



Research article

Stabilizing lead bullets in shooting range soil by phosphate-based surface coating

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Abstract: Soil lead (Pb) is well known as a threat to human health and ecosystem. Although relatively insoluble, lead bullets in shooting range soil can be readily released into soluble forms through natural weathering processes and thus pose significant human and environmental risks. In this study, laboratory experiments were conducted to investigate if the Pb bullets in shooting range soil can be stabilized through surface coating of phosphate-based materials. Results indicated that FePO₄ or AlPO₄ coatings, insoluble metal phosphates, have been successfully formed on the surface of the Pb bullets. The EPA Toxicity Characteristic Leaching Procedure (TCLP) test showed that FePO₄ or AlPO₄ surface coating would effectively reduce the Pb solubility or leachability of the bullets. The surface coating under pH of <5.5 for 7 days could achieve 92–100% reduction, with 85–98% by FePO₄ coating and 77–98% by AlPO₄ coating as compared with the non-coating. Leachable Pb concentration in the contaminated shooting range soil was reduced by 85–98% or 77–98% as a result of the FePO₄ or AlPO₄ solution treatment. This study demonstrated that the FePO₄ or AlPO₄-based surface coating on lead bullets can effectively inhibit the Pb weathering and significantly reduce the Pb release from soil through in situ chemical stabilization, which could be potentially applicable as a cost-effective and environmental-sound technology for the remediation of Pb-contaminated shooting range soil.

Keywords: Lead bullet; soil contamination; surface coating; lead stabilization; soil remediation

1. Introduction

Lead (Pb) has been listed as the most frequently encountered heavy metal contaminant at the Superfund sites by the National Priorities List (NPL) [The Agency for Toxic Substances and Disease Registry (ATSDR) 2013 Substance Priority List], which is identified as the most significant potential threat to human health, especially to children, due to its toxicity and human exposure potential by the United States Environmental Protection Agency (USEPA) and ATSDR [1]. Many studies showed that Pb exposure could cause damages to human brain and nervous system and lead to learning disabilities and behavior, reproductive, memory, or concentration problems as well as muscle and joint pain [2-4]. Lead in environment would also result in decreased survival, poor body condition, behavioral changes, and impaired reproduction of wildlife [5,6].

Most environmental Pb contaminations are resulted from anthropogenic activities such as mining, smelting and shooting activities. There are estimated about 9000 non-military outdoor shooting ranges in the United States, and approximately 80,000 tons of Pb were used for bullet and shot manufacture in later 1990s [7]. Although relatively insoluble in soil ecosystem, the fired Pb bullets are not inert and could be easily weathered and transformed into mobile forms under natural conditions. It has been confirmed that the Pb bullets in shooting range soil could last for several hundred years and usually release Pb^{2+} form into ecosystem through weathering reactions [8-12]. Smaller Pb particles resulting from abrasion could cause immediate contamination to the environment [13]. As a result, many civilian and military shooting ranges were contaminated with high Pb levels, usually greater than 10,000 mg Pb/kg soil [13]. For example, Manninen and Tanskanen [14] reported up to 54,000 mg Pb/kg soil in a shooting range in Viikinmäki, Finland.

Current remediation research of Pb-contaminated soil has been focused on in situ chemical immobilization using soil amendments, including phosphate minerals/salts [11,12,15-19], phosphoric acid [20], iron phosphate nanoparticles [21], poultry waste [22], bacteria [23-25], eggshell, mussel shell, cow bone, biochar [26-29], and peat moss [30]. The in situ immobilization is accomplished by transforming soluble Pb into insoluble forms through chemical, exchangeable, or adsorptive reactions, which significantly reduce Pb solubility, leachability, mobility, or bioavailability. The effectiveness of the technology is largely controlled by the dissolution or solubility of Pb solids in the soil ecosystem.

The remediation of Pb-contaminated shooting ranges by the in situ chemical immobilization has encountered two challenges: heterogeneity of Pb bullets and relatively large bullet size. In shooting range, fired bullets are usually present as isolated, relatively large solids with very slow weathering and limited dissolution, which prevents the weathered Pb bullets from the effective dissolution and transformation. Thus this remedial technology may not work for the contaminated shooting ranges. This study attempts to investigate if the surface coating approach using $FePO_4$ or $AlPO_4$ on the bullets can effectively prevent Pb weathering and stabilize Pb in shooting range soil. The hypothesis of this approach was that the weathering and Pb release from fired bullets could be inhibited through the in situ formation of $FePO_4$ or $AlPO_4$ surface coating on the Pb bullets, which would consequently reduce the Pb health and ecological risks and safeguard human and ecosystem from the contamination.

Iron (Fe) and aluminum (Al) are abundant elements in soil, and phosphate is often applied as a fertilizer in soil. Metal phosphates such as zinc, iron, aluminum, and chromium phosphates have been widely used as coating materials on the surface of both ferrous and non-ferrous metals because of their high corrosion resistance and superior adhesion with the metal substrate [31,32]. $FePO_4$ and

AlPO₄ are both insoluble phosphates often found in soil and nature as strengite (FePO₄·2H₂O) and variscite (AlPO₄·2H₂O) [33]. The solubility product (K_{sp}) of strengite is $\sim 10^{-33.5}$ [34] and variscite $\sim 10^{-27.7}$ [35]. If FePO₄ or AlPO₄ coatings could be successfully formed on the surface of Pb bullets, the surface coatings should be able to inhibit the bullets from further weathering and thus stabilize Pb in soil. The objectives of this study were: i) synthesize and characterize the FePO₄ or AlPO₄ materials; ii) in situ form and characterize the FePO₄ or AlPO₄ coatings on the surface of the Pb bullets; and iii) determine the effectiveness of the surface coating on the Pb solubility of the bullets and the contaminated soil through the EPA Standard Toxicity Characteristic Leaching Procedure (TCLP) test.

