Effect of slow-release phosphate on stabilization and long-term stability of Zn and Cd in soil

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Abstract: Slow-release phosphate materials were prepared by activating insoluble phosphate with organic acid to stabilize high concentrations of Cd and Zn in contaminated smelter soil. The results showed that oxalic acid (0.1 mol/L) activated tricalcium phosphate (TO-0.1) provided the most efficient stabilization of Cd and Zn. After 30 d treatment, leaching concentrations of Cd and Zn in soil were decreased from 3.17 and 16.60 mg/L to 0.078 and 0.32 mg/L, respectively. The acid-soluble fractions of Cd and Zn were transformed into reducible, oxidizable, and residual fractions. Notably, As mobility in TO-0.1 treated soils did not increase. In addition, acid rain leaching and 150 d of natural aging revealed that the slow-release phosphate material provided long-term stability for the stabilization of Cd and Zn. This study verifies the potential application of slow-release phosphate materials for the remediation of heavy metal contaminated soil at smelting sites.

Key words: smelting sites; Zn; Cd; phosphate; slow-release; long-term stability

1 Introduction

The impact of soil heavy metal pollution on environmental safety and human health has attracted widespread public attention. Long-term and excessive accumulation of heavy metals in soil ecosystems poses significant risks to agricultural productivity and groundwater [1]. For example, during the smelting process the release of residues, dust, waste gases, and water, causes serious heavy metal contamination at non-ferrous smelting sites but also to their surrounding soils [2,3]. According to investigations at the smelting sites and the surrounding areas, average concentrations of Cd, Cu, Pb, and Zn in soil were 19.8, 265, 1536, and 1371 mg/kg, respectively, which are significantly greater than the screening values of China's soil-environmental quality criteria [4,5]. Heavy metals accumulate in the surface soil and migrate downwards, thus endangering the surrounding ecological environment and human health [6,7]. Many researchers have noted that Cd, Zn, and Pb are predominantly in their mobile forms, thus confirming their elevated bioavailability within the soil and high pollution risk [8,9].

Phosphate materials are commonly used for the remediation of heavy metal contaminated soils [10,11]. They release phosphate ions and form precipitates with metals, which reduces their bioavailability and migration [12−14]. The addition of phosphate materials such as $CaHPO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$, and $MgHPO_4 \cdot 3H_2O$ reduces the TCLP (Toxicity Characteristic Leaching Procedure)

extractable concentrations of heavy metals in soil. Leachable concentrations of Cd, Cu, and Zn had a reduction of >95%, whereas Pb showed a reduction of 99% [15]. A composite material prepared with biochar (BC) and nano-hydroxyapatite (nHAP) had a stabilizing effect on Pb and Cd; the leaching concentration of Cd was reduced from 3.18 to 2.15 mg/L after 24 h [16]. Diammonium phosphate (DAP) is widely used for the remediation of heavy metal contaminated soils and can transform Pb and Cd into less soluble phosphate precipitates [17]. However, due to DAP's high solubility and leachability, it may cause eutrophication of water bodies [18]. Direct application of insoluble phosphate is cost-effective and environmentally friendly, but the release of phosphorus is too slow to meet most requirements [19]. Reasonable application rates and efficient utilization of phosphorus can not only reduce non-point source pollution but also protect phosphorus resources [20]. With increasing attention to phosphate materials, the focus of this research was to understand their efficient use for heavy metal stabilization.

Due to the low concentration of water-soluble phosphorus in insoluble phosphate and the limited binding sites for heavy metal adsorption and precipitation, practical application at the field scale requires large volumes, which leads to an increase in remediation costs [21,22]. Slow-release phosphate materials can be prepared as stabilization material for heavy metal contaminated soil. For example, biochar has been used as a carrier to deliver sustained-release phosphate [23]. Phosphate−biochar composites have also been used as slow-release fertilizers, thereby avoiding eutrophication of water bodies [24,25]. Biomass has also been used to prepare a new type of phosphorus-modified biochar by impregnating potassium dihydrogen phosphate, which can reduce the leaching of Cu(II) and Cd(II) in soil by 2−3 times, and promote the transformation of acid-soluble fractions to more stable fractions [26]. However, this method of adsorption and re-release increases the material preparation process and cost. In addition, insoluble phosphates can also promote the release of phosphate through activation [27]. Organic molecules with large functional groups can also be used to activate insoluble phosphates. Chemical recombination (valence bond) or physical interaction (adsorption/electrostatic interaction) is established between organic molecules and insoluble phosphates to accelerate the release of phosphorus [28]. Furthermore, active functional groups in soil organic components including —OH and —COOH contribute to the dissolution of insoluble phosphates when phosphate materials are applied to the soil [29]. Release characteristics and influencing factors of low relative molecular mass organic acids on phosphorus in low-grade phosphorites have revealed that the activation intensity of acid on phosphate rock was as follows: oxalic acid > citric acid > tartaric acid > formic acid > malic acid > succinic acid > acetic acid [30]. For example, the available phosphorus content of dolomite phosphate rock (DPR) activated by sodium lignosulfonate, lignin base, and humic acid increased by 6.86, 3.32, and 7.46 times, respectively [31,32].

A problem when considering phosphate as a remediation material is the occurrence of As contamination, which is generally present at lead−zinc smelting sites. Our previous study [5] revealed that the concentration of As in soil at an abandoned lead−zinc smelting site was much greater than the standard value; it mainly exists in the reducible and residual fractions, which are not easy to migrate. However, P and As have similar chemical properties and behaviors, and As is a chemical analog of P. Studies have revealed that after the application of phosphate modifiers, the close chemical similarity between PO_4^{3-} and AsO_4^{3-} causes the former to partially replace the latter, resulting in enhanced desorption and hence mobility of As. Therefore, it is necessary to determine how slow-release phosphates can affect As whilst stabilizing Zn and Cd at smelter sites.

The aim of this study was to prepare slow-release phosphate materials, having high-efficiency stabilization properties, for Cd and Zn stabilization in contaminated soil. The specific objectives of this study were: (1) to determine the effects of phosphate materials on the stabilization of Cd and Zn and their effect on As speciation; (2) to elucidate the stabilization mechanism by analyzing the physical structure and chemical composition of the materials and the remediated soil; (3) to evaluate the long-term stability of heavy metals in soil stabilized by the materials following natural aging and acid rain leaching. This research provides a theoretical basis and technical support for the

remediation of mixed metal(loid) contaminated soil at non-ferrous smelting sites.

