Subject Area 2.1: Methodologies of chemicals in soils/sediments**Research Article****Immobilization of Lead in Shooting Range Soils by Means of Cement, Quicklime, and Phosphate Amendments***Xinde Cao^{1,2**}, Dimitris Dermatas¹, Xuanfeng Xu¹ and Gang Shen¹¹ Center for Environmental Systems, Stevens Institute of Technology, Hoboken, NJ 07030, USA² Soil and Water Science Department, University of Florida, Gainesville, FL 32611, USA

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Abstract

Background, Aim, and Scope. Lead (Pb) contamination at shooting range sites is increasingly under environmental concern. Controlling Pb leachability from shooting range soil media is an important step to minimize Pb exposure to the surrounding environment. This study investigated stabilization of Pb in shooting range soils treated with cement, quicklime, and phosphate.

Materials and Methods. Two soils were used and collected from two shooting ranges, referred to as SR1 and SR2. The treatment additives were applied to the soils at rates from 2.5% to 10% (w/w). The effectiveness of each treatment was evaluated by Pb leachability, measured by the Toxicity Characteristic Leaching Procedure (TCLP). The possible mechanisms for Pb immobilization were elucidated using X-ray powder diffraction (XRPD).

Results. Cement and quicklime treatments were effective in immobilizing Pb in SR1 soil, with reduction of Pb concentration in TCLP leachate (TCLP-Pb) to be below the U.S. EPA non-hazardous regulatory limit of 5 mg L⁻¹ at application rates of ≥5% and 28-d incubation. By contrast, cement and quicklime amendments were less effective for Pb stabilization in SR2 soil because the TCLP-Pb levels in the treated soil were still higher than the limit of 5 mg L⁻¹ at all application rates, although they were significantly reduced in comparison with the untreated soil. Phosphate application was most effective in reducing Pb leaching in both soils. Even at an application rate as low as 5% and 1-d incubation, phosphate could reduce TCLP-Pb to be below the limit of 5 mg L⁻¹ in both soils.

Discussion. Immobilization of Pb in the SR1 soil amended with cement and quicklime was attributed to the formation of pozzolanic minerals (e.g., calcium silicate hydrate C-S-H and ettringite) that could encapsulate soil Pb. The pozzolanic reaction was limited in the SR2 soil upon the application of cement and quicklime. Reduction of the TCLP-Pb might result from complexation of Pb on the surface of the formed calcite. Phosphate-induced Pb immobilization was mainly attributed to formation of less soluble PbHPO₄.

Conclusions. The results indicate that effectiveness of cementitious treatments (cement and quicklime) in immobilizing Pb varies in two soils, being effective in SR1 soil but less in SR2 soil. For one given soil, no difference was observed of the effec-

tiveness between cement and quicklime treatments, whereas phosphate amendment emerges as a most effective treatment means for stabilizing Pb in both two soils, and it also shows a faster immobilization process and little effect on the soil acid buffering capacity.

Recommendations and Perspectives. Overall, our study reveals that immobilizing Pb can be one of the best management practices for Pb contamination at shooting range sites.

Phosphate amendment is most effective in immobilizing Pb in any kind of the soil ranges to minimize negative Pb impacts on the shooting range sites.

Keywords: Cement; immobilization; lead contamination; phosphate, quicklime; shooting range

Introduction

Shooting activities are one of the largest contributors of lead (Pb) to the environment (USGS 2002). More than 60,000 tons of Pb is annually deposited in U.S. shooting ranges (Craig et al. 1999). In the soil environment, metallic Pb can be rapidly transformed into active Pb species such as cerussite (PbCO₃) and hydrocerussite (Pb₃(CO₃)₂(OH)) (Lin 1996, Hardison Jr et al. 2004). These active Pb compounds increase the mobility of Pb in the surrounding environment (e.g., water, soil, and plant), thus posing a risk to the ecological system (Cao et al. 2003, Migliorini et al. 2004). Cao et al. (2003) has documented as high as 5% Pb occurring in the soils and up to 300 µg L⁻¹ Pb present in the retention pond water at shooting range sites. Migliorini et al. (2004) found that *Ocyrops olens* and *Armadillidium sordidum* in a shooting range accumulated as high as 75 µg Pb g⁻¹ and 520 µg Pb g⁻¹, respectively. Therefore, controlling Pb mobility from shooting range soil media is an important step to minimize Pb exposure to the surrounding environment.