2. Materials and Methods

2.1. Soil sampling and characterization

Soil samples were collected from top 30-cm of the high impact areas of a shooting range near St. Louis, Missouri. The soil was a clay loam (30.0% silt, 27.5% clay) with pH 7.3 and 3.2% organic matter. Scanning electron microscopy (SEM) analyses in conjunction with energy dispersive spectroscopy (EDS) indicated very high Pb content (4783 mg/kg) in the soil and a broad range of bullet size (μm to mm), suggesting the bullets were under highly weathering or corrosive conditions. Lead speciation analysis by the modified sequential extraction procedures [36] showed that the Pb fractions of water soluble and exchangeable (WE), carbonate-bound (CB), Fe-Mn oxides-bound (FM), organic matter-bound (OC), and residual (RS) forms were 448, 523, 523, 747, and 2541 mg/kg, respectively.

2.2. FePO₄ and AlPO₄ synthesis

FePO₄ and AlPO₄ were synthesized following the procedures described by Liu [37]. For the FePO₄ synthesis, 5.75 g NH₄H₂PO₄ and 6.56 g FeCl₃·6H₂O were separately dissolved in 50 mL MilliQ (18 M Ω ·cm) water. The two solutions were then dripped at the same rate into a beaker containing 50 mL 0.65 M H₃PO₄ solution, followed by adding 1.0 M Na₃PO₄ solution to adjust the pH to 1.3. The mixture was stirred for 2 h, and the FePO₄ solids were separated from the mixture using centrifugation at 3000 rpm for 20 min. The solids were washed twice with MilliQ water and heated at 850 °C for 6 h. For the AlPO₄ synthesis, 2.88 g NH₄H₂PO₄ and 9.76 g AlCl₃·6H₂O were individually dissolved in 50 mL MilliQ water, followed by same procedures of FePO₄ synthesis, but the pH of the mixture was adjusted to 2.2.

2.3. Coating procedure

The FePO₄ and AlPO₄ solutions were prepared separately by adding 2.7 g FePO₄ and 3.0 g AlPO₄ in 30 mL MilliQ water. Concentrated phosphoric acid was added slowly to dissolve the solid, and MilliQ water was added to the final volume of 50 mL (0.36 M FePO₄ or 0.45 M AlPO₄, pH~0.6). Five lead bullets (0.49 g each) were immersed into the FePO₄ or AlPO₄ solutions for 7 days. To assess the pH effect on coating, the solution pH value was adjusted with 1.0 M Na₃PO₄ to 1.0, 2.0, 3.0, 4.0, and 5.0, respectively.

For soil treatment, the coating solutions with various concentration of FePO₄ or AlPO₄ were prepared by dissolving 0.1 g to 3.0 g of FePO₄ or AlPO₄ in 50 mL of phosphoric acid solution. 1.0 g

of the collected soils was added in the solutions for 7 days. TCLP test was performed following the treatment for both coated bullets and treated soils to evaluate the efficacy of lead stabilization.

2.4. TCLP procedure

Lead stabilization by the surface coating was assessed by the modified toxicity characteristic leaching procedure (TCLP, EPA Method 1311 [38]). To prepare the leaching solution, 5.7 mL of glacial CH_3COOH and 64.3 mL of 1.0 M NaOH were added to 500 mL of MilliQ water. The mixture was diluted to 1.0 L with MilliQ water and the final pH was measured at 4.93.

Five uncoated or coated bullets were placed into a rotary agitation tube with 10 mL of the TCLP solution. The tube was agitated on a shaker for 18 hrs at a speed of 30 rpm under room temperature. The supernatant was filtered through a 0.45 μm pore-size polycarbonate filter (Fisher Scientific) and analyzed for the Pb concentration. The same TCLP procedures were applied to 1.0 g of untreated or coated soil. TCLP test was performed with triplicate per sample.

2.5. Analytical methods

2.5.1. X-ray diffraction analysis

The crystal structures of the synthesized FePO_4 and AlPO_4 were determined with Rigaku Mini Flex X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ (1.54 Å) radiation. The samples were scanned from 20° to 80° (2θ) at scan rate $1^\circ/\text{min}$ and step size of 0.02° . The crystalline phases were identified through comparing the collected XRD patterns with PDF2-2004 database of the International Center for Diffraction Data using a JADE software (www.ICDD.com).

2.5.2. SEM and XPS analysis

The coated bullets and soils were characterized by an FEI Quanta 600 FEG scanning electron microscope (SEM) under the high vacuum model. The samples were imaged with an Everhart-Thornley secondary electron detector (ETD) at 10 kV and working distance around 10 mm. Energy dispersive spectroscopy (EDS) analyses were performed at 10 kV for the AlPO_4 -coated samples and at 20 kV for the FePO_4 -coated samples.