2 Experimental

2.1 Soil sampling

Soil samples were collected from an abandoned Zn smelting site in South China from 0−1 m in depth. After removing stones, plant roots, and impurities, the soil samples were passed through a 2.0 mm nylon mesh, and then air dried before being placed in polyethylene bags. Soils were digested in concentrated acid system (HCl−HNO$_3$−HF) and subsequently determined by ICP-OES (ICAP 7000 Series, Thermo Scientific, USA) for metal(loid) concentrations. Soil pH was determined in a 1:2.5 (w/v) soil−water suspension. Available phosphorus was detected by using the molybdenum−antimony anti-spectrophotometric method. Soil characteristics are presented in Table S1 in the Supporting Information (SI).

2.2 Preparation of materials

As activators, 0.1 mol/L oxalic acid (OA) and 0.5 mol/L citric acid (CA) solutions were prepared. The activator was mixed with tricalcium phosphate (TCP) and phosphate rock (PR) at a liquid/solid ratio of 10:1. The mixture was then allowed to react and equilibrate for 7 d at room temperature, dried at 50 °C, and crushed. The stabilization materials used in the investigations were as follows: 0.1 mol/L oxalic acid activated tricalcium phosphate (TO-0.1), 0.5 mol/L oxalic acid activated tricalcium phosphate (TO-0.5), 0.1 mol/L citric acid activated tricalcium phosphate (TC-0.1), 0.5 mol/L citric acid activated tricalcium phosphate (TC-0.5), 0.1 mol/L oxalic acid activated phosphate rock (PO-0.1), 0.5 mol/L oxalic acid activated phosphate rock (PO-0.5), 0.1 mol/L citric acid activated phosphate rock (PC-0.1), 0.5 mol/L citric acid activated phosphate rock (PC-0.5).

2.3 Stabilization of contaminated soil

The effectiveness of slow-release phosphates for stabilization of Cd and Zn in soil was evaluated through batch experiments carried out at 25 °C. Phosphate materials (5 g) were mixed with the contaminated soil (100 g) in a beaker (200 mL), and the sample was prepared by wetting with deionized water and then cultured at a moisture content of 40%. In control treatments (CK), no stabilization materials were added. Samples were collected at the following time: 3, 7, 15, 30, 60, 120, and 180 d. Following the cultivation period, soil samples were air-dried, then ground and sieved for further analysis. Treatments were carried out in triplicate.

Leaching of Cd, Zn, and As from soil samples followed the solid waste extraction procedure for leaching toxicity sulphuric acid and nitric acid method (HJ/T 299—2007). The extraction agent was prepared by adding concentrated sulfuric acid and nitric acid with a mass ratio of 2:1 to deionized water until the pH reached 3.2. Soil (10 g) was added to the extract (100 mL), oscillated (18 h), and then filtered prior to determination of heavy metals and As by ICP-MS (Agilent 7500 Series, Thermo Scientific, USA). Zn, Cd, and As were determined using the four-step BCR sequential extraction procedure (Fig. S1 in SI) [33].

2.4 Leaching experiment

Plexiglass columns of the experimental device for the slow-release characteristic were prepared as follows: firstly, an aperture was created at the bottom of the glass column to collect the leachate in a beaker, then a filter cloth was laid across this opening. Quartz sand (2 cm) was added over the cloth and then the quartz sand (400 g) with 5% TO-0.1 or soil (400 g) with 5 % TO-0.1 was added. Finally, quartz sand (2 cm in depth) was added to the top of the column (Fig. S2 in SI).

Before the start of the experiment, about 100 mL of deionized water was passed through the columns using a peristaltic pump (BT101L, Baoding Reef Fluid Technology Co., Ltd., China) to achieve a saturated water holding rate and eliminate bubbles between the quartz sand in the column. The first leachate droplet was taken as the starting point of the test period, and then deionized water (50 mL) was slowly added every day, and leachate was collected in a beaker. The experiment was conducted over 12 d, and PO_4^{3-} concentration, pH, and electrical conductivity (EC) of leachate solutions were determined.

Simulated acid rain leaching was used to evaluate the long-term stability of Cd, Zn, and As in soil after remediation. The simulated acid rain solution was a mixture of H$_2$SO$_4$−HNO$_3$ (molar concentration ratio of 4:1) with a pH of around 5.6.

The simulated acid rain leaching volume for 1 d (Table S2 in SI) was obtained after subtracting surface runoff (obtained from the statistical year book from Hunan Province for average rainfall). The daily simulated acid rain leaching volume was determined as the total rainfall at the soil sample location for 30 d. The annual rainfall volume was then applied by continuous leaching for 12 d. The column was prepared as follows: firstly, an aperture was created at the bottom of the glass column to collect the leachate, and then a filter cloth was laid across this opening. Quartz sand (2 cm in depth) was added carefully over the cloth and then the contaminated soil (400 g) and/or 5% stabilizing material (TO-0.1 or TCP) was added. Finally, quartz sand (2 cm in depth) was added to the top of the column (Fig. S3 in SI). The interface between the upper layer of quartz sand and the mixture of quartz sand or soil was recorded as 0 cm, and the four sampling ports below it were −5, −10, −15, and −20 cm, respectively. The interface between the lower layer of quartz sand and the mixture of quartz sand or soil was recorded as −25 cm. The corresponding volume of simulated acid rain was injected every day to measure the concentrations of Cd, Zn, and As in leachates. The cumulative release (R_{CF}) of Cd, Zn, and As was determined as follows:

$$R_{CF} = \sum_{i=1}^{n} (\rho_i \cdot V_i) \tag{1}$$

where ρ_i is the concentration of heavy metals in the leaching solution on the ith day (mg/L); V_i is the volume of the leaching solution on the ith day (L).

