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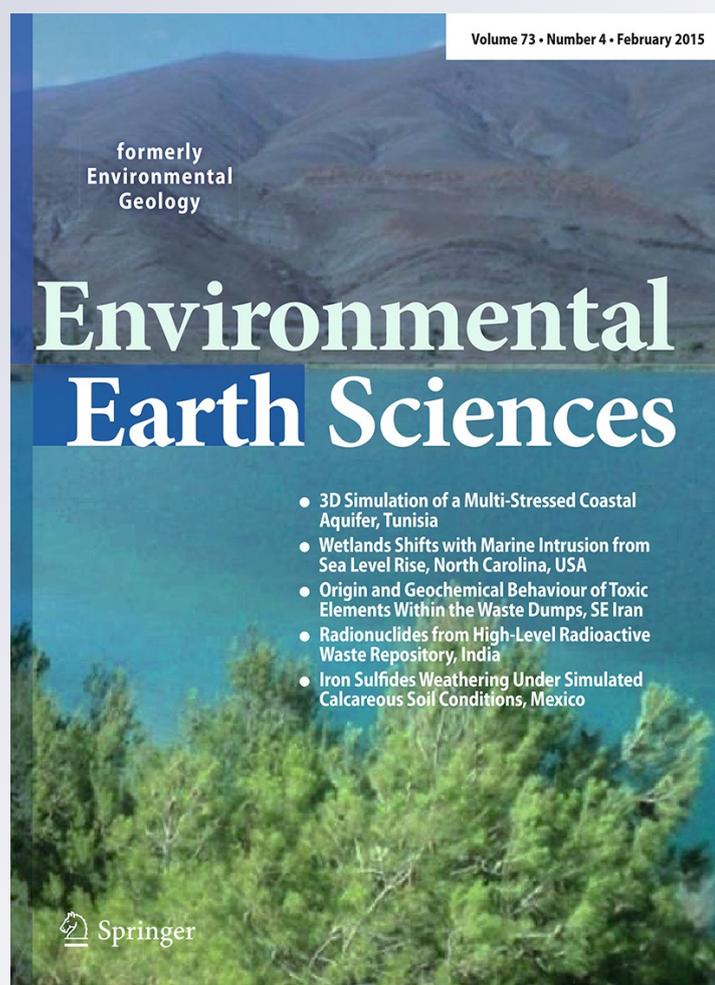
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A quantitative XANES evaluation of the TCLP applicability in phosphate-induced lead stabilization for firing range soils

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Abstract An acidic (pH 5.2) firing range soil, FDR26 in New Jersey, with Pb content of 6,017 mg kg⁻¹, was amended by adding 2.5 wt% fish bone grains. The leaching test, toxicity characteristic leaching procedure (TCLP), and spectroscopic technique, non-destructive X-ray absorption near edge structure (LCF-XANES), were employed to determine the leaching behavior and Pb speciation prior to and after the TCLP test. The TCLP-Pb was 209 mg L⁻¹ after the standard 18 h of tumbling and was increased to 288 mg L⁻¹ after an extended tumbling time of 96 h. The XANES of TCLP residue confirmed the existence of extractable Pb species following the 18 h extraction. TCLP-Pb was also reduced to 1.4 mg L⁻¹ after phosphate addition followed by 28 days of curing. LCF-XANES results revealed the transformation of metallic Pb into insoluble pyromorphite precipitates during the leaching test. The acidic extraction solution significantly increased the

dissolution of phosphate source and Pb species, and resulted in improved Pb immobilization.

Keywords Immobilization · Leachability · Tumbling · Spectroscopic · Pyromorphite

Abbreviations

APII	Apatite II
TCLP	Toxicity characteristic leaching procedure
DIW	De-ionized water
FDR26	Fort Dix range 26
HC	Hydrocerussite
HP	Hydroxypyromorphite
CP	Chloropyromorphite

Introduction

The significant accumulation of lead (Pb) in firing ranges from the use of Pb bullets has attracted much attention in recent years due to its potential negative environmental and health effects (USEPA 2001). In soil environments, Pb bullets can be partially or totally transformed into various Pb minerals, such as massicot (β -PbO), cerussite (PbCO₃) and hydrocerussite (Pb₃(CO₃)₂(OH)₂) (Jørgensen and Willems 1987; Lin 1996; Cao et al. 2003; Dermatas et al. 2006a; Zheng et al. 2011), which may increase Pb mobility in soils (Cao et al. 2003; Dermatas et al. 2006b). Environmental risk assessment of heavy metals in soils frequently involves testing metal leachability rather than total metal analyses (Hartley et al. 2004). The toxicity characteristic leaching procedure (TCLP), developed by the USEPA in 1986, has been widely applied as a regulatory test to determine the need for soil cleanup treatment and/or