Stabilization/solidification (S/S) is gaining prominence in the treatment and remediation of hazardous wastes and contaminated soils due to its cost-effectiveness, rapid implementation and its use of well-established techniques (Palomo & Palacios 2003, Dermatas & Meng 2003, Terzano et al. 2005). There are various techniques currently used for S/S, including pozzolanic, (cementitious or solidifying)-based solidifi-

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cation systems and chemical-based stabilization systems. The most commonly-applied pozzolanic materials are portland cement, lime, and/or fly ash (Palomo & Palacios 2003, Dermatas & Meng 2003, Terzano et al. 2005). The pozzolanic-based S/S techniques immobilize contaminants by adsorption, incorporation into the pozzolanic products (e.g., calcium alumina hydrate C-A-H or calcium silicate hydrate C-S-H), or via precipitation as metal hydroxides under alkaline pH associated with cement and lime (Gougar et al. 1996, Moulin et al. 1999). Physical entrapment of heavy metals adsorbed to particle surfaces in a low permeability cementitious matrix is also very likely (Moulin et al. 1999, Badreddine et al. 2004). Chemical-based S/S approach is based on the formation of thermodynamically stable and insoluble precipitate end-products with the contaminants. More effective chemical additives include phosphates and Fe-Mn oxides (Ma et al. 1995, Hettiarachchi et al. 2000, Basta et al. 2001, Seaman et al. 2001, Cao et al. 2002). Phosphate has been proven to be effective in immobilizing Pb from labile soil Pb forms via formation of lead phosphate compounds such as pyromorphite-like minerals ($\text{Pb}_5(\text{PO}_4)_3\text{X}$, $\text{X}=\text{F}, \text{Cl}, \text{OH}$) by scavenging Pb from soluble Pb compounds such as cerussite (PbCO_3) and litharge (PbO) (Zhang & Ryan 1999, Cao et al. 2002, Scheckel & Ryan 2004). Field application of this stabilization method was demonstrated at an abandoned battery recycling site by Cao et al. (2002) who found that phosphate rock significantly reduced leachability and phytoavailability of Pb due to formation of hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$).

The purpose of the present study was to reduce the leachability of Pb in shooting range soils via cement, quicklime, and phosphate amendments as a function of soil properties and incubation time as well as to identify possible mechanisms responsible for Pb stabilization/solidification.

1 Materials and Methods

1.1 Soil sampling and characterization

Two soils were used in this study and collected from the surface (top 20 cm) of the berms (backstops) at two shooting ranges, referred to as SR1 and SR2 which were located at California and New Jersey, USA, respectively. After being air dried to a constant, SR1 soil was passed through a 4.75 mm screen, and SR2 soil through a 0.075 mm sieve. Note, soil particles are generally ≤ 2 mm. Our preliminary experiments indicated that there is a significant amount of Pb present

between the 2 and 4.75 mm fraction in SR1 soil and SR2 soil, while Pb is concentrated in the ≤ 0.075 mm fraction (Data not shown). Therefore, these two fractions: ≤ 4.75 mm for SR1 soil and ≤ 0.075 mm for SR2 soil were selected and subjected to the treatment. Soil pH was measured at a 1:1 soil:water ratio and organic carbon content was determined using the Walkley-Black procedure (Nelson & Sommers 1982). The measurement of total soil metal concentrations was performed by digesting 1 g soil using USEPA Method 3050B, followed by using inductively coupled plasma-optical emission spectrometry (ICP-OES; Thermo Varian Vista-MPX, Varian, Palo Alto, CA) analysis. Quality assurance/Quality control (QA/QC) followed U.S. EPA program by a blank, a replicate and a spike every 20 samples. Quality control samples included 2710 Montana soil standard reference materials (US NIST, Gaithersburg, MD). Selected soil properties are presented in Table 1.