Mathematical models of heavy metal release were used to fit the cumulative release of heavy metals under leaching conditions. The common first-order kinetic equation (Eq. (2)), modified Elovich equation (Eq. (3)), parabolic equation (Eq. (4)) and double-constant rate equation (Eq. (5)) were used to fit the concentrations of Cd, Zn and As in soil with the leaching solution, and the correlation coefficient (R^2) and root mean square error (RMSE) were used to judge the advantages and disadvantages of the model.

$$\ln R_{CF} = a + bV_{CF} \tag{2}$$

$$R_{CF} = a + b\ln V_{CF} \tag{3}$$

$$R_{CF} = a + bV_{CF}^{1/2} \tag{4}$$

$$\ln R_{CF} = a + b\ln V_{CF} \tag{5}$$

where a and b are constants; V_{CF} was the cumulative leaching solution volume (mL); R_{CF} was the cumulative release of heavy metals (mg).

2.5 Chemical analysis

The microstructures and surface element distribution of slow-release phosphate materials were investigated using scanning electron microscopy (SEM, TESCAN MIRA4, Czech Republic) with an energy dispersive system (EDS, Xplore, Holland). The specific surface areas of the materials were measured by Brunauer−Emmett−Teller (BET, TriStar II 3020, USA). The mineral determination was assessed by X-ray diffraction (XRD, BrukerAXS D8 Advance, Germany) using Cu K$_\alpha$ radiation at 2θ of 10°−85° and scanning rate of 5 (°)/min. Data were analyzed using Jade 6.5 software. Fourier transform infrared spectroscopy (FTIR, NICOLET, USA) was used to determine chemical bonds and functional groups of the material, and the resulting data were analyzed using OMNIC software.

3 Results and discussion

3.1 Stabilization of Cd and Zn

According to the soil environmental quality standards of China (GB 36600—2018) and the US superfund soil screening guidelines, screening values for Zn, Cd, and As were 300, 65, and 60 mg/kg, respectively. Total concentrations of Zn, Cd, and As in the test soil were 76110, 1233, and 409 mg/kg, which greatly exceeded the screening values. Previous investigations revealed that there was a risk of heavy metal pollution in the groundwater at this site [34]. Standard values of leaching concentrations for Zn, Cd, and As in soil were 5, 0.01, and 0.05 mg/L, respectively, which were based on The Chinese Level IV Groundwater Quality Standard (GB/T 14848 − 2017). The leaching concentrations of Cd and Zn in untreated soil were 3.17 and 16.60 mg/L (Table S1 in SI). However, the leaching concentration for As was 0.0026 mg/L, which was below the standard value.

The effects of insoluble phosphate activated by oxalic acid and citric acid on heavy metal concentrations are presented in Fig. S4 in SI. Insoluble phosphate activated by oxalic acid had a greater effect on the stabilization of heavy metals. After remediation by TO-0.1, leaching concentrations of Cd and Zn were reduced from 3.17 and 16.60 mg/L to 0.078 and 0.32 mg/L, respectively. Organic acids can promote the release

of phosphorus and increase the available phosphorus content of phosphorus-based materials [13]. In addition, the activation effect of organic acids on phosphorus was revealed as tricarboxylic acid > dicarboxylic acid > monocarboxylic acid [35]. Oxalic acid can activate soil phosphorus more efficiently than citric acid, which is consistent with the results of this experiment [36]. At the same time, the concentration of organic acids will also affect the behavior of materials and heavy metals in soil [37]. The effect of 0.5 mol/L oxalic acid and citric acid activated material on the stabilization of heavy metals was not as efficient as the 0.1 mol/L treatment. This may be because the organic acids do not react with phosphate during material preparation. They may have entered the soil and combined with heavy metals instead, hence reducing phosphate reaction efficiency. Therefore, during material preparation, the appropriate organic acid concentration should be selected to reduce the migration risk of heavy metals in soil.

The effectiveness of different phosphate materials for stabilization of Cd and Zn in soil is shown in Fig. 1. After the addition of TCP, the leaching concentrations of Cd and Zn decreased to 0.52 and 2.10 mg/L, respectively, which indicated that TCP had great potential in remediating heavy metal contaminated soil. The effectiveness of TO-0.1 for Cd and Zn stabilization was higher than that of TCP. Although KH_2PO_4 also demonstrated effective heavy metal stabilization, it dissolved rapidly and was easily lost following leaching. In addition, there was a clear release of As into the soil solution after KH_2PO_4 stabilization. Significant PO_4^{3-} release will compete for adsorption sites with AsO_4^{3-} and AsO_3^{3-}, leading to increased As mobility. However, As concentrations in leachate were not excessive following stabilization with other materials. It has been shown that in acidic soil, an increase in Ca^{2+} concentration will promote As adsorption and reduce its solubility. Therefore, compared with other phosphate materials, calcium-based phosphate is more suitable as a stabilizing material for heavy metal and As contaminated soils. At the same time, the slow release of phosphorus may also be a reason for the decrease in competition between As and P.

Figure 2 shows the stabilization effect of two insoluble phosphates activated by oxalic acid on heavy metals after natural aging for 150 d.

