific surface area and higher surface energy, which assist the adsorption of heavy metal

ions, and which may simultaneously stabilize metal ions through wrapping and chemically incorporation (FS Zha et al. 2013). In addition, the high alkali environment formed by the hydrolysis and hydration reactions of cement enables metal ions to be either adsorbed on the surface of the hydrated gel or to exist in the pores of the soil in the form of hydroxide precipitation. Thus, under the same number of freeze-thaw cycles, the concentration of Pb^{2+} concentration in leachate decreases as the cement content increases.

Fig. 3 also shows that the concentration of lead ions in the leachate increases continuously with the increase of the number in freeze-thaw cycles, but that this increase rate may be fast or slow. When the lead content is low (5000 mg/kg), the concentration of Pb^{2+} in the leaching solution of the lead-contaminated soils treated with composite binders increases slowly with increasing number of the freeze-thaw; however, when the lead content in the samples is higher (15,000 mg/kg), the Pb^{2+} concentration in the leachate increases rapidly.

Long-term freeze-thaw cycles increase the number of large pores, leading to the formation of internal cracks in soils and the destruction of structural integrity (Chamberlain and Gow 1979; Rui et al. 2019). This increases the contact area between the Pb^{2+} and water, causing a decrease in the ability of calcium silicate hydrate gel (C-S-H) and calcium aluminate hydrate (C-A-H) to adsorb and encapsulate the Pb^{2+} . The pH balance of these solidified lead-contaminated soils is thus destroyed, and the hydrated gel is dissolved while the chemical form of lead changes, leading to large quantities of Pb^{2+} precipitating out. In terms of the reasons why the solidified lead-contaminated soil with a high concentration of lead developed a higher rate of precipitation of Pb^{2+} under freeze-thaw cycles than the solidified lead-contaminated soils with lower concentrations of lead, this is mainly because the initial Pb^{2+} concentration was too high, exceeding the adsorption capacity of the hydrated gel and leading to the excess Pb^{2+} dissolving in the pore water, hindering the hydrolysis and hydration processed and thereby reducing the stability of solidification (Gineys et al. 2010). Moreover, these soils could not provide enough OH^- to precipitate Pb^{2+} due to the drop in pH; the excess Pb^{2+} thus mostly exists in the pores of the soil in a free state.

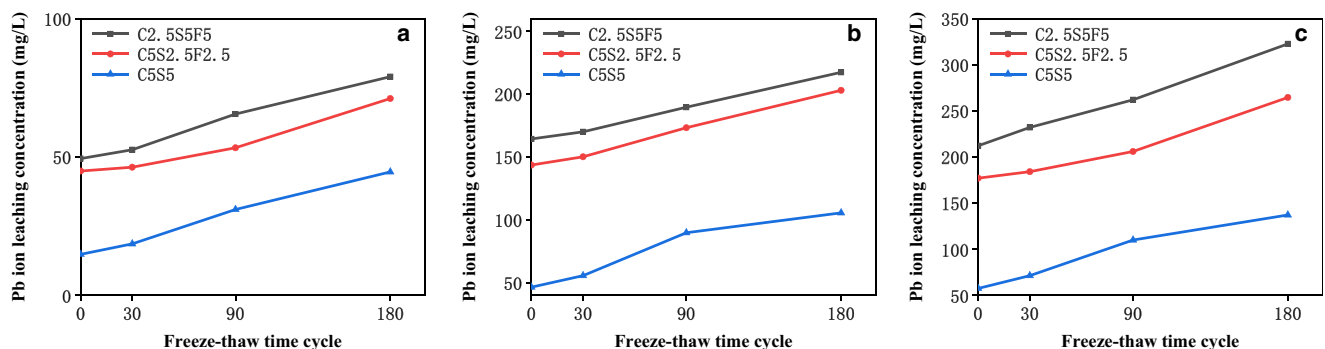


Fig. 3 Pb^{2+} concentration in leachate as a function of the number of freeze-thaw cycles: (a) 0.5% Pb, (b) 1.0% Pb, and (c) 1.5% Pb

Fig. 3 also shows that in the case of the same cement content, the precipitation concentration of lead ions in the solidified lead-contaminated soil with 2.5% fly ash is much greater than that of the solidified lead-contaminated soil without fly ash, which is mainly attributed to two reasons. The first one is that a large number of harmful substances (such as unburned carbon) and fine particles in fly ash would cause a delay in the hydration reaction of cement. The second one is fly ash mainly composed of CaO, SiO₂, and Al₂O₃, which is not like alkaline activators, such as cement and lime, and only effectively hydrates in an alkaline environment.