X-ray photon spectroscopy (XPS) analyses were performed by a Kratos Axis 165 photoelectron spectroscopy system. To reduce the sample charging effects, the samples were placed on a conductive carbon tape in sample holders. Charge neutralizer was used to further reduce the charging effects. The analyzed area was set to be 120 microns, and the samples were positioned at 0° take-off angle. The analysis was performed under ultra high vacuum level of at least 1.0 e^{-8} Torr. For a best elemental resolution, monochromatic Al source was used for the excitation. Single sweep and high sensitivity broad surveys were used for elemental identification. Multiple sweeps with low sensitivity, but high resolution were performed for elemental scans. The number of sweeps was determined by the strength or signal/noise ratio for each element. Surface sputtering was performed with a Perkin Elmer differential gun using argon, charged at 2000 volts with an emission level of 10 mA, and 12 milli-pa at a sputter rate of 12 angstroms/minute on Au surface. Sputtered scans were 0, 5, and 10-minute for the FePO_4 -coated samples and 0 and 5-minute for the AlPO_4 -coated samples. The

quantification was determined by the specific Kratos Axis Vision Processing software with appropriate Relative Sensitivity Factor for this particular XPS system.

2.5.3. Colorimetric lead analysis

A modified dithizone colorimetric method in the presence of triton X-100 procedure by Hu et al. [39] was used to determine the Pb concentration in aqueous solution with the detection limit of 0.1 mg/L.

3. Results

3.1. Synthesized coating materials and coating surface characterization

The XRD pattern of the synthesized FePO_4 (Figure 1A) matched the single-phase hexagonal rodolicoite, with a P321 space group (PDF# 29-0715). The strong, sharp peaks, i.e., 100, 102, 104, and 200, were indicative of good crystallinity of the synthesized FePO_4 . A few diffraction peaks, i.e., P1, P2, and P3 (Figure 1A), might be resulted from the impurity in the chemicals used for the synthesis. The XRD pattern of the synthesized AlPO_4 (Figure 1B) matched the single-phase orthorhombic berlinite with a C2221 space group (PDF# 72-1161). The strong narrow peaks of 111, 021, 112, and 220 also demonstrated good crystallinity of the synthesized AlPO_4 .

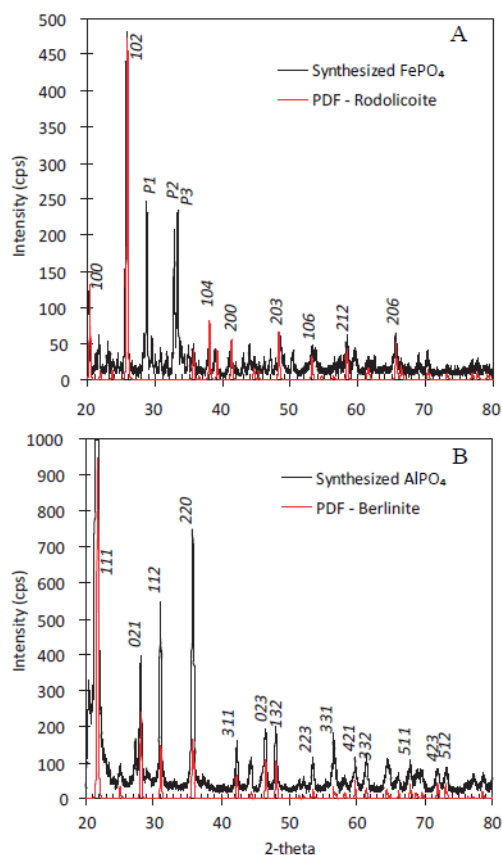


Figure 1. X-ray diffraction patterns of synthesized FePO_4 and AlPO_4 as well as PDF of standard rodolicoite and berlinite.

The SEM comparison between the uncoated bullet (Figure 2a) and the coated bullets (Figure 2b and 2c) indicated a successful surface coating coverage. The crystals of the AlPO_4 -coated surface spot D in Figure 2b (Figure 2d) were seed-like tiny particles or patches on the surface with primarily elemental composition of Pb, P, O, and Al at the point 1 and 2 (Figure 2d-1 and 2d-2). The coating spot E (Figure 2e) on the FePO_4 -coated surface (Figure 2c) contained two types of iron phosphate crystals: platelets and needle-like crystals, primarily containing Pb, P, O, and Fe at the point 3 and 4 (Figure 2e-3 and 2e-4). The solution pH for the Figure 2b and 2c coatings were 1.2 and 0.9, respectively.