Concentrations of Cd and Zn were effectively reduced following treatment with TO-0.1 and PO-0.1, which was mostly stable at 30 d. Furthermore, there was no obvious activation within 150 d. The adsorption of phosphate in soil can promote coordination chelation between heavy metals and generate insoluble metal minerals, thus significantly reducing the leaching concentration of heavy metals [17]. In general, the effectiveness of TCP as an activated precursor to remove metal cations is greater than that of PR. In addition, the concentration of low relative molecular mass
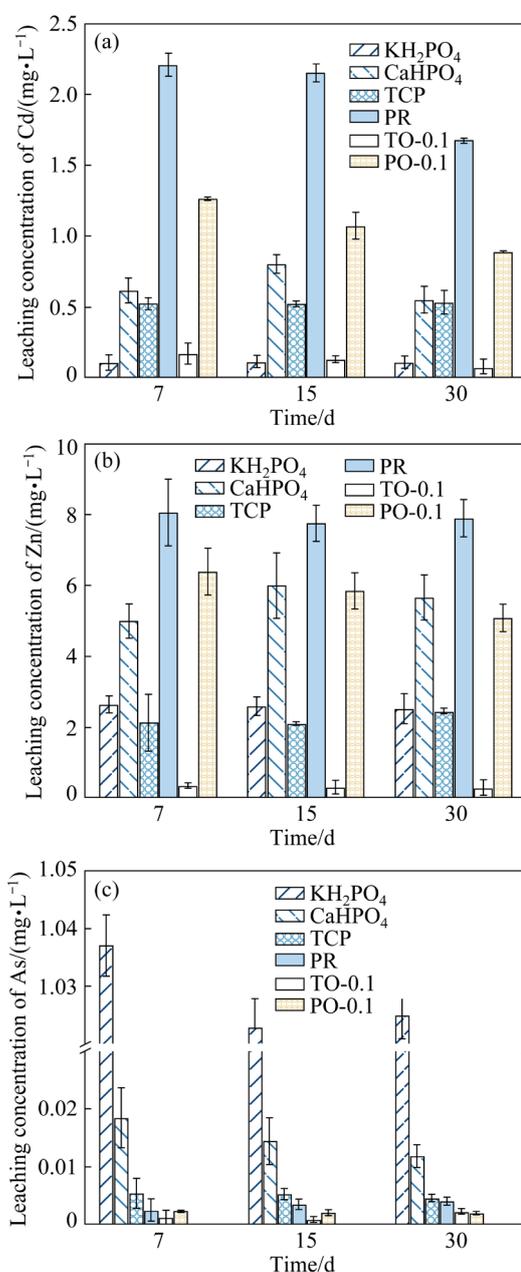
Fig. 1 Leaching concentrations of Cd (a), Zn (b), and As (c) in soils treated by KH_2PO_4, $CaHPO_4$, TCP, PR, TO-0.1, and PO-0.1
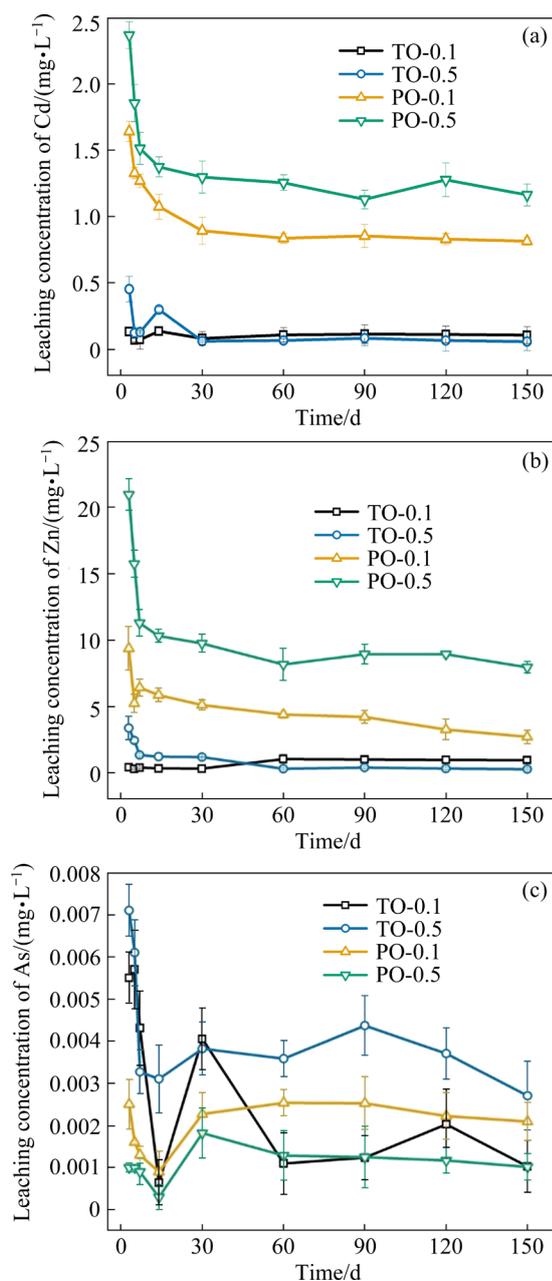
Fig. 2 Leaching concentrations of Cd (a), Zn (b), and As (c) in soil following long-term natural aging

organic acids, complexation ability, and other factors, all have a significant effect on the release of phosphorus in insoluble phosphate minerals [30].

3.2 Chemical speciation of Cd, Zn, and As

Heavy metal fractions after remediation for 30 d are displayed in Fig. 3. All phosphate materials converted the acid-soluble fractions of Cd and Zn into reducible, oxidizable, and residual forms. The reducible, oxidizable, and residual fractions of Cd increased with the addition of KH$_2$PO$_4$, CaHPO$_4$, TCP, and PR, whilst the acid-soluble fraction was
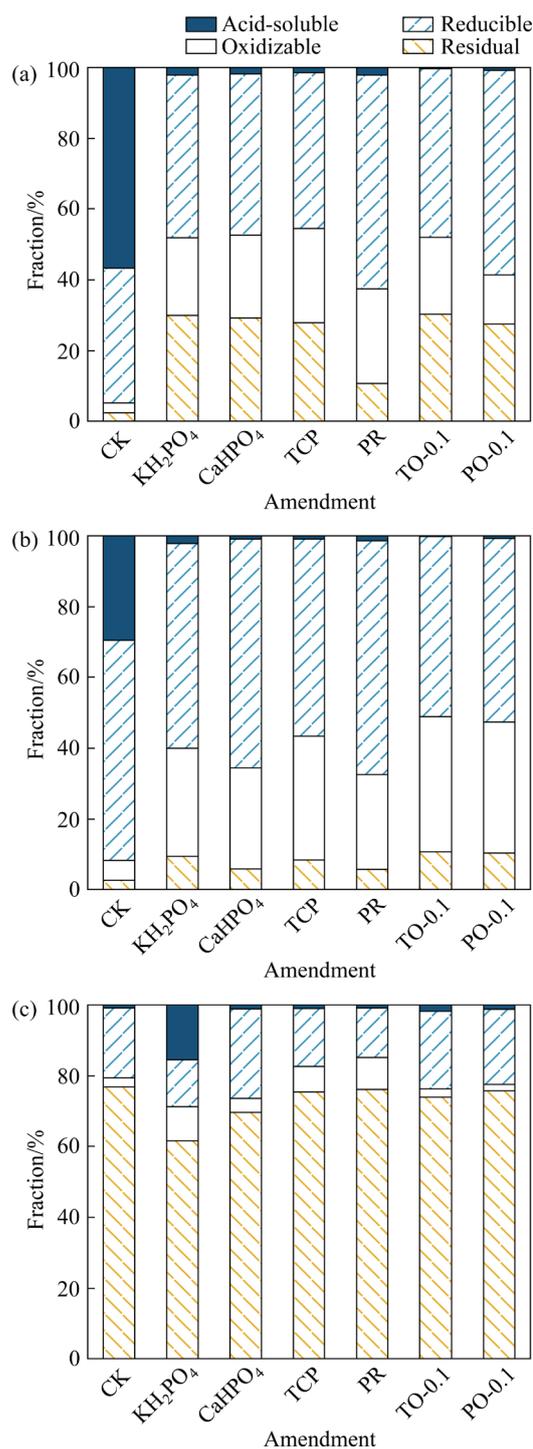
Fig. 3 Fractions of Cd (a), Zn (b), and As (c) following amendment additions