1.2 Soil treatments

Three amendment additives, including Portland cement (type 1&2), quicklime (CaO), and monocalcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) were used in this study for immobilizing soil Pb. The treatment rates were 2.5%, 5.0%, 7.5%, and 10% by soil weight. Specifically, 200 grams of the soil were placed in a stainless steel mixing bowl and hand homogenized for 30 seconds. Pre-weighed additives and 40wt% de-ionized H_2O were added to the material simultaneously. Materials were well-mixed for 30 min and incubated in sealed bags at room temperature for up to 28 days. Control experiments were also performed in the same way as the treatment tests except that amendment additives were not added. Each treatment was conducted in triplicate, and soil samples were collected at day 1 and after 28 days.

1.3 Toxicity characteristic leaching procedure

The treatment effectiveness was assessed by soil Pb leachability, measured by Toxicity Characteristic Leaching Procedure, following the U.S. EPA Method 1311 (USEPA 1992) with minor modifications. Briefly, 25 g soil was mixed with 500 g of either of two leaching fluids ($\text{pH}=4.93$ and $\text{pH}=2.88$) in a 500 ml high-density polyethylene (HDPE) bottle. The mixture was tumbled at a speed of 30 rpm for 18 hrs. At the conclusion of extraction, pH of leachate solution was determined prior to filtration through a 0.45- μm membrane. The filtrate was then acidified with nitric acid to a $\text{pH}<2$ prior to Pb determination.

Table 1: Selected physico-chemical properties of the shooting range soils

	pH 1:1	Org C ^a (wt%)	Fines ^b (wt%)	Al ^c (wt%)	Ca (wt%)	Fe (wt%)	Mn (mg/kg)	Pb (mg/kg)	TCLP-Pb (mg/L)	TCLP Leachable Pb ^d (%)
SR1	7.53 $\pm$ 0.21 ^e	0.43 $\pm$ 0.02	90.1 $\pm$ 8.21	7.77 $\pm$ 0.12	3.54 $\pm$ 0.11	3.30 $\pm$ 0.12	750 $\pm$ 46.7	2,520 $\pm$ 130	16.5 $\pm$ 0.22	13.1 $\pm$ 0.12
SR2	8.47 $\pm$ 0.15	0.50 $\pm$ 0.03	100 $\pm$ 9.22	2.24 $\pm$ 0.08	0.68 $\pm$ 0.04	2.40 $\pm$ 0.09	250 $\pm$ 21.1	35,868 $\pm$ 1551	466 $\pm$ 10.2	26.0 $\pm$ 2.31

^a Organic carbon

^b Soil particles passing through a 0.075-mm sieve

^c Total metal concentrations

^d Percentage (%) of Pb concentration in TACLP extraction (mg/kg) with respect to total in the soil (mg/kg)

^e All data were expressed as mean $\pm$ standard deviation (n=3)

1.4 X-ray powder diffraction

Minerals in the selected soils were determined by X-ray Powder Diffraction (XRPD) using a Rigaku DXR-300 computer-automated diffractometer. Analytical samples were prepared by grinding the selected soils into $\leq 75\mu\text{m}$ powder followed by mounting these fine powders into a quartz sample holder. The X-ray source was a Cu anode operating at 40 kV and 30 mA using $\text{CuK}\alpha$ radiation with a diffracted beam graphite-monochromator. Step scanned data was collected between 5° and 65° in 2θ with a step size of 0.05° and count time of 5 seconds per step using Bragg-Brentano geometry. XRPD patterns were analyzed by using the Jade Software (Ver.7.1), with a reference to the Inorganic Crystal Structure Database. Phase quantitation was obtained by the Rietveld refinement, using the Whole Pattern Fitting Function of Jade (Rietveld 1969). In this study, the SIROQUANT software was applied, in combination with XRPD patterns, to quantify composition change of minerals, especially for the amount change of Pb-derived minerals in soils upon phosphate treatments.

1.5 Statistical analysis

All results were expressed as an average of three replicates with standard deviation, and treatment effects were determined by analysis of variance according to general linear model procedure of the Statistical Analysis System (SAS Institute Inc.). Differences among the means were separated by least significant difference at $p \leq 0.05$.