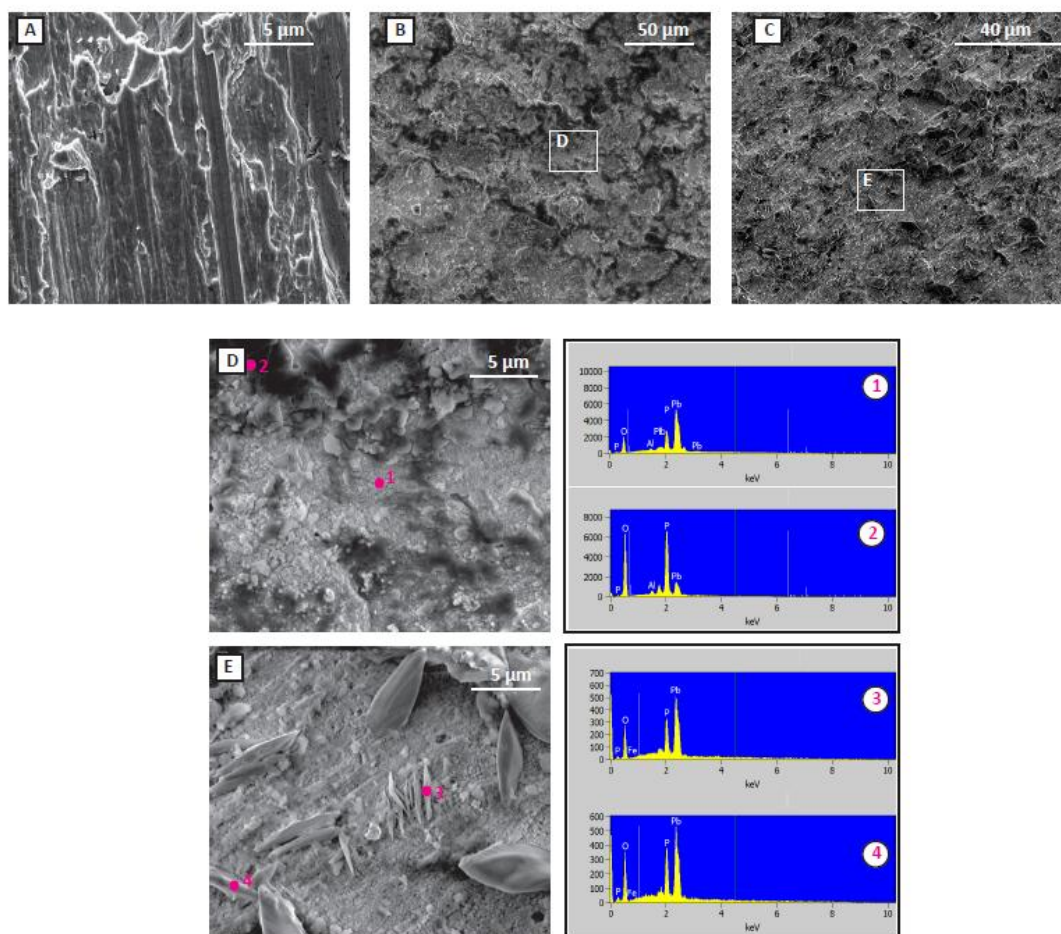


Figure 2. SEM micrograph and EDS patterns (a) uncoated lead bullet; (b) AlPO_4 -coated bullet; (c) FePO_4 -coated bullet; (d) micrograph of the D spot and elemental composition of the point #1 and #2; and (e) micrograph of the E spot and elemental composition of the point #3 and #4.

XPS patterns on the AlPO_4 -coated bullet surface demonstrated both Al (III) and PO_4 (III) characteristic peaks (Figure 3a, 3b) including Al (III) $2p$ (74.8 eV), and P $2p$ (134.0 eV), which was consistent with the values of AlPO_4 in the NIST XPS database (<http://srdata.nist.gov/xps/selectEnergyType.aspx>). The pattern on the FePO_4 -coated surface showed Fe (III) and PO_4 (III) characteristic peaks including Fe (III) $2p$ (712.4 eV), and P $2p$ (133.9 eV) (Figure 3c, 3d), which was also in a good agreement with those of FePO_4 in the NIST XPS database. In addition, characteristic peaks of Pb, O, and C were also identified in the patterns for both coated surfaces.

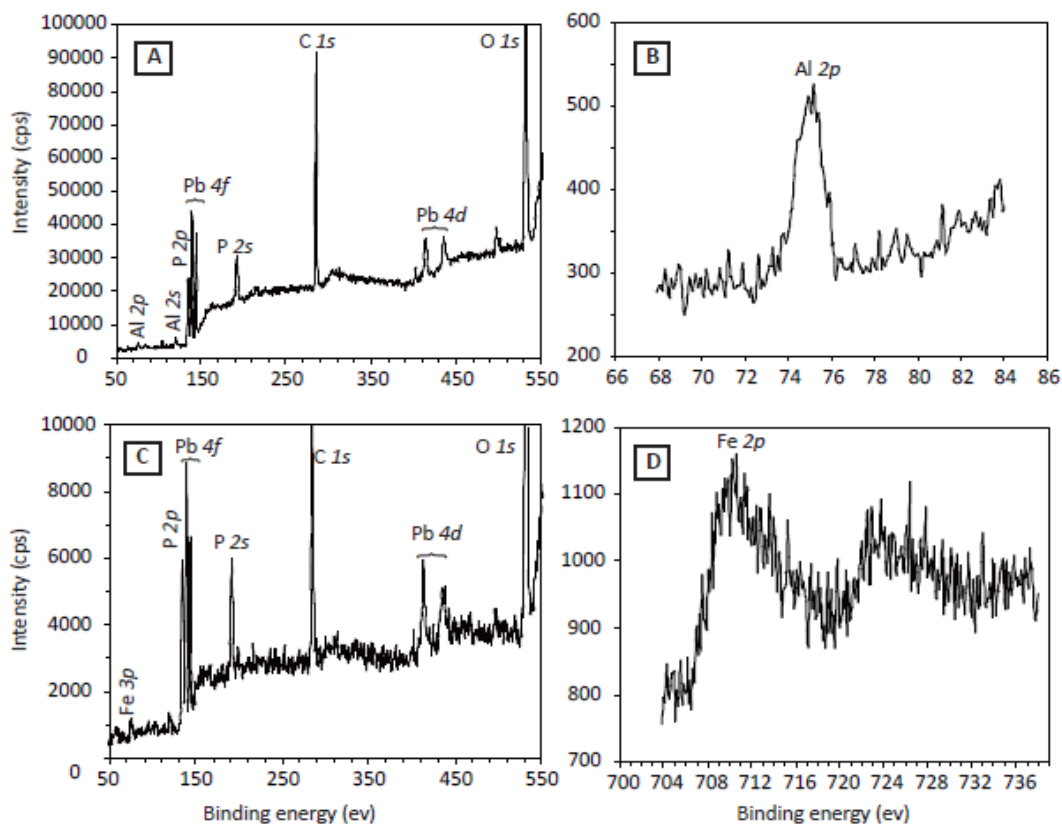


Figure 3. XPS patterns of 0-minute (a) and 5-minute (b) sputtered scan for the AlPO_4 coating surface; 0-minute (c) and 5-minute (d) sputtered scan for the FePO_4 coating surface.