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disposal. The use of phosphate as a Pb stabilization agent has been extensively studied, beginning with Nriagu (1974). The USEPA Best Management Practices manual (US 2005) includes phosphate spreading as a migration control method for lead at outdoor shooting ranges and TCLP was performed to evaluate the effectiveness of this treatment.

However, the relevance of TCLP to the evaluation and regulation of waste materials is still subject to criticism for several reasons. First, in a standard TCLP test, two types of extraction fluids are utilized (acetic acid solution, pH 2.88; and acetate buffer solution, pH 4.93) to simulate the presence of organic compounds/phases in landfill leachates. Such a low pH extraction environment may yield conservative results for the prediction of the in situ leaching behavior of most contaminants as TCLP was designed to simulate the worst-case leaching scenario. In general, the conservative results are not dangerous as they overestimate leachability. However, in some cases, the TCLP may also underestimate the leaching of contaminants from particular wastes, which could increase the risk of improper waste management. For example, Halim et al. (2004) found that the TCLP underestimated the leaching of Pb and Cd from cementitious wastes compared to municipal solid waste (MSW) leachates, postulating that the complexation of the Pb and Cd with organics in the MSW leachates was responsible for their increased mobility. Ghosh et al. (2004) indicated that TCLP underestimated arsenic leaching from arsenic-containing solids under landfill conditions and they demonstrated that equilibrium concentrations were not achieved within the 18 h standard exposure time. Furthermore, Chrysochoou et al. (2007) and Dermatas et al. (2008) pointed out that, in phosphate-treated Pb contaminated soils, a significant shift of extractable Pb to the residual phase may occur due to the formation of insoluble pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{X}$, where $\text{X} = \text{OH}^{-1}, \text{Cl}^{-1}, \text{F}^{-1}$) during the extraction process under a low pH environment.

The main goal of this study was to evaluate the applicability of TCLP for examining Pb contaminated firing range soils. The extended TCLP test (up to 96 h of tumbling) was performed to examine the Pb leaching behavior as a function of tumbling time. The non-destructive X-ray absorption near edge structure (XANES) spectroscopy technique was employed to determine the Pb spatial distribution and speciation. Other parallel methods, such as X-ray diffraction (XRD) analysis, are unable to detect amorphous or microcrystalline Pb phases and have a detection limit (~ 1 wt% of total Pb concentration); electron microprobe analysis (EMPA) and scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) can both provide quantitative or semi-quantitative elemental composition over a large beam spot size; however, both of these techniques have difficulty distinguishing

chemical associations with Pb. X-ray absorption fine structure (XAFS) and XANES have been approved as reliable methods to quantitatively determine the proportion of each Pb mineral (either crystalline or non-crystalline/poor-crystalline) present in soils through fitting measured Pb spectra with linear combinations (LCF) of XANES spectra of known Pb reference spectra (Beauchemin et al. 2002; Roberts et al. 2002; Scheinost et al. 2002; Scheckel and Ryan 2004; Takahashi et al. 2002; Vantelon et al. 2005). In this study, LCF-XANES was implemented to analyze the Pb speciation in both untreated and biogenic phosphate (industrial processed fishbone grains, Apatite II)-treated firing range soil prior to and after TCLP tumbling to provide insight into the relevance of TCLP to the evaluation of Pb leachability of phosphate amended firing range soils.

Materials and methods

Soil preparation

Soil samples were collected from the surface (upper 60 cm) of a berm at a military firing range site located in New Jersey. The soil samples were air dried, passed through No. 4 sieves (4.75 mm) and stored in capped containers to maintain the soil moisture. The soil pH was measured using a 1:1 soil to water ratio according to the ASTM method D4980-89. Water-soluble anions were measured according to the procedure reported by Huerta et al. (2005). The total carbon content was determined using the Rock-Eval method (Hetényi et al. 2005). The samples were digested according to U.S. EPA standard method 3050B and the total concentrations of Al, Ca, Fe, Mg, Mn, and Pb metals were determined using inductively coupled plasma (ICP) optical emission spectrometry (Thermo Varian Vista-MPX, Varian).