Comparing the lead ion leaching concentration of solidified lead-contaminated soil under the action of short-term freeze-thaw cycles (the number of freeze-thaw cycles is less than 30) and the action of long-term freeze-thaw cycles (the number of freeze-thaw cycles is greater than 30), it is found that when the number of freeze-thaw cycles is less than 30 times, the rate of Pb²⁺ leaching concentration is relatively low. This is mainly because the low temperature during freezing (Liu et al. 2017) and high initial lead ion content have delayed the hydration reaction and the pozzolanic reaction, resulting in the short-term freeze-thaw cycle, the solidification/stabilization process is still not completed, and the adsorption of Pb²⁺ by the newly produced hydration products offsets some of the Pb²⁺ that are eventually desorbed due to repeated freeze-thaw cycles, which affect the obligatory and non-specific adsorption of heavy metals by the soil. Therefore, if the leaching characteristics of solidified heavy metal contaminated soil are studied only under the action of short-term freeze-thaw cycles, it is impossible to obtain such a significant influence of the number of freeze-thaw cycles on the leaching ion concentration under the action of long-term freeze-thaw cycles. And we can clearly draw a conclusion that the leaching concentration of lead ions continues to increase as the number of freeze-thaw cycles increases, which is not as assumed that it will not stabilize after the number of freeze-thaw cycles reaches a certain number.

Chemical form

Fig. 4 shows the chemical forms of lead found in sample C5S2.5F2.5 before it was subjected to freezing and thawing and after 90 times of alternate freezing and thawing.

For lead-contaminated soil not affected by freeze-thaw cycles, the carbonate-bound lead (F3) content was the highest, at up to 84.21%. The second most common was humic acid-bound lead (F4), at 9.175%, followed by iron-manganese oxide-bound lead (F5) at 3.099%. This shows that cement-based binders, such as cement, quicklime, and fly ash, work to repair lead-contaminated soil mainly by relying on alkaline products produced by hydration reactions to react with Pb²⁺ to form hydroxide or by initiating carbonate precipitation to stabilize Pb²⁺.

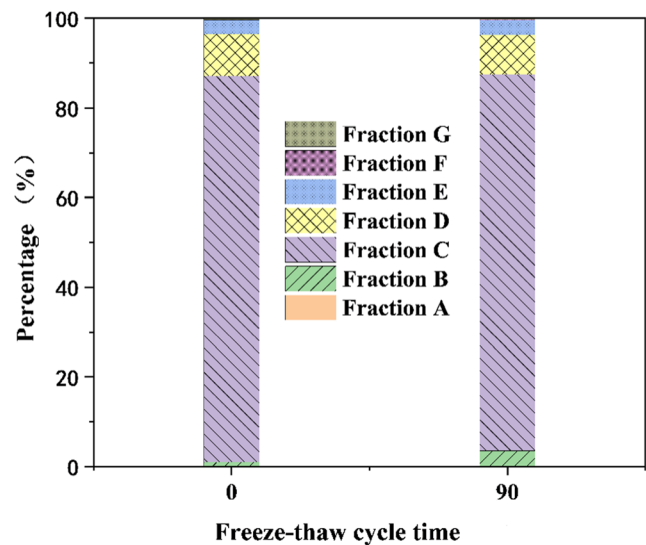


Fig. 4 Chemical forms of lead in solidified lead-contaminated soils at 0- and 90-time freeze-thaw cycles

For the solidified lead-contaminated soils subjected to 90 times of alternate freezing and thawing, the highest proportion was still carbonate-bound lead (F3), though the content level was lower than that seen in solidified lead-contaminated soils without freezing and thawing; this could be attributed to the fact that, with the increase in number of the freeze-thaw cycle, the pH value of the TCLP leachate of the solidified lead-contaminated soils was decreased, creating an environment not conducive to the formation of OH⁻ and CO₃²⁻. It is worth noting that the percentage content of ion-exchanged lead (F2) in the solidified lead-contaminated soil after freezing and thawing was significantly increased, exceeding even that of iron-manganese oxidized bound lead and reaching to up to 3.412%; it could be attributed to the fact that there are several endothermic and exothermic heat processes which occur during long-term freeze-thaw cycles and, according to the principles of soil adsorption thermodynamics, such temperature changes affect the specific and non-specific adsorption of heavy metals by the soil, ultimately promoting the desorption of Pb attached to the surface of the soil and the surface of cement hydration products (Wei et al. 2015b).