3.2. TCLP Pb leachability

TCLP leachable Pb from uncoated bullets was $1059 \mu\text{g/g}$ Pb. The surface coatings by both FePO_4 and AlPO_4 significantly reduced the Pb leachability. The FePO_4 coating resulted in the leachable Pb ranging from 6.2 to $82.2 \mu\text{g/g}$ Pb under the coating solution pH of <5.5 (Figure 4a). The reductions were 92% to 99% in compared with the uncoated bullet, while the AlPO_4 coating had the leachable Pb from 0 to $59.5 \mu\text{g/g}$ Pb (Figure 4b), with the reductions of 94% to 100%.

TCLP leachable Pb concentration from the shooting range soil before the coating was $2865 \mu\text{g/g}$ of soil. The coating treatments with various dosages of AlPO_4 or FePO_4 (0.2–6.0 g/100 mL) have resulted in reduced leachable Pb in the soil. Leachable Pb in the soils treated with high FePO_4 dosage (≥ 2.0 g/100 mL) was 3.4%~0.9% of the untreated soils, as compared to 8.6%~5.0% for the soil treated with relatively low dosage (<2.0 g/100 mL) (Figure 5a), while leachable Pb in the soils treated with high AlPO_4 dosage (≥ 2.0 g/100 mL) decreased to 2.7%~0.9% of the untreated soils, in contrast to 13.8%~12.7% of the soils treated with relatively low dosage (<2.0 g/100 mL) (Figure 5b).

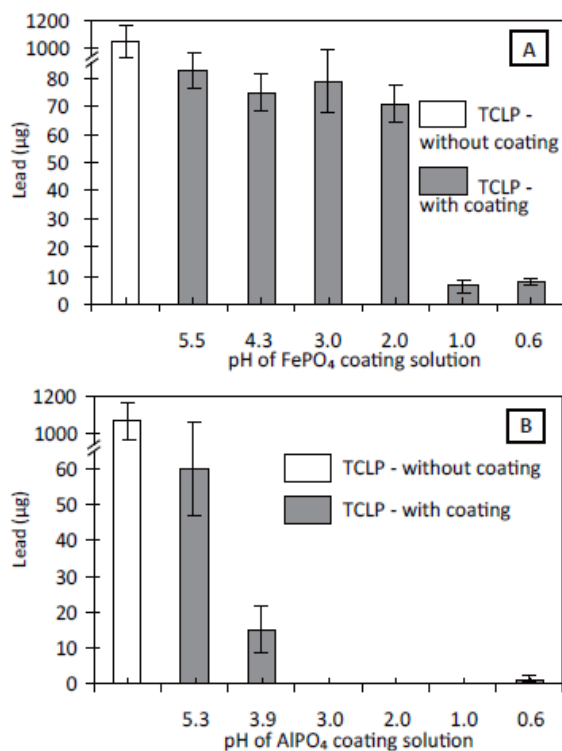


Figure 4. TCLP leachable Pb concentration of (a) FePO_4 -coated and (b) AlPO_4 -coated bullets under various coating pH values.

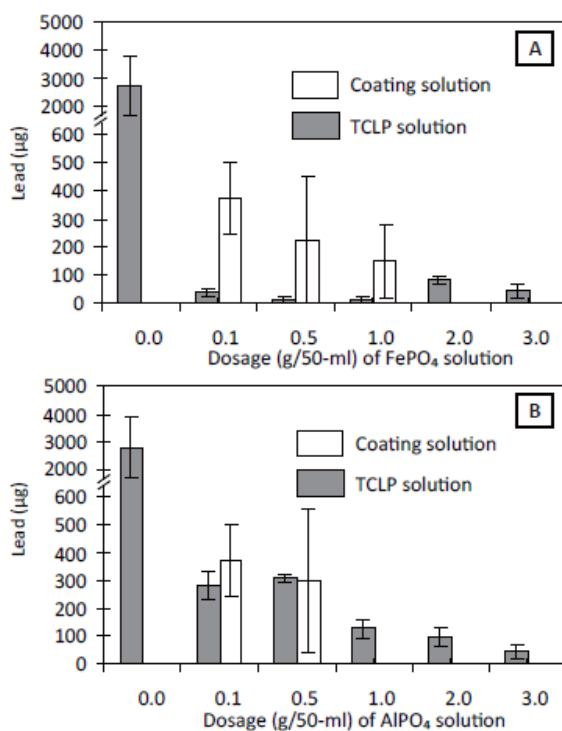


Figure 5. TCLP leachable Pb concentration of the shooting range soil treated with various concentrations of (a) FePO_4 and (b) AlPO_4 coating.

4. Discussion

4.1. Characterization of $\text{FePO}_4/\text{AlPO}_4$ coating

Characterization of the $\text{FePO}_4/\text{AlPO}_4$ coating on lead bullets was performed to determine morphological features, elemental compositions, and mineral phases of the coating layers. The elemental composition in Figure 2d-1 included Al, P, O, and Pb. The binding energies of Al, P, and O further suggested that AlPO_4 coating was successfully formed on the bullet surface. Similarly, the elemental composition in Figure 2d-2 included Fe, P, O, and Pb. The binding energies of Fe, P, and O further implied that the synthesized coating was FePO_4 . The synthesized materials were confirmed by XRD as rodolicoite (FePO_4) or berlinite (AlPO_4) (Figure 1a and 1b). Thus it was reasonably speculated that the coating on the bullet surface was as strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) or variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) based on the synthesis conditions. These two hydrated minerals could be transformed to rodolicoite or berlinite at high temperature (850 °C) [37]. The low pH conditions of the coating process would also facilitate the formation of lead phosphates, and coexistence of Pb and P in Figures 2d-1 to 2e-4 implied the formation of lead phosphates on the surface. Although previous studies have indicated that the successful Pb immobilization was heavily dependent on the formation of pyromorphites, in this study, the lead phosphate formation on the surface would not be a primary mechanism for the Pb stabilization based on the experimental conditions.