Phosphate amendment

Duplicate phosphate amendment samples were prepared by mixing 100 g of air-dried soil with Apatite II, the processed fishbone grains ($\text{Ca}_{10-x}\text{Na}_x(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_2$, where $x < 1$ (US Patent #6217775). No other trace metals were detected, including Pb. Calcium and phosphorus content varies slightly from samples to samples. In 2001, the method of utilizing fish bones and fish hard parts to treat metal-contaminated leachates was patented. The chemical composition of fish bones is similar to the Apatite Mineral Group and the patent inventor used the name of Apatite II to separate it from the Apatite mineral group as it carries its own biochemical and structural characteristics. Apatite II is

a waste product from the commercial fish industry. It has low solubility, $K_{sp} < 10^{-20}$, adding no phosphate loading to the environment (Wright et al. 2004; Conca and Wright 2006). The calcium cation along with PO_4^{-3} , OH^{-1} , and CO_3^{-2} from the dissolution reaction of the fish bones provides strong buffering capacity to the solution, buffering around neutral pH, which helps precipitate many metals. The processed fishbone grain sizes ranged from 0.25 to 1 mm (supplied by Slater, UK). A series of dosages from 1.0 to 7.5 wt% (wt. fish bone/wt. dry soil) were added for Pb stabilization. Following thorough mixing with 35 mL of deionized water, the specimens were stored in sealed high-density polyethylene (HDPE) 125 mL bottles and cured for 28 days at 21 ± 1 °C. The soils were sampled at 28 days for TCLP leaching and spectroscopic analyses. Soil moisture content of each specimen was kept in the range of 25.3 to 25.7 %.

TCLP experiment

Batch experiments using TCLP were conducted according to USEPA Method 1311 with minor modifications. Specifically, 3 g of a thoroughly homogenized soil sample (≤ 4.75 mm) was mixed with 60 g of leaching fluid (acetate buffer, pH 4.93) in 60 mL HDPE bottles. The selection of leaching fluids was based on the pH and buffering capacity of the soil. The mixture was tumbled at a speed of 30 rpm for 18 h. Following pH determination, the aliquots were filtered through 0.45 μm membrane filters prior to ICP-OES analyses. The TCLP filter residue was collected for spectroscopic XANES analysis. Given the concerns reported in the literature that TCLP may be time-dependent, longer extractions (up to 96 h) were performed by tumbling 50 g soil with 1,000 g of leaching fluid in 1,000 mL HDPE bottles for the specified intervals. Each sample was run in duplicate.

LCF-XANES analysis

Pb L_{III} -XANES data were collected at the Pohang light source (PLD) in South Korea on beamline BL7C1 using Si (111) double monochromator crystals. High-order harmonic contamination was eliminated by detuning the monochromator to reduce the incident X-ray intensity by approximately 30 %. All spectroscopic data were recorded over the energy range of -200 to 200 eV about the L_{III} -edge of Pb with a 0.4 eV step size in the fluorescence mode using a N_2 gas-filled ionization chamber as a detector. Energy was calibrated to 13,035 eV (the first inflection of a Pb metal foil standard) and was collected simultaneously with the respective spectrum for each sample. The collected spectrum data were then converted to $\mu(\text{E})$ and

normalized to the atomic absorption following a background subtraction using the ATHENA program in the IFEFFIT computer package (Newville 2001). The normalized spectra of the soil samples were analyzed by linear combination fitting (LCF) of Pb reference spectra to the soil sample spectra to identify and quantify the major Pb species present in the soil. The goodness of fit was judged by the *R*-factor, which is the misfit scaled to the data itself ($R\text{-factor} = \text{sum}(\text{data-fit})^2 / \text{sum}(\text{data}^2)$). Generally, a *R*-factor < 0.05 indicates a good fit (Toby 2006).