2 Results and Discussion

Table 1 shows that both SR1 and SR2 soils were alkaline (pH 7.5–8.5) and contained low organic carbon ($<0.50\%$). The SR1 contained 90% fines (see Table 1) and was mainly composed of quartz, montmorillonite, illite 2M1, muscovite 2M1, cristobalite, and albite, with a little amount of

calcite and calcium silicate hydrate (C-S-H) (Fig. 1). The broad hump of the XRPD pattern between $2\theta = 5\text{--}10^\circ$ further demonstrated the presence of amorphous clay minerals (Montmorillonite, Illite 2M1 and Muscovite 2M1). Although the SR2 soil was well fine-grained due to 100% of the soil passing through a 0.075-mm sieve (Table 1), no clay minerals were determined, and predominant mineral was quartz (Fig. 1). The SR1 soil contained $\sim 16\%$ Al, Ca, Fe, and Mn, about three times than that ($\sim 5.6\%$) in the SR2 soil. Lead concentrations in SR1 and SR2 soils were $\sim 2,500\text{ mg kg}^{-1}$ and $36,000\text{ mg kg}^{-1}$, respectively (see Table 1), far exceeding the U.S.EPA soil screening level of 400 mg kg^{-1} (USEPA 1996). XRPD analysis of the SR2 soil revealed dominant presence of Pb as cerussite (PbCO_3). However, not any Pb species were identified in the SR1 soil (see Fig. 1). High leachability of Pb was also observed in both soils, with 13.1 and 26.0% of Pb being extracted by TCLP from SR1 and SR2 soils, respectively (see Table 1). Lead concentrations in the TCLP leachate (TCLP-Pb) of SR1 and SR2 soils were 16.5 and 466 mg L^{-1} , respectively, thereby over the U.S. EPA non-hazardous regulatory limit of 5 mg L^{-1} . Remediation of these soils is necessary and imperative from an environmental concern.

2.1 Cement treatment

In both soils, cement treatment significantly reduced TCLP-Pb except at low dosages ($\leq 5.0\%$) of cement, compared to in the untreated (Figs. 2a and 3a). At 1-d incubation, addition of 2.5% and 5.0% cement increased the TCLP-Pb in the SR1 soil, most probably due to pH reduction that enhanced Pb desorption from Fe-Mn oxides and/or increased dissolution of Pb-particles in the soil (see Fig. 2a). Addition of 2.5% and 5.0% cement reduced the TCLP leachate pH from 5.8 observed in the untreated to 4.6 and 5.2, respectively (see Fig. 2a). Reduction of pH in these treated soils

Fig. 1: X-ray powder diffraction (XRPD) patterns of SR1 and SR2 soils. Mn, Montmorillonite; I, Illite 2M1; Mu, Muscovite 2M1; Gy, Gypsum; Q, Quartz; Cr, Cristobalite; Al, Albite; Ca, Calcite; CSH, Calcium silicate hydrate; and Ce, Cerussite

Fig. 2: Lead concentrations and pH in the TCLP leachates of SR1 soil amended with (a) cement, (b) quicklime, and (c) phosphate for 1-d and 28-d incubation. The dot horizontal line shows the U.S. EPA TCLP Pb regulatory limit of 5 mg L⁻¹. Y-axis is a log scale

with lower dosages might be related to the stronger acidity of TCLP extractant (pH=2.99) used, compared to pH=4.88 used in the control soil. Pozzolanic reactions were probably limited at lower cement application ($\leq 5.0\%$). Thus, leachate pH in the treated soils was controlled by the TCLP extractant (pH=2.99) itself and remained lower than that in the control soil. The observation suggests that, at lower cement rates, the pH effect was mainly responsible for the Pb leaching.