4.2. Pb leachability of coated bullet

TCLP tests for the lead bullets treated with the FePO_4 or AlPO_4 solution at various initial pHs (0.6–5.5) indicated that the FePO_4 or AlPO_4 coating could effectively prevent the Pb dissolution and leaching from the bullets under acidic conditions (Figure 4a and 4b). It was speculated that the Pb stabilization was achieved as the FePO_4 or AlPO_4 surface coatings act as an inhibitive barrier to prevent bullet from direct contacts with oxygen and water and consequently inhibit further weathering. The formation of metal phosphate coating usually can be divided into four steps—ionization, hydrolysis, oxidation, and crystallization [40]. Thus the concentration of the coating materials becomes the most important factors governing the extent and speed of coating film growth. Many studies revealed that the corrosion resistance by metal phosphate coating increased with phosphate salt content in coating solutions [41,42]. In general, the higher phosphate salt concentration would result in faster phosphoric reactions during coating process, which could lead to the formation of thick, fine-grained coating film. Leachable Pb was found to increase with increasing the pH of the coating solutions (Figure 4). This might reflect the pH effect on the FePO_4 or AlPO_4 content that was favored under acidic conditions. At relatively low pH values, more metal phosphates were dissolved in the coating solutions. By contrast, as the pH value increased, the less solid metal phosphate dissolved. As a result, thinner, less coating was formed, leading to higher leachable Pb. Nevertheless, even under $\text{pH} > 5$, the surface coating could still reduce leachable Pb by over 90% (Figure 4).

4.3. Soil treatment efficacy

In compared to untreated soil, leachable Pb concentration in the soil treated with FePO_4 or

AlPO₄ solution was reduced by 85–98% and 77–98%, respectively (Figure 5a and 5b). The reduction could be attributed to two possible mechanisms: the first was the formation of FePO₄ or AlPO₄ coating layers on the weathered lead bullets as well as Pb-bearing soil particles. In shooting range soil, leachable Pb primarily came from lead bullets that were in contact with soil constituents and subject to oxidation, carbonization, and hydration reactions, ultimately leading to the weathered crust around the bullets. Hydrocerussite, cerussite (PbCO₃), and small amount of massicot (PbO) are predominantly present in the weathered crusts [10]. The solubility product (K_{sp}) of massicot and cerussite is $10^{12.72}$ and $10^{4.65}$ [10,43]. The solubility calculated with Mineql+4.6 indicated two minerals are highly soluble under acidic conditions (pH < 6, in equilibrium with atmospheric CO₂), with a value of $\sim 10^{0.7}$ M for massicot and $\sim 10^{-4}$ M for cerussite. Whereas, the simulated solubility of FePO₄ (strengite, $K_{sp} = 10^{-33.5}$) [34] or AlPO₄ (variscite, $K_{sp} = 10^{-27.7}$) [35] were $\sim 10^{-9}$ and $\sim 10^{-6}$ M at pH 6, respectively. Therefore, FePO₄ or AlPO₄ coating layers are much more resistant to leaching under acidic conditions, which was confirmed by our TCLP data (Figure 5). The second mechanism could be attributed to the reactions of dissolved or adsorbed Pb ions with phosphate ions, leading to the formation of lead phosphates, i.e., pyromorphite. This mechanism is dominant for conventional Pb immobilization in literature [10,20,30].

TCLP test demonstrated a slight decrease in leachable Pb in the soil after treatment with increasing the coating solution concentration from 0.2 g to 6.0 g of FePO₄ or AlPO₄/100 mL (Figure 5). Generally, the higher the coating concentration, the smaller the FePO₄/AlPO₄ crystals. As a result, higher phosphate concentration could result in more uniform coating on the lead fragments, which is conducive to the reduction of leachable Pb. Meanwhile, the pyromorphite formation appears to be kinetically limited rather than thermodynamically constrained at pH < 8 [44]. The pyromorphite formation in soil is affected by the dissolution rate of soil-adsorbed Pb²⁺ and supply of soluble phosphate [20,45]. Under the coating pH conditions, soil-adsorbed Pb can be easily desorbed and transformed to insoluble lead phosphates in higher phosphate concentration. In addition, the study by Ruby et al. [46] suggested that the Pb²⁺-laden mineral phases formed under acidic conditions tend to be more stable in acidic conditions, such as PBET solution (pH 2.0~3.0). It should be more efficient to use FePO₄/AlPO₄ solutions with lower pH values for soil treatment at initial stage, because more dissolved Pb²⁺ was available, more stable lead phosphates was formed, leading to more uniform coating on soil Pb fragments.