reduced to 2.23%, 1.90%, 1.58%, and 2.37%, respectively. The acid-soluble fraction of Cd was reduced to 0.31% after the addition of TO-0.1, whilst the residual fraction of Cd increased to 30.2%. Stabilization was improved further compared with TCP. Zinc fraction revealed the same change to that of Cd. The increase in the

oxidizable fraction of heavy metals following the addition of modified phosphates may be attributed to the adsorption of Cd and Zn by phosphate minerals. Organic functional groups on the surface of modified phosphate material can be complexed with Cd and Zn to form oxidizable compounds, and precipitation of phosphate will produce an increase in heavy metals in the residual fraction [38,39]. Considering the low solubility of TCP materials, the transfer of Cd and Zn from mobile to residual fractions was due to their incorporation into the lattice of phosphate minerals [40]. The acid-soluble fraction of As increased from 1.01% to 15.69%, 1.27%, 1.13%, 1.03%, 1.88%, and 1.22% following remediation by KH_2PO_4, $CaHPO_4$, TCP, PR, TO-0.1, and PO-0.1, respectively. The acid-soluble fraction of As increased significantly following remediation by KH_2PO_4, which was consistent with the leaching toxicity results. This effect indicated that the slow release of P may reduce the potential risk of As migration when phosphate materials are used to remediate heavy metal contaminated soil.

3.3 Characteristics of amendments

According to the results above, oxalic acid has a greater capacity for activation than citric acid. Therefore, characterization and analysis of TO-0.1 and PO-0.1 were selected to investigate the mechanism of heavy metal stabilization by slow-release phosphate materials. The results of SEM−EDS indicated that TCP and PR had compact structures, whereas TO-0.1 and PO-0.1 had loose, porous structures, which increased the specific surface area (Fig. 4). BET specific surface area is presented in Table S3 in SI. After organic acid activation, the specific surface area of TO-0.1 increased from 5.4847 to 7.0095 m^2/g, and the total pore volume increased from 1.7991 to 2.3015 cm^3/g. The etching impact of oxalic acid on TCP was the main indicator of the increase in porosity and specific surface area. Low relative molecular mass organic acids accelerate the dissolution of insoluble phosphorus by reducing pH. Oxalic acid causes the surface of the material to release phosphate and increase binding sites [41]. The agglomerated porous structure was created from the initial crystal structure. This was caused by the electrostatic repulsion of anions after oxalic acid reacted with phosphate, which encouraged the development of a complex 3D lamellar structure. Through EDS analysis it was discovered that TO-0.1 and PO-0.1 had a greater Ca/P ratio than TCP and PR, indicating that some had amorphous properties (Fig. S5 in SI). The surface of TO-0.1 contained a greater number of exogenous O, most likely occurring in oxygen-containing active groups, as evidenced by the increase in the O/C ratio from 0.60 to 1.61 compared to TCP. Oxalic acid molecules on the surface of the material had functional groups such as 一COOH and 一OH,
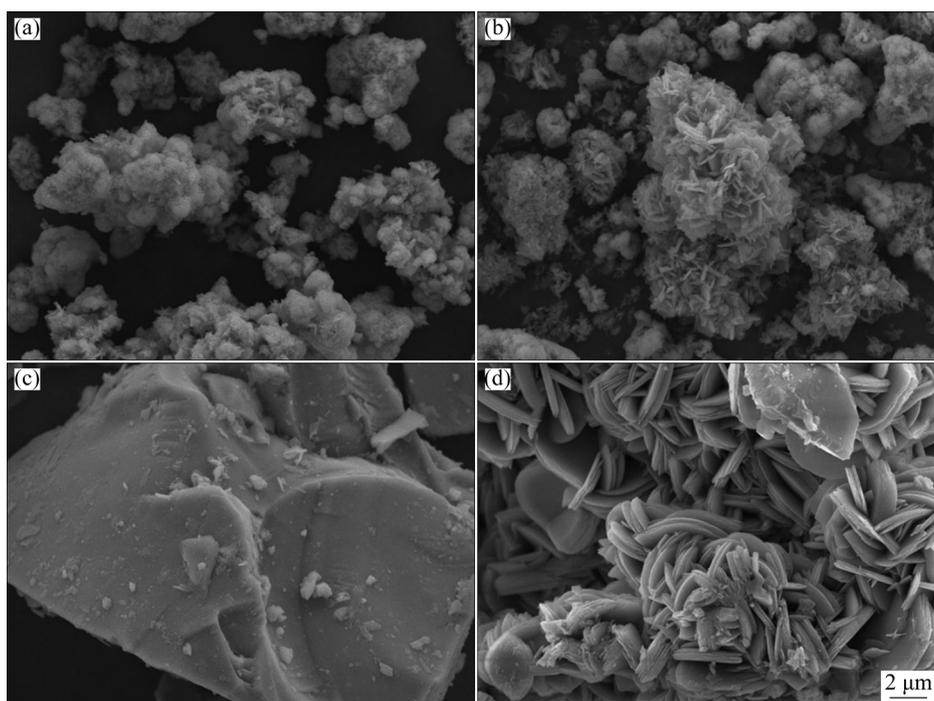

Fig. 4 SEM images of TCP (a), TO-0.1 (b), PR (c), and PO-0.1 (d)

which increase binding sites with metals. The stabilizing effect of metals in soil is improved by the formation of the organic−metal surface complexes [42,43].