When cement was applied at $>5\%$, TCLP-Pb was lower than that in the untreated soil and even below the U.S. EPA criteria of 5 mg/L for non-hazardous waste materials at 10% cement (Fig. 2a). Lead leaching percentage (referred to as

Fig. 3: Lead concentrations and pH in the TCLP leachates of SR2 soil amended with (a) cement, (b) quicklime, and (c) phosphate for 1-d and 28-d incubation. The dot horizontal line shows the U.S. EPA TCLP Pb regulatory limit of 5 mg L⁻¹. Y-axis is a log scale

Soil Pb leachability) showed a similar trend to the TCLP-Pb, i.e., increased at low dosage ($\leq 5.0\%$) and decreased beyond 5% dosage (Table 2). As shown in Fig. 2a, increasing addition of cement from 5.0% to 10% increased leachate pH, which may result from the inherent alkalinity of cement (Kamon & Nontananandh 1991). Elevated pH would induce solubilization of silica and alumina from the soil clay minerals (Keller 1964), promoting the formation of cementitious hydrates, calcium alumina hydrate (C-A-H) and calcium silicate hydrate (C-S-H) (Gougar et al. 1996). XRPD analysis on the treated soils showed that cement induced formation of calcium silicate hydrate (C-S-H) (20~29 and 47) and ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) (20~9 and 15.6)

Table 2: Percentage (%) of TCLP extractable Pb in the treated SR1 and SR2 soils within 1-d incubation

Dosage (%)	SR1			SR2		
	Cement	Quicklime	Phosphate	Cement	Quicklime	Phosphate
0.0	13.1±1.23b ^a	13.9±1.12b	13.1±0.23b	31.1±4.56a	31.5±2.67a	31.1±2.31a
2.5	26.7±3.25b	30.6±2.47b	0.19±0.02c	48.4±3.47a	51.2±5.88a	1.89±0.22c
5.0	23.3±2.89c	20.6±3.01c	0.18±0.03d	27.2±2.34b	39.8±4.67a	0.23±0.02d
7.5	16.2±1.65a	8.55±0.56b	0.17±0.03c	5.18±0.46b	5.53±0.21b	0.14±0.02c
10	1.19±0.22b	0.38±0.02c	0.22±0.02c	1.34±0.08b	4.34±0.11a	0.14±0.01c

^a All data were expressed as mean ± standard deviation (n=3); data following the same letter in the same row and same soil are not significantly different ($p \leq 0.05$)

(Fig. 4a). Ettringite can immobilize heavy metals through isomorphous substitution of the ions in the mineral product (Kamon & Nontananandh 1991). Gougar et al. (1996) suggested that Pb can generally replace Ca in the ettringite phase. The C-S-H was often identified as the more prevalent component of the cement-induced stabilization/solidification (S/S) samples (Gougar et al. 1996). It was asserted that the C-S-H phases were responsible for the retention of Pb. Direct evidence showed that Pb in the investigated S/S samples was mainly incorporated into C-S-H phases. Moulin et al. (1999) employed ^{29}Si NMR and EXAFS to demonstrate the pres-

ence of Si-O-Pb in the C-S-H species. Cocke (1992) and Badreddine et al. (2004) have also reported fixation of Pb by C-S-H under ^{29}Si NMR and SEM-EDS analysis.

Increasing incubation from day 1 to after 28 days consistently increased the leachate pH for all dosage rates (see Fig. 2a). Elevated pH would enhance the pozzolanic reaction, resulting in a further decline of the TCLP-Pb concentrations. For example, TCLP-Pb concentration at 5.0% cement was reduced from 20mg L⁻¹ to 4.3mg L⁻¹ when the soil was incubated from 1 day to 28 days (see Fig. 2a). As a

Fig. 4: XRPD patterns of the cement or quicklime-treated (a) SR1 and (b) SR2 soils. Et, Ettringite; Ca, Calcite; CSH, Calcium silicate hydrate; and Ce, Cerussite

fact, upon addition of the cement beyond 5.0%, TCLP-Pb was all below the U.S. EPA limit of 5 mg L⁻¹ after a 28-d incubation (see Fig. 2a).