X-ray adsorption spectra of standard Pb compounds that are considered to be the dominant species in the untreated and phosphate-treated soil samples were recorded and used in LCF analysis. These Pb reference compounds, either purchased or synthesized, included: (1) $\text{Pb}(\text{NO}_3)_2$ (ACS certified; Fisher Scientific); (2) $\beta\text{-PbO}$ (massicot) (ACS certified; Fisher Scientific); (3) PbCO_3 (cerussite) (ACS; EM Science); (4) $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite) (Alfa Aesar); (5) PbSO_4 (Anglesite) (ACS certified; Fisher Scientific); (6) PbHPO_4 (Lab synthesized); (7) $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ (chloropyromorphite) (Lab synthesized); and (8) $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ (hydroxypyromorphite) (Lab synthesized). The purity of commercially obtained chemicals (1–5) was confirmed by X-ray powder diffraction (XRPD). The Pb phosphate minerals (6–8) were prepared under controlled laboratory conditions and their purity was also confirmed by XRPD. Four soil samples were analyzed in our study, which include: (1) untreated FDR26; (2) untreated FDR26 TCLP residue; (3) 2.5 wt% fishbone-treated FDR26 followed by 28 days of curing; and (4) treated FDR26 TCLP residue.

Results and discussion

Soil characterization and soil pH

The physical and chemical properties of the FDR26 range soil are summarized in Table 1. FDR26 is an open, active range. The berm materials were sandy/silty loamy coastal plain soils with limited buffering capacity that were exposed to acidic rainfall, resulting in an acidic soil condition (pH 5.2). Total Pb concentration of the FDR26 range soil was $6,017 \text{ mg kg}^{-1}$, far exceeding the soil screening regulatory limit of 400 mg kg^{-1} established by the USEPA (USEPA 1996a, b), which was classified as a hazardous waste. Upon phosphate addition, the soil acidity was depleted through the release of PO_4^{-3} , OH^{-} , and CO_3^{-2} ions from the fishbone dissolution followed by a 24 h incubation. Soil pH was neutralized from 5.2 to 7.0, a value at which most metals have the minimal leachability.

Table 1 Selected physico-chemical and mineralogy properties of the bulk firing range soils

	Range soil
pH 1:1	5.2
Water content (wt%)	0.3
Major metals (wt%)	
Al	0.69
Ca	0.01
Fe	0.80
Trace elements (mg kg ⁻¹)	
Mn	2
Mg	71
Pb	6,017
Soluble anions (mg L ⁻¹)	
PO ₄ ⁻³	<0.01
Cl ⁻¹	0.33
SO ₄ ⁻²	1.69
Total carbon (wt%)	0.21
Fines (wt%)	14
Bulk mineralogy ^a (wt%)	
Quartz	87
Kaolinite	6
Mica	7
Leachability (mg L ⁻¹)	
TCLP-Pb (18 h)	209

Bulk soils are the <No. 4 sieve (4.75 mm) size fraction of the range soils

^a Bulk mineralogy quantified weighted percentage was determined by XRPD employed with software Jade 7.0 (MDI (Material's Data Inc) 2005)

Untreated soil sample

The TCLP-Pb concentration of untreated FDR26 soil after 18 h of tumbling was 209 mg L⁻¹. Theoretically, the maximum leachable Pb concentration of FDR26 soil would be the total Pb concentration, 6,017 mg kg⁻¹ divided by 20 (liquid-to-solid ratio), which is 301 mg L⁻¹. In other words, approximately 30.5 % of Pb remained in the TCLP residue following 18 h of tumbling at a leachate pH of 4.9. Therefore, the potential for further dissolution of Pb minerals is expected. By performing the extended (up to 96 h) TCLP, the results (Fig. 1a) showed that the Pb concentration increased to 270 mg L⁻¹ at 48 h and continued to increase to 288 mg L⁻¹ at 96 h. Apparently, TCLP-Pb concentration was not stabilized at a standard tumbling time of 18 h. The one-point TCLP test (18 h) underestimated Pb leaching from the FDR26 soil. A previous research showed that Pb dissolution exhibits an amphoteric characteristic of a “V” shaped pH-dependency, in which Pb solubility is lowest at mid-range pH values (~6–10) and is highest in the acidic (pH < 6) and alkaline (pH > 10) ranges (Dermatas and Meng 2003). This

