Immobilization of Lead by Phosphate Amended Polonite

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Abstract

Polonite is an alkaline material that has been used to remove nutrients from domestic wastewater and it has been evaluated as a fertilizer. Stabilization of Pb by Polonite and Polonite amended with PO_4 (Polonite-P) was studied. Octacalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) was a primary species of PO_4 formed on the surface of Polonite-P. Lead was found to be associated with pozzolanic reaction products in Pb treated Polonite and Pb treated Polonite-P samples. Formation of Pb oxides, as precipitates or surface complexes, were substantial constituents of Pb treated Polonite. Dissolution of $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ followed by formation of $\text{Pb}_4\text{O}(\text{PO}_4)_2$ was a probable mechanism of Pb removal by Polonite-P. Polonite-P could be a suitable replacement for current PO_4 sources as a Pb stabilization agent. Finally, LDI-TOF was an effective technique for evaluating forms of Pb on Polonite and Polonite-P.

Keywords: Polonite, Lead, Phosphate, Stabilization

1. Introduction

Lead contamination of soils and groundwater in the environment is a significant environmental challenge. Lead particles in soil undergo weathering processes, which result in the formation of Pb oxides and Pb carbonates (Jørgensen and Willems, 1987). Nriagu (1974) proposed the use of phosphate (PO_4) to immobilize Pb *in situ* via the formation of low solubility pyromorphites and this approach has become an accepted remediation strategy (*cf.* Chrysochoou et al., 2007). Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$; hereafter referred to as HA) has been used as a source of PO_4 for *in situ* Pb immobilization, but is limited by its dissolution rate, especially in the neutral to alkaline pH range (Hashimoto and Sato, 2007). Similarly, stabilization of Pb with PO_4 rock has been limited by dissolution rate (Park et al., 2011). Consequently, the extensive incubation times required by these PO_4 sources may not be practical under some field conditions. Soil acidification has been recommended for *in situ* stabilization of Pb with HA to facilitate dissolution of the HA amendment (Suzuki et al., 1984; Hashimoto and Sato, 2007). While some studies have demonstrated that PO_4 can retard movement of Pb in the environment, some forms of PO_4 treatment have been reported to increase Pb concentrations in field water leaching tests (Kilgour et al., 2008; Park et al., 2011). Butkus and Johnson (2011a) reported that transport of Pb bearing intermediates formed in the presence of HA exceeded that of a Pb control at low pH, which indicates that acidic pH can be a drawback when attempting to stabilize heavy metals in soil. Phosphoric acid and highly soluble phosphate salts can be used to overcome HA dissolution limitations (Ryan et al., 2004; Butkus and Johnson, 2011a and 2011b), but cultural eutrophication concerns are a significant detriment (*cf.* Park et al., 2011). Although some non-

apatite forms of calcium phosphates have demonstrated a greater Pb stabilization efficacy (*cf.* Sugiyama et al., 2002), an ideal phosphate amendment to immobilize Pb has yet to be identified.

Polonite (trade mark Polonite®) is a substance that results from heating (900 °C) Opoka, a naturally occurring sedimentary rock (Renman and Renman, 2010). Opoka is mainly comprised of SiO₂ and CaCO₃ and heating converts some CaCO₃ to reactive CaO (Renman and Renman, 2010). Renman et al. (2009) reported that Polonite is primarily comprised of the following compounds: SiO₂ (45%); CaO (45%); Al₂O₃ (4%); Fe₂O₃ (2%); and, K₂O (1%). Recently, Kolosov (2014) reported that Polonite contains substantial amounts of CaCO₃. The incongruity between these reports has not been resolved. Cucarell et al. (2009) reported that untreated Polonite contains 0.4 g P/kg Polonite. Due to the PO₄ sorption capacity of Polonite, it has been considered for use as substrate for wastewater nutrient removal (Renman and Renman, 2010). Polonite has also been evaluated as a multicomponent fertilizer (Cucarella et al, 2008) and for treating landfill leachate (Kietlińska and Renman, 2005). Kietlińska and Renman (2005) reported that Polonite had 99%, 93%, 86%, and 67% removal efficiencies for Mn, Fe, Zn, and Cu, respectively in column leaching tests. Therefore, it was hypothesized that Polonite could be used for stabilization of Pb. Further, it was hypothesized that PO₄ amended Polonite (Polonite-P) could serve as PO₄ source for Pb stabilization via formation of Pb-PO₄ precipitates and overcome the limitations of other PO₄ sources, including those described above. These hypotheses were tested by evaluation of the speciation of Pb in aqueous systems comprised of Polonite and Polonite-P. The effectiveness of laser desorption ionization mass spectrometry with

62 time of flight detection (LDI-TOF), as a tool for evaluating inorganic surface speciation, was
63 also evaluated.