Cement addition to the SR2 soil was not as effective in immobilizing Pb as that in the treated SR1 soil, which was reflected by the fact that the treated SR2 soil retained higher TCLP-Pb and soil Pb leachability than the treated SR1 soil (see Fig. 3a and Table 2). At 1-d incubation, addition of 2.5% cement increased TCLP-Pb and soil Pb leachability which resulted from pH reduction (see Fig. 3a and Table 2). Again, pH effect determined Pb leachability at a lower addition of cement to the SR2 soil. Although there was a drastic decrease in TCLP-Pb from 835 mg L⁻¹ to 6.1 mg L⁻¹ for the addition of cement from 2.5% to 10% (Fig. 3a), the levels of TCLP-Pb were still above the U.S. EPA regulatory limit of 5 mg L⁻¹. This could be explained by the fact that the formation of the pozzolanic products that contributed to the immobilization of Pb was limited due to low clay content in the SR2 soil. Instead, a substantial amount of calcite (20–29) was formed (Fig. 4b). Calcite was also established as a major component in the cementitious-treated wastes by IR and XRD spectrograms (Badreddine et al. 2004). Lead can be immobilized by calcite via replacement of Ca site or formation of Pb mononuclear inner-sphere complexes at the calcite surface or precipitation of hydrocerussite and cerussite secondary phases (Rouff et al. 2004, Sturchio et al. 1997). It has been observed, using X-ray standing wave and X-ray reflectivity methods, that Pb²⁺ ions exchanged at the calcite (1014) interface occupy Ca²⁺ site at the surface (Sturchio et al. 1997). In a study conducted by Rouff et al. (2004), EXAFS data showed the formation of Pb mononuclear inner-sphere complexes at the calcite surface with a first-shell Pb-O bond length of 2.34 Å at low Pb concentration of 1 μM. It was interesting to emphasize that cerussite disappeared after cement or quicklime were added to the SR2 soil (see Fig. 4b). However, XRPD patterns didn't show any Pb minerals appearance in the treated soil in consequence to the disappearance of cerussite (see Fig. 4b). It further confirmed the hypothesis that Pb was adsorbed on the calcite surface. However, this adsorption-based immobilization may not be stable and readily re-dissolve upon acidic TCLP extraction, thus leaving high Pb leaching.

Soil incubation didn't enhance the decline of TCLP-Pb, and on the contrary, it increased the Pb leaching, and all treatments failed the regulatory limit of 5 mg L⁻¹ (see Fig. 3a). The enhanced Pb leaching is probably attributed to pH reduction when incubation increased to 28 days (see Fig. 3a). It is surprising that pH decreased with incubation time from 1 day to 28 days especially at a cement addition of ≥7.5%. The possible explanation is that the SR2 soil had a low acid buffer capacity due to quartz predominance and the 18 hours of TCLP extraction was not enough for the mixture to equilibrate and the leachate pH was still controlled by the TCLP extractant solution itself.

2.2 Quicklime treatment

Like the cement treatment, quicklime significantly reduced TCLP-Pb in both two soils except at low dosages (≤5.0%) of quicklime (Figs. 2b and 3b). At 1-d incubation, addition of 2.5% and 5.0% quicklime to the SR1 soil reduced the

TCLP leachate pH from 5.8 in the untreated soil to 4.76 and 5.39, respectively (see Fig. 2b). As a result, TCLP-Pb concentrations were increased to 38.5 mg/l and 26.0 mg/L, higher than 16.5 mg/L in the untreated soil (see Fig. 2b). Soil Pb leachability was increased from 17% in the control to 20–30% (see Table 2). Upon increasing quicklime addition, however, TCLP-Pb and soil Pb leachability were significantly decreased (see Table 2 and Fig. 2b). XRPD analysis on the treated soils showed that quicklime induced the formation of the C-S-H and ettringite (see Fig. 4a). Therefore, precipitation or incorporation of Pb into these pozzolanic products may control reduction of TCLP extractable Pb. Note, with lime addition increasing from 7.5% to 10%, pH increased to more than 9 (see Fig. 2b). Generally, at highly alkaline condition (pH>9), Pb leachability was enhanced due to a dissolution of Pb particles (Dermatas & Meng 2003). However, this case was not true in this study. It again confirmed the hypothesis that precipitation or incorporation of Pb into the pozzolanic products was mainly responsible for Pb immobilization at high level of lime application.