The mineral composition of the materials was revealed by alteration of the diffraction peak in the XRD patterns (Fig. 5). Fluorapatite ($Ca_5(PO_4)_3F$) was the main component of PR [35]. The weak peak intensity and broad peak shape of fluorapatite revealed that fluorapatite loses crystallinity after oxalic acid activation. Characteristic peaks of calcium oxalate were observed in both TO-0.1 and PO-0.1, indicating that PR and TCP dissolved and released Ca^{2+}, and combined with $C_2O_4^{2-}$ in oxalic acid to form calcium oxalate monohydrate ($CaC_2O_4·H_2O$) [44]. In addition, the formation of insoluble calcium oxalate revealed that oxalic acid could promote the dissolution of insoluble phosphate and reduce the activation of heavy metals. Therefore, oxalic acid was more suitable as an activator of insoluble phosphate than citric acid. The appearance of characteristic peaks of TO-0.1, hydroxyapatite ($CaPO_3(OH)·H_2O$), and calcium hydrogen phosphate ($CaHPO_4$) revealed that tricalcium phosphate dissolved in oxalic acid to release Ca and P [35].
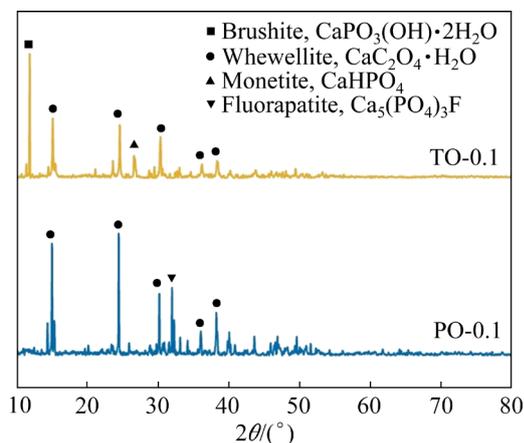

Fig. 5 XRD patterns of TO-0.1 and PO-0.1

FT-IR spectroscopy was used to analyze chemical bonds and functional groups of TO-0.1 and PO-0.1 (Fig. S6 in SI). It was discovered on the surface that there were mainly oxygen-containing functional groups, aromatic functional groups, and phosphorus-containing functional groups. The peak at 1317 cm^{-1} corresponds to a stretching peak of metal carboxylate. The peak at 1620 cm^{-1} conforms to the bending vibration mode and the corresponding

O—C—O bending vibration peak at 519 cm^{-1}. Five peaks between 3000 and 3500 cm^{-1} were consistent with the asymmetric and symmetric stretching peaks of water molecules coordinated by calcium oxalate. Compared with PO-0.1, the absorption peak intensity of TO-0.1 at 1317 cm^{-1} was weakened, indicating that the oxygen-containing active groups in TO-0.1 were more involved in the reaction and consumed calcium oxalate during the activation process [45]. Furthermore, the absorption peaks of $H_2PO_4^-$ at 889 and 958 cm^{-1} disappeared, suggesting that phosphate was to some extent consumed during the activation process.

3.4 Slow-release leaching characteristics of amendments

PO_4^{3-} concentration in the leachate of TO-0.1 treatment is presented in Fig. 6. Due to weak phosphorus adsorption in quartz sand, a significant amount of phosphorus was leached. After 5 d, the concentration of PO_4^{3-} in the leaching solution slowly decreased, but PO_4^{3-} was still steadily released following leaching, which suggested sustained release of TO-0.1. The release of PO_4^{3-} was relatively slow in the first 2 d, but at 3 d a larger quantity was released, with a growth rate of 540%. It was released slowly, and the concentration subsequently was maintained at approximately 0.015 mg/L. This may be due to the formation of preferential flow in the soil at the initial stage of leaching. The loss of leaching solution at the initial stage may have led to the formation of pores, and phosphorus was more likely to have leached into the lower soil through these pores [46]. Phosphorus was not fully immobilized by soil colloids at the initial stage, resulting in most PO_4^{3-} being leached. Furthermore, compared with quartz sand, heavy metals in the soil also had a stabilization effect on phosphorus.

Leaching solution pH in the quartz sand system showed an upward trend at the initial stage (Fig. S7 in SI), with lower pH (6.04) on the first day being attributed to the introduction of low molecular organic acids. With an increase in leaching time, pH increased continuously, which was probably caused by hydrolysis of PO_4^{3-} in the leaching solution. After 7 d, it was almost stable, mainly due to the buffering effect of phosphate. pH revealed a trend of decreasing and then increasing, and this may be attributed to the buffering effect of

the soil. At the same time, carboxyl groups introduced by low relative molecular mass organic acids reduced pH at the initial stage of leaching. pH began to increase at 3 d and stabilized at 8 d. Leaching solution EC decreased by 29% at 7 d, which was due to the gradual exchange of ion-exchangeable components [47]. The EC was significantly higher at 1 d with quartz sand, but then gradually decreased and finally stabilized, which was consistent with PO_4^{3-} in the leaching solution.

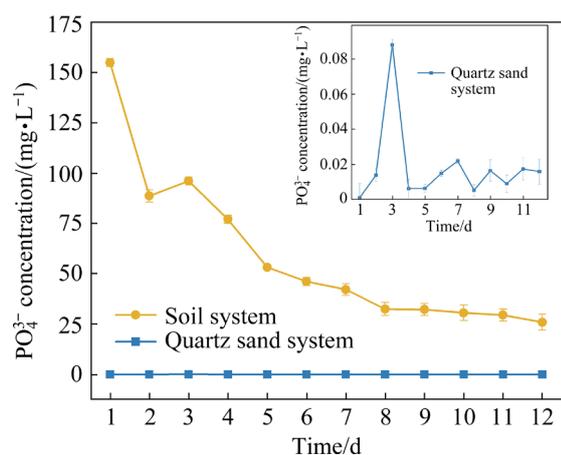**Fig. 6** PO_4^{3-} concentration in leaching solution