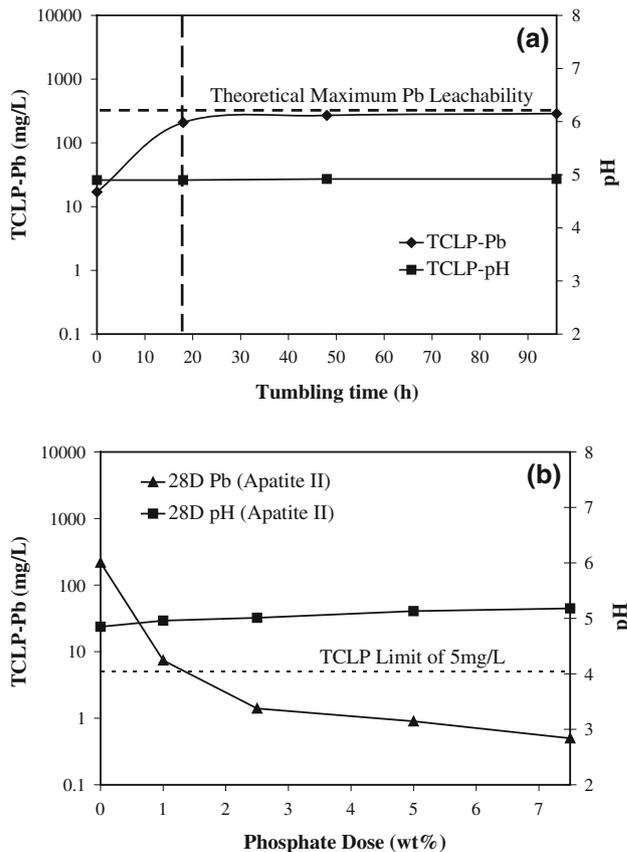


Fig. 1 a Lead concentrations and pH of the TCLP leachates from the FDR26 soil amended with phosphate with a curing time of 28 days. Dotted horizontal line shows the USEPA TCLP-Pb regulatory limit (5 mg L⁻¹). b Solution pH and Pb concentration in TCLP leachates of FDR26 as a function of contact time

suggests that, for most of the firing range soils with soil pHs between 6 and 8, an extended tumbling time beyond the standard 18 h may be necessary for the TCLP test to reach an equilibrium Pb leaching behavior due to the presence of soluble Pb species in the solid residue.

The LCF-XANES results (Table 2) further supported our TCLP finding through quantitative spectroscopic analysis. The results indicated that the untreated FDR26 soil is mainly composed of metallic Pb and its weathering products, massicot, cerussite and hydrocerussite (HC). Although FDR26 soil was exposed to acidic rainfall, the weathered Pb minerals coated the metallic surface, which inhibited the weathering rate of metallic Pb with little disturbance (Dermatas et al. 2006a). After 18 h of tumbling, the weight proportion of each Pb species remaining in the residue shifted, which implied a difference in the dissolution rate between the Pb species during extraction. Since 69.5 % of the total Pb concentration was extracted, only 30.5 % of Pb remained in the residue. We applied the 30.5 % ratio to the Pb composition and the corresponding

Table 2 Linear combination fitting (LCF)- X-Ray absorption near edge spectroscopy (XANES) analysis of soil samples on solid-phase Pb speciation

Sample	Metallic Pb	Massicot	Cerussite	HC	HP	CP	R-factor
A	21.1	32.2	21.8	24.9	–	–	0.000015
B	19.9	17.0	15.2	48.0	–	–	0.000030
C	14.1	18.0	7.6	40.2	20.1	–	0.000017
D	–	–	1.0	33.1	49.5	16.4	0.000026

Values are weighted fraction percentage (%)

A Untreated FDR26; B Untreated FDR26 TCLP residue; C 2.5 % fishbone-treated FDR26 soil followed 28 days curing; D Treated FDR26 TCLP residue

HC Hydrocerussite, HP Hydroxylpyromorphite, CP Chloropyromorphite

weight percentage converted into: metallic Pb (6.1 wt%), lead oxide (5.2 wt%), cerussite (4.6 wt%) and hydrocerussite (14.6 wt%). Obviously, none of the predominant Pb species dissolved completely, which quantitatively implied that 18 h of tumbling was not sufficient for FDR26 soil.

Treated soil samples

Various amounts of fishbone grains, from 1.0 to 7.5 wt%, were used to treat the FDR26 soil (Fig. 1b). The TCLP results showed that a 2.5 wt% fish bone dosage was sufficient to minimize more than 99 % of the TCLP-Pb concentration from 209 to 1.4 mg L⁻¹ followed by 28 days curing, in compliance with the RCRA regulatory limit of 5 mg L⁻¹ for Pb. Use of the TCLP leaching test to evaluate the in situ outdoor shooting range phosphate treatment effectiveness was suggested in the BMP manual as a testing procedure (USEPA 2005). However, it may provide a misleading assessment of treatment efficacy since the TCLP extraction fluid mimics the landfill leachate condition, which favors the dissolution of both Pb and phosphate sources during the extraction process.