4.4. Environmental impacts

The application of FePO₄ or AlPO₄ for the remediation of Pb-contaminated shooting soil should be environmental-sound. Soil naturally contains abundant Fe and Al in the constituents, and phosphorus is often applied to soil as a fertilizer for plant growth. FePO₄ and AlPO₄ are existing inorganic minerals with various crystal phases in the soil system and non-toxic to human beings and animals. FePO₄ is one of a few molluscicides approved for use in organic farming, while AlPO₄ has even been used for medical treatment. The application of FePO₄ or AlPO₄ could potentially cause the elevation of P level in surface aquatic system through runoff and leaching, which has been environmentally concerned because of water quality and potential eutrophication [47,48]. However, the P leaching in soil ecosystem could be minimized due to strong adsorption by soil minerals [49]. Another potential negative impact of the FePO₄ or AlPO₄ treatment is the Al release to the environment under acidic conditions, threatening the aquatic life and plants. Theoretically, FePO₄

and AlPO_4 are insoluble in pH 3 to 8 as simulated with Mineql+4.6. Studies also showed that FePO_4 and AlPO_4 are hardly soluble in natural soil ecosystem [33]. Consequently, FePO_4 or AlPO_4 coating would be potentially effective technique to prevent Pb release from weathered bullets in shooting range. For practice and successful implementation of this application, maintaining aerobic condition of soils is critical, because Fe(III) may be reduced to Fe(II) under anoxic conditions [50], which increases the solubility of the compound and destabilize the coating. However, anoxic conditions of soil do not affect the AlPO_4 stability. Thus, AlPO_4 coating would be more stable than FePO_4 coating under anoxic soil environment.

5. Conclusion

Surface coatings using FePO_4 and AlPO_4 were tested for the Pb stabilization of shooting bullets in the contaminated soil. The two metal phosphates were synthesized and successfully coated on the surface of lead bullets. When bullets were treated with FePO_4 or AlPO_4 coating solutions for 7 days under pH range of <5.5 , the TCLP leachable Pb was substantially reduced by 92–100%. Treatment with FePO_4 or AlPO_4 coating solutions on Pb-contaminated shooting soil also demonstrated significant reduction of the leachable Pb, with the reduction of 85–98% for FePO_4 and 77–98% for AlPO_4 . Lead stabilization was achieved by forming FePO_4 or AlPO_4 coating on the surface of lead fragments that protected bullets from being exposed directly to oxygen and water, consequently inhibiting the weathering and corrosive process. During the coating processes, lead phosphates such as pyromorphites could also be potentially formed. This study demonstrated that application of AlPO_4 and FePO_4 coating technology would be a cost-effective and environmental-sound solution to remediate Pb-contaminated shooting soil, especially under lower pH and aerobic conditions, and safeguard human and ecosystem from the contamination.

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Conflicts of interest

The authors declare no conflict of interest.

References

1. ATSDR, 2013. Available from: <http://www.atsdr.cdc.gov/SPL/index.html>.
2. National Research Council (US) (1993) Measuring lead exposure in infants, children and other sensitive populations, Washington DC: National Academy Press.
3. Ramsés García-Niño W, José Pedraza-Chaverrí J (2014) Protective effect of curcumin against heavy metals-induced liver damage. *Food Chem Toxicol* 69: 182-201.

4. Lanphear BP (2015) The impact of toxins on the developing brain. *Annu Rev Pub Health* 36: 211-230.
5. Tavecchia G, Pradel R, Lebreton JD, et al. (2001) The effect of lead exposure on survival of adult Mallards in the Camargue, southern France. *J Appl Ecol* 38: 1197-1207.
6. Schulz JH, Gao X, Millspaugh JJ, et al. (2007) Experimental lead pellet ingestion in Mourning Doves (*Zenaida macroura*). *Am Midl Nat* 158: 177-190.
7. USEPA (2001) Best management practices for lead at outdoor shooting ranges. USEPA, New York.
8. Jorgensen SS, Willems M (1987) The fate of lead in soils: the transformation of lead pellets in shooting range soils. *Ambio* 16: 11-15.
9. Lin Z (1996) Secondary mineral phases of metallic lead in soils of shooting ranges from Orebro County, Sweden. *Environ Geol* 27: 370-375.
10. Cao X, Ma LQ, Hardison Jr DW, et al. (2003) Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *J Environ Qual* 32: 526-534.
11. Sanderson P, Naidu R, Bolan N (2013) Effectiveness of chemical amendments for stabilization of lead and antimony in risk-based land management of soils of shooting range. *Environ Sci Pollut Res* 20: 1-15.
12. Sanderson P, Naidu R, Bolan N (2014) Ecotoxicity of chemically stabilised metal(loid)s in shooting range soils. *Ecotoxicol Environ Saf* 100: 201-208.
13. Hardison Jr DW, Ma LQ, Luongo T, et al. (2004) Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering. *Sci Total Environ* 328: 175-183.
14. Manninen S, Tanskanen N (1993) Transfer of lead from shotgun pellets to humus and three plant species in a Finnish shooting range. *Arch Environ Contam Toxicol* 24: 410-414.
15. Ma QY, Logan TJ, Traina SJ (1995) Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. *Environ Sci Technol* 29: 1118-1126.
16. Cao X, Ma LQ, Chen M, et al. (2002) Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environ Sci Technol* 36: 5296-5304.
17. Hashimoto Y, Takaoka M, Oshita K, et al. (2009) Incomplete transformation of Pb to pyromorphite by phosphate-induced immobilization investigated by X-ray absorption fine structure (XAFS) spectroscopy. *Chemosphere* 76: 616-622.
18. Park JH, Bolan NS, Chung JW, et al. (2011a) Environmental monitoring of the role of phosphate compounds in enhancing immobilization and reducing bioavailability of lead in contaminated soils. *J Environ Monit* 13: 2234-2242.
19. Liu R, Zhao D (2013) Synthesis and characterization of a new class of stabilized apatite nanoparticles and applying the particles to in situ Pb immobilization in a fire-range soil. *Chemosphere* 91: 596-601.
20. Yang J, Mosby DE, Casteel SW, et al. (2001) Lead immobilization using phosphoric acid in a smelter-contaminated urban soil. *Environ Sci Technol* 35: 3553-3559.
21. Liu R, Zhao D (2007) Reducing leachability and bioaccessibility of lead in soils using a new class of stabilized iron phosphate nanoparticles. *Water Res* 41: 2491-2502.
22. Hashimoto Y, Matsufuru H, Sato T (2008) Attenuation of lead leachability in shooting range soils using poultry waste amendments in combination with indigenous plant species. *Chemosphere* 73: 643-649.
23. Wu SC, Luo YM, Cheung KC, et al. (2006) Influence of bacteria on Pb and Zn speciation, mobility and bioavailability in soil: a laboratory study. *Environ Pollut* 144: 765-773.