Like cement treatment, addition of quicklime to the SR2 soil was not as effective in immobilizing Pb as that in the treated SR1 soil (see Fig. 3a and Table 2). Lower levels of quicklime treatments (2.5% and 5.0%) increased the concentrations of TCLP-Pb and soil Pb leachability due to the pH reduction (see Fig. 3b and Table 2). Upon the treatments beyond 5.0%, pH increased up to 11.5 that resulted in decrease of TCLP-Pb and soil Pb leachability (see Fig. 3b and Table 2). As shown in Fig. 4b, a considerable amount of calcite was formed in the lime-treated SR2 soil. High pH would enhance adsorption of Pb on the calcite surface. Increasing incubation from day 1 to 28 days enhanced the TCLP-Pb decrease, especially at higher application (≥7.5%) (see Fig. 3b). Nevertheless, this adsorption-based immobilization may not be stable and readily re-dissolve upon acidic TCLP extraction, thus leaving high Pb leaching. All treatments failed the regulatory limit of 5 mg L⁻¹.

2.3 Phosphate treatment

Figs. 2c and 3c show Pb concentrations and equilibrium pH in TCLP leachates from the MCP-treated SR1 and SR2 soils, respectively. Phosphate treatment had little effect on the leachate pH in both soils at all application rates, with a decrease of pH from 5.78 in the untreated down to 5.22 for SR1 (see Fig. 2c) and from 5.35 in the untreated down to 5.13 for SR2 (see Fig. 3c). It appears that phosphate amendment had little effect on the acid buffering capacity of the soils. However, even within one day and at such a low pH (5.1–5.8), Pb concentration in the TCLP leachate was significantly decreased at all rates of MCP application and even below the non-hazardous level of 5 mg/L, except at the lowest dosage of 2.5% in the SR2 soil (Figs. 2c and 3c). Soil Pb leachability was also significantly reduced, with only 0.14–0.22% of Pb being extracted by TCLP from two soils upon 10% MCP application, compared to 13.1–31.1% in untreated soil (see Table 2).

Lead immobilization may be attributed to the P-induced conversion of Pb from soluble cerussite to insoluble Pb phosphate minerals (Ma et al. 1995, Laperche et al. 1997). XRPD

Fig. 5: XRPD patterns of the SR2 soil treated with 5.0%, 7.5%, and 10% MCP. Ce, cerussite; LP, PbHPO₄

analysis showed that phosphate treatment induced a formation of less soluble PbHPO₄ ($2\theta=30.5$) in the SR2 soil, along with a reduction of cerussite peaks at $2\theta=24.9$ and 25.1 (Fig. 5). Thus, it was expected that PbHPO₄ formation would increase with increasing addition of phosphate (see Fig. 5). Table 3 shows the results of the SIROQUANT quantification analysis of XRPD for composition change of minerals in the SR2 soil upon phosphate treatments. It should be pointed out that the data in Table 3 was very approximate since brushite (CaHPO₄·2H₂O) and metaswizerite (Mn₄Fe_{1.75}(PO₄)₄·8H₂O) minerals were not included in quantification due to the unavailable structure database in the SIROQUANT program. Nevertheless, it did indicate an increase of conversion of Pb from cerussite to PbHPO₄. For example, upon phosphate treatment from 5% to 10%, cerussite was reduced from 1.7% to 0.1%, whereas PbHPO₄ was increased from 0.2% to 3.4% (see Table 2). Note, many of previous studies have shown *in situ* or *ex situ* formation of most stable pyromorphite-like minerals (Pb₅(PO₄)₃X,

X=Cl, OH, F) in the contaminated soils upon phosphate addition (Laperche et al. 1997, Zhang & Ryan 1999, Cao et al. 2002, Scheckel & Ryan 2004). However, pyromorphite-like minerals were not identified in the present study. Instead, PbHPO₄ formation was detected. Although the solubility product of PbHPO₄ ($K_{sp}=10^{-23.8}$) is higher than that of pyromorphite-like minerals ($K_{sp}=10^{-71.6}$ – $10^{-84.4}$), it is still much lower than that of cerussite ($K_{sp}=10^{-12.8}$) (Traina & Laperche 1999). Therefore, PbHPO₄ formation would be responsible for the reduction of Pb leachability.