The investigation of Pb speciation that is altered during leaching was carried out by conducting LCF-XANES analysis on the 2.5 wt% fishbone-treated sample prior to and after the TCLP test. The results (Table 2) show that the 28-day cured soil sample mainly consisted of metallic Pb, massicot, cerussite, hydrocerussite (HC) and hydroxylpyromorphite (HP). Compared to the untreated sample, about 20 % of the total Pb was converted into the insoluble lead phosphate mineral, HP (Fig. 2).

Upon addition of fishbone, the soil acidity (soil pH 5.2) triggered the dissolution reaction of the Apatite II and induced phosphate release. The dissolved phosphate reacted with the available free Pb²⁺ and precipitated as HP (Conca and Wright 2006). Vantelon et al. (2005) showed that Pb oxide was formed near the metallic Pb core and was successively transformed to hydrocerussite and then cerussite as the outer layer. The precipitation reaction

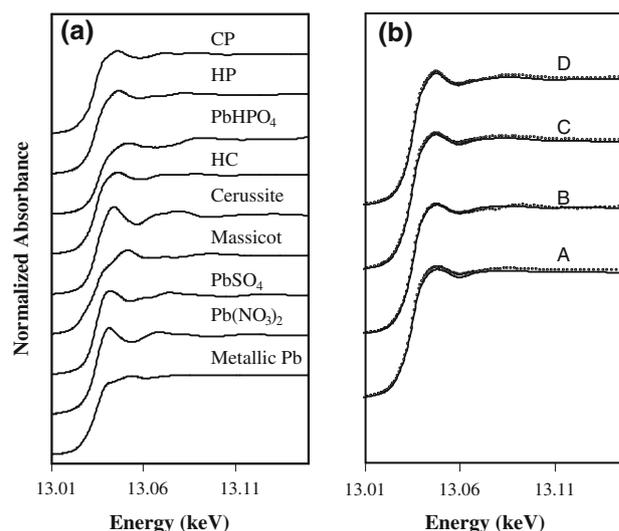


Fig. 2 Normalized Pb_{L-III} XANES spectra of selected samples in this study. **a** reference materials including cerussite (PbCO₃), (hydrocerussite (Pb₃(CO₃)₂(OH)₂), and some laboratory synthesized lead sulfate; **b** measured sample spectra (dotted line) and the corresponding linear combination fits (solid line)

stimulated further dissolution of the exposed cerussite and fishbone to form more HP. Theoretically, neither the precipitation nor the dissolution reactions would cease until the soil environment reaches a new equilibrium. The transformation of cerussite into HP released carbonates into the solution and formed HC. Hence, the weight percentage of HC increased significantly after treatment, which was in agreement with previous reports by Vantelon et al. (2005) and Lin (1996) that hydrocerussite is the first carbonated species formed in the weathered crust.

The LCF results (Table 2) of the treated TCLP residue showed that metallic Pb, Pb oxide and cerussite were almost completely dissolved after the extraction process. It suggests that the tumbling process mechanically accelerated the peel-off of Pb carbonates from the bullet fragment surfaces. Consequently, the relatively soluble metallic Pb and Pb oxides were exposed to the phosphate solution and

resulted in a dramatically increased Pb dissolution compared to the untreated soil sample. More importantly, the quantitative results showed that about 66 % of total Pb was transformed into pyromorphite, including HP and CP. Interestingly, Chloropyromorphite (CP) was not detected in the treated soil sample prior to TCLP tumbling. According to the nucleation theory, when saturation exceeds a critical value, homogeneous nucleation can occur spontaneously. Although CP is several orders of magnitude less soluble than HP (Nriagu 1974), HP was formed initially instead of CP, possibly because the available soil chloride concentration in the FDR26 soil may have been too low. Under low saturation conditions, spontaneous homogeneous nucleation of CP would not occur; however, heterogeneous nucleation could take place after HP was formed. The similarity of HP and CP structures made the heterogeneous nucleation of CP suitable (Schwertmann and Cornell 1991). Hence, the presence of HP likely reduced the energy barrier for CP nucleation (Steeffel and van Cappellen 1990). As a result, HP converted to CP during the extraction by isomorphous substitution.