These observed phenomena suggest that long-term freeze-thaw cycles mainly affect the ion exchange form and the carbonate bound form in terms of the chemical forms of lead in solidified lead-contaminated soils; this reduces the carbonate bound state proportions while increasing ion exchange state content. The ion-exchange form is sensitive to changes in the soil environment, easily develops into migration and transformation, and can be absorbed by plants, which is the most mobile and most biologically toxic form among the heavy metal forms. That is to say, the freeze-thaw cycle effect transforms the lead in the solidified lead-contaminated soil into a more active chemical form, making it easier to leaching.

SEM

A scanning electron microscope (SEM) was used to test and analyze microstructure change characteristics of samples before and after freeze-thaw cycles, with test results as shown in Fig. 5.

Fig. 5 shows that when the number of freeze-thaw cycles is 0, the solidified lead-contaminated soil with Pb-5000 mg/kg has a good degree of cementation; the surface is relatively flat, and there are almost no cracks and pores. However, for samples that had not undergone freeze-thaw cycles, which had a higher initial lead content of 15,000 mg/kg, as shown in Fig. 5(c), displayed plate crystalline portlandite ($\text{Ca}(\text{OH})_2$). This further confirms that the presence of a high Pb^{2+} content can delay the progress of cement hydration reactions (Gineys et al. 2010; Liu et al. 2019), and where the hydration reaction of cement is delayed, it cannot provide a good alkaline environment for the pozzolanic reaction of fly ash. This explains why spherical unreacted fly ash particles can be seen in Fig. 5(c). After samples undergo 90 freeze-thaw cycles, however, the plate-shaped portlandite ($\text{Ca}(\text{OH})_2$) content is greatly reduced, with gel formed in large quantities covering the surface of the particles and spreading in the pores, indicating that the hydrolysis and hydration reactions of the cement-based binders

(cement, quicklime, and fly ash) and the physical and chemical interactions between their products and the lead-contaminated soils continue to proceed at this stage.

Fig. 5(b) and (d) shows that after 90 freeze-thaw cycles, the hydrated gel formed in the solidification/stabilization process is broken up and dispersed, with more pores and local cracks appearing, demonstrating that the structure of solidified lead-contaminated soils is significantly damaged by freeze-thaw cycles. Analyzing these two photos also suggests that the surface of the hydrated gel is relatively rough, indicating that, after the adsorption structure is destroyed, the metal ions previously encapsulated or chemically bonded are exposed, resulting in the increase in the concentration of heavy metals in the filtrate and in the proportion of lead in the ion-exchange state, a finding consistent with the TCLP test results and chemical speciation analysis results obtained previously.

Conclusions

In this work, attempts were made to evaluate the long-term stability of lead in composite solidified lead-contaminated soil under long-term freeze-thaw cycles based on toxicity characteristic leaching procedure (TCLP) tests, chemical speciation