3.5 Long-term stability of Cd, Zn, and As in simulated acid rain leaching

Following remediation, the stability of Cd, Zn, and As was evaluated by simulated acid rain leaching, and their cumulative release is presented in Fig. 7. Untreated soil leached the most Cd and Zn (1.68 and 23.2 mg, respectively), and the cumulative release was much greater than that of remediated soil (0.45 and 2.99 mg for TO-0.1, respectively, which decreased by 73.2% and 87.1%, respectively). Cd and Zn were therefore stabilized as a result of TO-0.1 and their release was lower than that of TCP, which was consistent with results presented in Section 3.1. Treatments with TO-0.1 and TCP demonstrated two stages of rapid and slow release. After being treated with TO-0.1 and TCP, the release of Cd during the first 7 d accounted for 75.6% and 75.7% of the total, and Zn accounted for 71.7% and 87.5%, respectively. Due to the continuous leaching of acid rain, competitive adsorption between H^+ and metal cations increased, resulting in the gradual release of heavy metals originally adsorbed on the soil surface. Carbonate- and organic-bound heavy metals were also gradually released due to low pH conditions, resulting in

rapid to slow release. However, in treated soil, cumulative release of As was greater than that in untreated, signifying that As was activated.
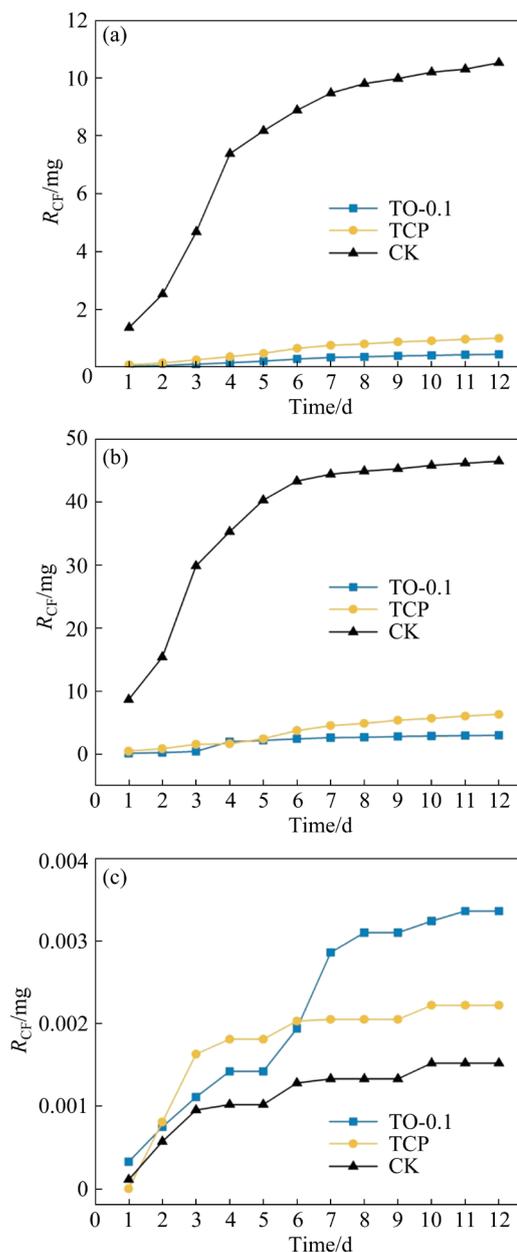

Fig. 7 Cumulative release (R_{CF}) of Cd (a), Zn (b), and As (c) in soils following acid rain leaching

Figure S8 in SI shows the distribution of Cd, Zn, and As at different soil depths following 12 d of acid rain leaching. Cd and Zn concentrations were lower with TO-0.1 treatment than those with TCP treatment. TO-0.1 therefore had greater stabilization effects on Cd and Zn. Leaching was significantly weaker on the surface (0−10 cm) than in the lower layer (15−25 cm). Following remediation with TO-0.1 and TCP, As mobility increased compared with that of the untreated soil, although it did not

exceed 0.05 mg/L (Chinese Level IV Groundwater Quality Standard (GB/T 14848−2017)). Furthermore, the concentration of As was greater in the upper layer (0−10 cm) compared to the lower layer, demonstrating that As did not easily migrate following remediation. As dissolution may also be due to a decrease in redox potential as a result of excess water in the soil column.

The leaching and release of heavy metals may be due to a variety of reactions including adsorption and ion exchange. First-order kinetics can describe the simple surface process of the diffusion mechanism [48]. The parabolic equation was suitable for describing the process controlled by multiple factors [49]. Elovich equation described a

series of reaction mechanisms, such as solute diffusion in the solid phase or interface, surface activation, and deactivation. It is suitable for reaction processes with large changes in activation energy but is not suitable for reaction processes with single surface diffusion mechanism [50]. The double-constant rate equation is an empirical formula, which is suitable for more complex dynamic reaction processes. It can describe the process of uneven energy distribution on soil particle surfaces and the affinity of different adsorption sites for heavy metals [51].