Under realistic field conditions (soil pH 6–8), the transformation into less soluble pyromorphite could take years to reach the equilibrium state with limited disturbance, especially within alkaline soil. Scheckel and Ryan (2004) reported that a maximum of 45 % of total Pb transformed into pyromorphite after 32 months in 1 % phosphoric acid-treated soil. On the contrary, a high transformation yield was achieved during the 18 h TCLP extraction process. As a result, the TCLP testing of phosphate amended firing range soil may underestimate Pb leaching under real-world field conditions as the acidic TCLP solution acted as a “catalyst” which promote the transformation of insoluble pyromorphite. Therefore, for in situ remediation of Pb contaminated soils using phosphate, simply relying on TCLP testing to determine the phosphate dosage remains questionable and requires further investigation.

Conclusion

Performing a TCLP leaching test to evaluate the waste leachability or the waste treatment effectiveness is a widely accepted procedure. It is also a popular and standard method the environmental remediation industry uses to determine the quantity of phosphate addition required in the field to stabilize the Pb in the soils. However, based on our recent study, it is suggested that the TCLP test may not be the “perfect” way to be applied in the field and we concluded our findings as follows:

1. The extended (up to 96 h) TCLP test of the untreated FDR26 soil indicated that the standard TCLP 18 h tumbling time was not sufficient for the Pb-soil-solution system to achieve the equilibrium. Pb concentration continued to increase with the tumbling time, up to 96 h. This finding was further confirmed by the quantitative spectroscopic LCF-XANES analysis as a small amount of metallic Pb fragments and its related weathering products remained in the residue after the 18 h extraction period. The remaining Pb residues resumed to dissolve further in the acidic TCLP solution as tumbling process continued.
2. The TCLP extraction solution significantly improved Pb immobilization. The accelerated dissolution of phosphate and Pb promoted the formation of insoluble Pb minerals. This hypothesis was evidenced by the comparison of Pb speciation transformation prior to and after the TCLP test by LCF-XANES, which revealed the conversion of metallic Pb into insoluble pyromorphite. This finding, again, implied that TCLP may underestimate the in situ Pb leaching behavior and thus the application of using TCLP to determine the necessary dosage of phosphate additive, as a remediation alternative for Pb contaminated firing range soils, may be unreliable.

Overall, a single-point TCLP test, when applied to examine phosphate-induced Pb leaching under field conditions, may result in a misleading or unreliable assessment. Accordingly, another USEPA developed leaching test, synthetic precipitate leaching procedure (SPLP) (1994), which simulates the rainfall, may be more meaningful for the phosphate-treated firing range soil, if left in situ for both Pb and phosphate leaching.

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References

- Beauchemin S, Hesterberg D, Beauchemin M (2002) Principal component analysis approach for modeling sulfur K-XANES spectra of humic acids. *Soil Sci Soc Am J* 66:83–91