It can also be seen from Figs. 2c and 3c that the TCLP-Pb concentration did not decrease further with increasing incubation time from day 1 to 28 days for all phosphate addition rates. It was possible for these treated soils that the conversion of Pb from cerussite to PbHPO₄ may be complete within just one day because the formation of Pb phosphate minerals is a rapid process and often happens within seconds (Rabinowitz 1993).

Table 3: Percentage (%) of the mineral phases in the P-treated SR2 soils

Mineral	Chemical formula	Untreated soil	5.0 % MCP ^a	7.5 % MCP	10 % MCP
Albite	NaAlSi ₃ O ₈	3.81±0.23b ^b	7.52±0.24a	7.62±0.14a	8.40±0.56a
Anorthoclase	NaAlSi ₃ O ₈	8.62±0.34c	19.1±3.21a	12.7±2.32ab	7.68±1.23c
Brushite	CaHPO ₄ ·2H ₂ O	– ^c	NQ ^d	NQ	NQ
Cerussite	PbCO ₃	3.79±0.15a	1.74±0.18b	0.30±0.02c	0.11±0.01c
PbHPO ₄	PbHPO ₄	<0.01d	0.19±0.02c	2.51±0.16b	3.42±0.23a
Metaswizerite	Mn ₄ Fe _{1.75} (PO ₄) ₄ ·8H ₂ O	–	NQ	NQ	NQ
Quartz	SiO ₂	83.8±4.56a	71.5±8.33a	76.8±8.31a	80.4±7.88a

^a MCP, monocalcium phosphate [Ca(H₂PO₄)₂·H₂O]

^b All data were expressed as mean ± standard deviation (n=3)

^c –, Not present

^d NQ, Not quantified by SIROQUANT program, Data following the same letter in the same row are not significantly different ($p\leq 0.05$)

3 Conclusions

Cementitious-based treatments, i.e., with cement and quicklime, were more effective in immobilizing Pb in the SR1 soil than in the SR2 soil. In the SR1 soil, the cementitious agents reacted with silicate, aluminum, calcium, and sulfate sources from the soil clay to form pozzolanic products (C-S-H and ettringite) that capture soil Pb. In the SR2 soil, the pozzolanic reactions were limited due to less silicate, aluminum, calcium, and sulfate sources from the quartz-dominated soil. Reduction of Pb leaching may result from adsorption of Pb on the calcite surface, following the dissolution of cerussite. However, this adsorption-based immobilization may not be stable and may readily re-dissolve upon acidic TCLP extraction, thus maintaining high Pb leaching. Phosphate amendment was most effective in stabilizing Pb in both soils. Lead immobilization in the P-treated soils was mainly attributed to transformation of soluble cerussite to less soluble PbHPO_4 . In all, the effectiveness of the cement and quicklime treatments varies with the soil properties. For one given soil, no difference was observed of the effectiveness between cement and quicklime treatments, whereas phosphate amendment is most effective in immobilizing Pb in any kinds of shooting range soils, and P-induced Pb immobilization is a fast process and has little effect on the soil acid buffering capacity.

4 Recommendations and Perspectives

To operate an outdoor range that is protective of human health, the environment, and wildlife, each range should have a site specific, well designed best management practices (BMPs) plan. Several BMPs have been proposed including (1) control and contain Pb bullets and bullet fragments; (2) prevent migration of Pb to the subsurface and surrounding surface water bodies; and (3) remove Pb from the range and recycling (USEPA, 2001). The results from the current study demonstrate that Pb immobilization can be one option of the BMPs for reducing Pb contamination in shooting range sites via physical and chemical amendment, because a sufficient amount of additives can reduce TCLP-Pb to be below the U.S. EPA non-hazardous regulatory limit of 5 mg L⁻¹. Phosphate amendment is most effective in immobilizing Pb in any kind of the range soils to minimize Pb negative impact on the shooting range sites.

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