24. Park JH, Bolan N, Megharaj M, et al. (2010) Isolation of phosphate-solubilizing bacteria and characterization of their effects on lead immobilization. *Pedologist* 53: 67-75.
25. Park JH, Boland N, Megharaj M, et al. (2011b) Bacterial-assisted immobilization of lead in soils: Implications for remediation. *Pedologist* 54: 162-174.
26. Ahmad M, Hashimoto Y, Moon DH, et al. (2012a) Immobilization of lead in a Korean military shooting range soil using eggshell waste: An integrated mechanics approach. *J Hazard Mater* 209-210: 392-401.
27. Ahmad M, Lee S, Yang JE, et al. (2012b) Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. *Ecotoxicol Environ Saf* 79: 225-231.
28. Moon DH, Cheong KH, Khim J, et al. (2013a). Stabilization of Pb²⁺ and Cu²⁺ contaminated firing range soil using calcined oyster shells and waste cow bones. *Chemosphere* 91: 1349-1354.
29. Moon DH, Park JW, Change YY, et al. (2013b) Immobilization of lead in contaminated firing range soil using biochar. *Environ Sci Pollut Res* 20: 8464-8471.
30. Lee S, Lee M, Chung J, et al. (2013) Immobilization of lead from Pb-contaminated soil amended with peat moss. *J Chem* 509-520: 1-6.
31. Lazzarotto L, Maréchal C, Dubar L, et al. (1999) The effects of processing bath parameters on the quality and performance of zinc phosphate stearate coatings. *Surf Coat Technol* 122: 94-100.
32. Roncal-Herrero T, Rodríguez-Blanco JD, Benning LG, et al. (2009) Precipitation of iron and aluminum phosphates directly from aqueous solution as a function of temperature from 50 to 200 °C. *Cryst Growth Des* 9: 5197-5205.
33. Stumm W, Morgan JJ (1996) Aquatic chemistry: Chemical equilibria and rates in natural waters, 3 Eds., New York: John Wiley and Sons.
34. Iuliano M, Ciavatta L, De Tommaso G (2007) On the solubility constant of strengite. *Soil Sci Soc Am J* 71: 1137-1140.
35. Iuliano M, Ciavatta L, De Tommaso G (2008) The solubility constant of variscite. *Soil Sci Soc Am J* 72: 343-346.
36. Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51: 844-851.
37. Liu H (2010) Synthesis of nanorods FePO₄ via a facile route. *J Nanopart Res* 12: 2003-2006.
38. USEPA (1992) Method 1311. *Toxicity Characteristic Leaching Procedure (TCLP)*, Washington, DC: USEPA.
39. Hu L, Chen J, Wang L, et al. (2007) Rapid determination of micro lead with dithizone water phase by spectrophotometry. *J Kunming Univ Sci Tech* 32: 81-83.
40. Kouisni L, Azzi M, Zertoubi M, et al. (2004) Phosphate coatings on magnesium alloy AM60 Part 1: Study of the formation and the growth of zinc phosphate films. *Surf Coat Technol* 185: 58-67.
41. Górecki G (1992) Iron phosphate coatings—Composition and corrosion resistance. *Corrosion* 48: 613-616.
42. Chen TT, Ke ST, Liu YM, et al. (2005) The study on optimizing the zinc phosphate conversion coating process and its corrosion resistance. *J Chung Cheng Inst Technol* 34: 1-11.
43. Lindsay WL (1979) *Chemical equilibria in soils*, New York, USA: John Wiley.
44. Laperche V, Traina SJ, Gaddam P, et al. (1996) Chemical and mineralogical characterizations of Pb in a contaminated soil: reactions with synthetic apatite. *Environ Sci Technol* 30: 3321-3326.
45. Ryan JA, Zhang P, Hesterberg D, et al. (2001) Formation of chloropyromorphite in a

-
- lead-contaminated soil amended with hydroxyapatite. *Environ Sci Technol* 35: 3798-3803.
46. Ruby MV, Schoof R, Brattin W, et al. (1999) Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environ Sci Technol* 33: 3697-3705.
47. Bennett EM, Carpenter SR, Caraco NF (2001) Human impact on erodable phosphorus and eutrophication: A global perspective. *Bioscience* 51: 227-234.
48. Oelkers EH, Valsami-Jones E (2008) Phosphate mineral reactivity and global sustainability. *Elements* 4: 83-87.
49. Tang X, Yang J (2012) Long-term risk reduction of lead contaminated mill waste by phosphate treatments. *Total Environ Sci* 438: 299-303.
50. Pratt AJ (2006) The curious case of phosphate solubility. *Chem New Zeal* 70: 78-80.



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