- Cao X, Ma LQ, Chen M, Hardison DW Jr, Harris WG (2003) Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *J Environ Qual* 32:526–534
- Chrysochoou M, Dermatas D, Grubb DG (2007) Phosphate application to firing range soils for Pb immobilization: the unclear role of phosphate. *J Hazard Mater* 144:1–14
- Conca J, Wright J (2006) An Apatite II permeable reactive barrier to remediate groundwater containing Zn, Pb and Cd. *Appl Geochem* 21:1288–1300
- Dermatas D, Meng X (2003) Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils. *Eng Geol* 2189:1–18
- Dermatas D, Menounou N, Dadachov M, Dutko P, Shen G, Xu X, Tsaneva V (2006a) Lead leachability in firing range soils. *Environ Eng Sci* 23:88–101
- Dermatas D, Shen G, Chrysochoou M, Grubb DG, Menounou N, Dutko P (2006b) Pb speciation versus TCLP release in army firing range soils. *J Hazard Mater* 136:34–46
- Dermatas D, Chrysochoou M, Grubb DG, Xu X (2008) Phosphate treatment of firing range soils: lead fixation or phosphate release? *J Environ Qual* 37(1):47–56
- Ghosh A, Mukiibi M, Ela W (2004) TCLP underestimates leaching of arsenic from solid residuals under landfill conditions. *Environ Sci Technol* 38:4677–4682
- Halim CE, Scott JA, Natawardaya H, Amal R, Beydoun D, Low G (2004) Comparison between acetic acid and landfill leachates for the leaching of Pb(II), Cd(II), As(V), and Cr(VI) from cementitious wastes. *Environ Sci Technol* 38:3977–3983
- Hartley W, Edwards R, Lepp NW (2004) Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. *Environ Pollut* 131:495–504
- Hetényi M, Nyilas T, Toth TM (2005) Stepwise Rock-Eval pyrolysis as a tool for typing heterogeneous organic matter in soils. *J Anal Appl Pyrolysis* 74:45–54
- Huerta VD, Sánchez MLF, Sanz-Medel A (2005) Qualitative and quantitative speciation analysis of water soluble selenium in three edible wild mushrooms species by liquid chromatography using post-column isotope dilution ICP–MS. *Anal Chim Acta* 538(1–2):99–105
- Jørgensen SS, Willems M (1987) The fate of lead in soils: the transformation of lead pellets in shooting range soils. *Ambio* 16:11–15
- LaGrega MD, Buckingham PL, Evans JC (1994) Hazardous waste management. McGraw-Hill, New York
- Lin Z (1996) Secondary mineral phases of metallic lead in soils of shooting ranges from Orebro County, Sweden. *Environ Geol* 27:370–375
- MDI (Material's Data Inc) (2005) Jade Version 7.1. California, USA
- Newville M (2001) IFEFFIT: interactive XAFS analysis and FEFF fitting. *J Synchrotron Radiat* 8:322–324
- Nriagu JO (1974) Lead orthophosphates. IV. formation and stability in the environment. *Geochim Cosmochim Acta* 38:887–898
- Roberts DR, Scheinost AC, Sparks DL (2002) Zn speciation in a smelter contaminated soil profile using bulk and micro-spectroscopic techniques. *Environ Sci Technol* 36:1742–1750
- Scheckel KG, Ryan JA (2004) Spectroscopic speciation and quantification of lead in phosphate-amended soils. *J Environ Qual* 33:1288–1295
- Scheinost AC, Kretzschmar R, Pfister S (2002) Combining selective sequential extractions, X-ray absorption spectroscopy, and principal component analysis for quantitative zinc speciation in soil. *Environ Sci Technol* 36:5021–5028
- Schwertmann U, Cornell RM (1991) Iron oxides in the laboratory: preparation and characterization. VCH Weinheim, Germany
- Steefel C, Van Cappellen P (1990) A new kinetic approach to modeling water-rock interaction: the role of nucleation, precursors, and Ostwald ripening. *Geochim Cosmochim Acta* 54:2657–2677
- Takahashi Y, Usui A, Okumura K, Uruga T, Nomura M, Murakami M, Shimizu H (2002) Application of XANES for the determination of oxidation states of Co and Pb in natural ferromanganese nodules. *Chem Lett* 31:366–367
- Toby BH (2006) R factors in rietveld analysis: how good is good enough? *Powder Diffr* 21(1):67–70
- USEPA (1992) Test methods for evaluating solid waste, physical/chemical methods, SW-846 3rd Ed, Method 1311, Washington, DC
- USEPA (1996a) Test methods for evaluating solid waste, physical/chemical methods, SW-846 3rd Ed, Method 1312, Washington, DC
- USEPA (1996b) Soil screening guidance: user's guidance. USEP-A540/R-96/018 US Gov Print Office, Washington, DC
- USEPA (2001) Best management practices for lead at outdoor shooting ranges. EPA-902-B01-001 Region 2, New York
- USEPA (2005) Best management practices for lead at outdoor shooting ranges. EPA-902-B-01-001 Revised
- Vantelon D, Lanzirotti A, Scheinost AC, Kretzschmar R (2005) Spatial distribution and speciation of lead around corroding bullets in a shooting range soil studied by micro-x-ray fluorescence and absorption spectroscopy. *Environ Sci Technol* 39:4808–4815
- Wright J, Conca J L, Rice R K, Murphy B (2004) PIMS using Apatite IITM: how it work to remediate soil and waste. In: Proceedings of the Conference on sustainable range management. Available from: <http://www.battelle.org/book-store>, ISBN1-57477-144-2, B4-05
- Zheng G, Xu S, Liang M, Dermatas D, Xu X (2011) Transformations of organic carbon and its impact on lead weathering in shooting range soils. *Environ Earth Sci* 64(8):2241–2246