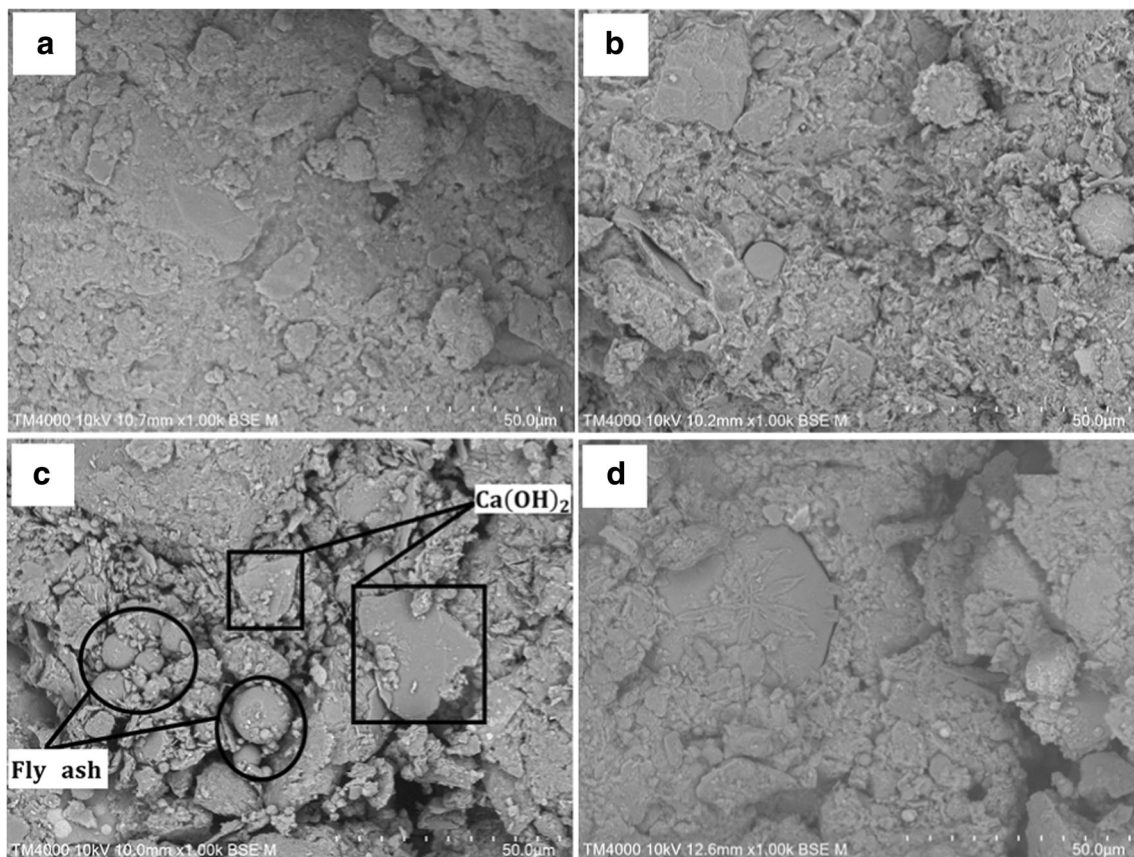


Fig. 5 SEM micrographs of the samples stabilized with compound binder C5S2.5F2.5: with 0.5% Pb and (a) without freeze-thaw cycle and (b) at 90-time freeze-thaw cycles; with 1.5% Pb and (c) without freeze–thaw cycle and (d) at 90-time freeze-thaw cycles

analysis (Tessier sequential extraction correction method), and scanning electron microscopy (SEM) analysis. In this manner, the study investigated the leaching characteristics and chemical speciation of lead in solidified/stabilized lead-contaminated soils with different initial lead concentrations under the effects of long-term freeze-thaw cycles. The main conclusions were, thus, as follows:

For the same number of freeze-thaw cycles, the pH value of leachate increases with an increase in either or both of cement and quicklime content. However, once fly ash is used to replace part of cement as a binder to repair lead-contaminated soil, the pH value of the leachate decreases as the fly ash content increases. The concentration of lead ions filtered out also decreases with the increase of cement and quicklime content. Where fly ash is used to replace a part of cement used as a binder to repair lead-contaminated soils, the concentration of leached lead ions also increases with the increase in fly ash content.

Under the action of long-term freeze-thaw cycles, when the number of freeze-thaw cycles reached 180 times, the pH value of the extracts of different samples was reduced by about 2.04% to 6.58% compared with those without freeze-thaw cycles.

The concentration of lead ions in leaching solution continues to increase with the increase in the number of freeze-thaw cycles, indicating that long-term freeze-thaw cycles increase the leachability of solidified lead-contaminated soil. Simultaneously, the pH value of the leaching solution decreases as the freeze-thaw cycle increases in duration.

Long-term freeze-thaw cycles mainly affect the ion-exchange state and carbonate-bound state with regard to lead-occurring forms. The main manifestation of this is that, as the number of freeze-thaw cycles increases, the carbonate-bound lead content becomes lower despite strong metal stability, and the ion-exchange lead content, with poor metal stability, increases significantly.

After long-term freeze-thaw cycles, microstructure change characteristics in solidified soils can be observed that are consistent with the change rule of the leaching characteristic index, thus revealing the mechanism of solidified lead-contaminated soil change under long-term freeze-thaw cycles. Comparing the scanning electron microscope images of solidified lead-contaminated soil samples with varying initial concentrations of lead ions under the same freeze-thaw cycle also suggests that high concentrations of lead ions may delay hydration reactions.

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Author's contribution Yang Zhongping guided the writing of this manuscript and provided conditions for the development of all experiments. Wang Yao was the main contributor to the writing of this manuscript. Ren Shupe provided most of the data for this study, while both Li Xuyong and Change Jiazhao made suggestions for this manuscript. Xu Hui provided the data for the chemical speciation analysis.

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Data availability Data sharing is not applicable to this article as no datasets were generated or analyzed during the current study.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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