The four equations were used to fit the release process for Cd, Zn and As under simulated acid rain leaching conditions (Fig. 8). The fitting effects of
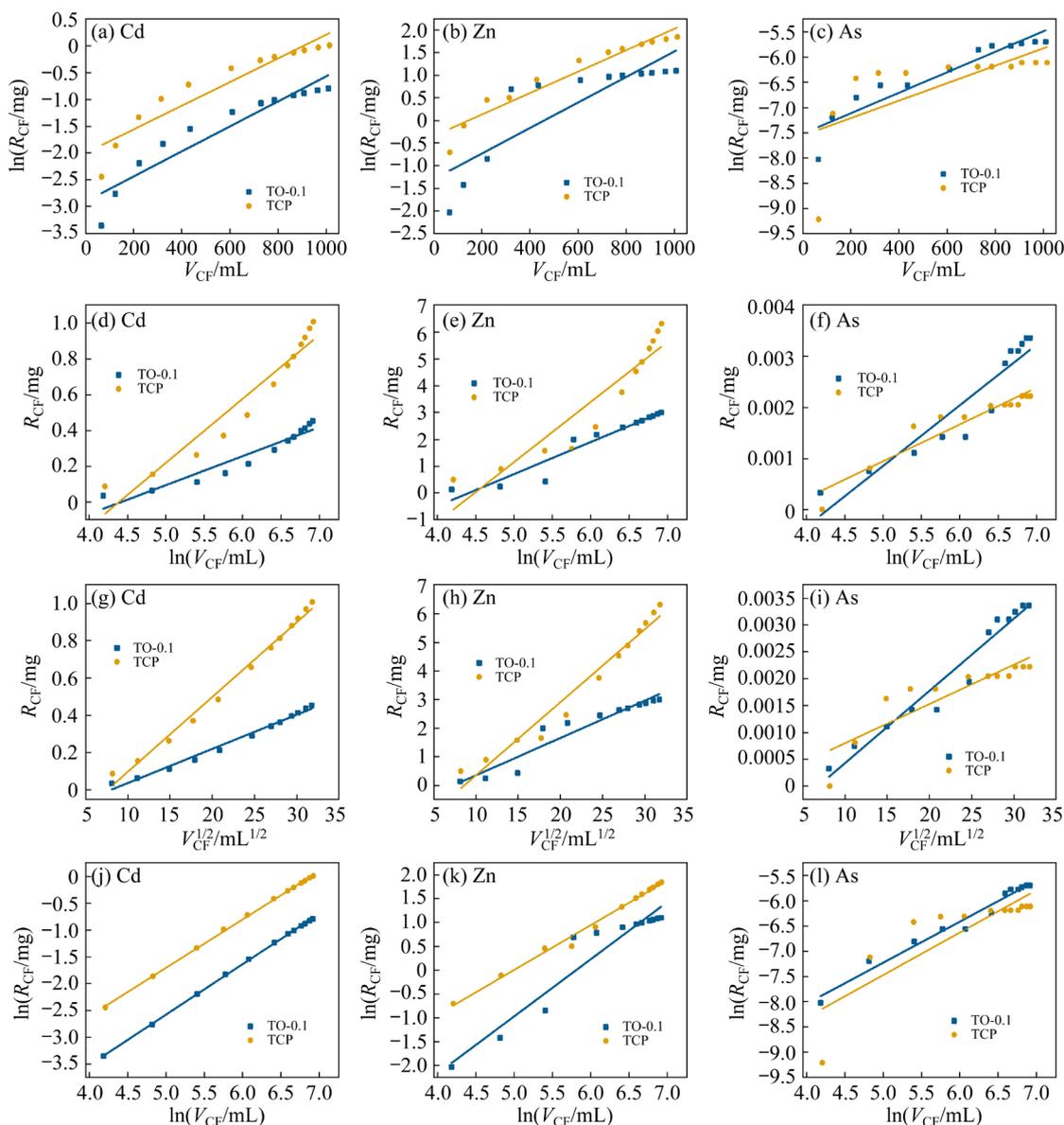
Fig. 8 Model fitting results for release of heavy metals following leaching: (a−c) First-order kinetics equation; (d−f) Modified Elovich equation; (g−i) Parabolic equation; (j−l) Double-constant rate equation

the first-order kinetic equation and the modified Elovich equation were generally inferior to those of the other models, and the R^2 for both were almost less than 0.95. Following acid rain leaching, the release behavior of Cd in the soil treated by TO-0.1 or TCP conformed to the double constant equation. Zn conformed to the modified Elovich equation respectively following acid rain leaching with TO-0.1 treatment, whilst Zn conformed to the parabolic equation with TCP treatment. As conformed to the double-constant rate equation following treatment with TO-0.1. In summary, the release behaviors of Zn and As in the soil treated with different materials have changed. The control of complex reaction rates and multiple diffusion factors was the common kinetic characteristic of these heavy metals [52].

4 Conclusions

(1) Leaching concentrations of Cd and Zn were effectively reduced following treatment with slow-release phosphate materials, being mainly stable at 30 d. Greatest stabilization efficiency for heavy metals was demonstrated by TO-0.1. The acid-soluble fractions of Cd and Zn were transformed into more stable forms: reducible, oxidizable, and residual fractions. The analysis of speciation and leaching concentrations revealed that TO-0.1 did not increase the mobility of As and demonstrated long-term Cd and Zn stability after 150 d of natural aging.

(2) Characterization of slow-release phosphate materials revealed that the addition of oxalic acid promoted the dissolution of insoluble phosphate and increased the specific surface area of the material. With continuous leaching, TO-0.1 demonstrated sustained release of PO_4^{3-}.

(3) Following acid rain leaching, TO-0.1 considerably increased the stability of Cd and Zn. TO-0.1 demonstrated improved heavy metal stabilization compared to TCP. The release behaviors of Zn and As in the soil treated with different materials have changed. The control of complex reaction rates and multiple diffusion factors was the common kinetic characteristic of these heavy metals.

CRediT authorship contribution statement
Chu-xuan LI: Conceptualization, Methodology,

Investigation, Validation, Data curation, Formal analysis, Writing − Original draft, Review & editing; **Shan-xin YUAN:** Resources, Writing − Review & editing; **Hai-feng LI**, **Yong-ping LU**, **Wei-chun YANG**, **Wen-shun KE**, **Lu TANG**, **Chong-jian TANG** and **William HARTLEY:** Investigation; **Sheng-guo XUE:** Conceptualization, Methodology, Supervision, Resources, Writing − Review & editing, Project administration.

Declaration of competing interest

Acknowledgments

Supplementary Information

Supplementary Information in this paper can be found at: http://tnmsc.csu.edu.cn/download/25-p2091-2023-1175-Supplementary_Information.pdf.

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缓释磷酸盐对土壤中锌和镉的稳定化及长效性的影响

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摘　要：采用有机酸活化难溶性磷酸盐制备缓释磷酸盐材料以稳定冶炼场地土壤中高浓度的 Cd 和 Zn。结果表明，经 0.1 mol/L 草酸活化的磷酸三钙(TO-0.1)对 Zn 和 Cd 的稳定化效果最佳，经 30 d 处理后土壤中 Cd 和 Zn 的浸出浓度分别从 3.17 和 16.60 mg/L 降低至 0.078 和 0.32 mg/L。Cd 和 Zn 的弱酸提取态转化为可还原态、可氧化态和残渣态。同时，TO-0.1 未提高土壤中 As 的迁移性。此外，酸雨淋溶和 150 d 自然老化的结果证明了缓释磷酸盐材料对土壤中 Cd 和 Zn 的稳定具有长效性。该研究证明，缓释磷酸盐材料具有修复冶炼场地重金属污染土壤的潜力。

关键词：冶炼场地；锌；镉；磷酸盐；缓释；长效性

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