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2. Materials and Methods

2.1 *Polonite*

Polonite, Biotech (Sigtuna, Sweden) was received as dry media with a size range of *ca.* 2-6 mm. Polonite-P was prepared as follows. Four grams of Polonite were combined with a 16 mL solution comprised of 1010 mg KNO₃/L, Fisher Scientific (Fair Lawn, NJ), and 7320 mg K₂HPO₄/L, Fisher Scientific (Fair Lawn, NJ). The PO₄ concentration was based on PO₄ adsorption capacity (15 mg PO₄/g Polonite) that was measured for Polonite (data not shown), which is comparable to values reported in the literature (Herrmann et al., 2014). The resulting suspensions were incubated under constant shaking, 200 RPM, at 25 °C for 48 hours. This incubation time was based on kinetics studies, which revealed that equilibrium was achieved in *ca.* 18 hrs and it is consistent with other studies using similar solid to liquid ratios and sorbents (*cf.* Cucarella and Renman, 2009). Following incubation, the suspensions were washed with 1010 mg KNO₃/L, dried, and stored.

2.2 *Sorption experiments*

Sixteen mL solutions of 1010 mg KNO₃/L, Fisher Scientific (Fair Lawn, NJ), and Pb(NO₃)₂, Fisher Scientific (Fair Lawn, NJ), with initial concentrations ranging from 1 mg Pb/L to 10x10³ mg Pb/L were prepared on the day of the experiment. These 16 mL solutions were combined with *ca.* 4 g of Polonite or *ca.* 4 g of Polonite-P. (In each sample, the mass of sorbent was recorded with a precision of 1/10,000 of a gram and subsequently used in sorption

calculations.) The pH of each sample was measured following 20 minutes of reaction time at room temperature. The resulting suspensions were incubated under constant shaking, 200 RPM, at 25 °C for 48 hours, which is longer than the typical incubation time of 24 hours for similar studies (*cf.* Elzinga and Sparks, 2002; Cao et al., 2004; Hashimoto and Sato, 2007; Yin et al., 2013). Following incubation, pH was measured and then 10 mL aliquots of the suspension were filtered through 0.45 µm Millipore nylon filters (Bedford, MA). Eighty micro-liters of 16 *N* HNO₃ was added to the filtrate, which was then analyzed for Pb, P, and Ca. Stock Pb suspensions were also combined with 80 µL of 16 *N* HNO₃ prior to Pb analysis.

Lead, Ca, and P concentration were quantified using inductively coupled plasma optical emission spectrometry, ICP-OES, (Optima 2100DV, PerkinElmer, Shelton, CT). Continued calibration verification (CCV) was conducted with a midrange standard: 1.00 mg Pb/L, 1.00 mg Ca/L and 4.89 mg P/L. The detection limits for ICP-OES were 0.003 mg Pb/L, 0.03 mg Ca/L, and 0.05 mg P/L.

2.3 *LDI-TOF*

Polonite was ground to power with a mortar and pestle and used as a sorbent as described above and then subsequently analyzed by LDI-TOF. LDI was performed on the samples using a 50 Hz N₂ laser ($\lambda=337\text{nm}$) source with TOF detection, Shimadzu Axima Confidence (Shimadzu Biotech, Kratos Analytical Limited, Manchester, UK). Samples were prepared for analysis by first suspending them in methanol and then loading them onto a 384-sample-well stainless steel plate, which had been previously acid washed, rinsed with DI water, rinsed with methanol and allowed to air dry in a controlled atmosphere. One micro-liter of suspended sample was

deposited on the plate and solvent was allowed to evaporate. The plate was then loaded into the mass spectrometer. Laser power was optimized by observing signal intensity. At lower laser intensities, the samples are considered to be desorbed and ionized; and, at higher laser intensities they are considered to be ablated or evaporated. Due to the inherent variability in shot to shot spectra, most of the reported spectra are averages of more than 100 profiles, which are co-added spectra from at least 10 laser shots. For both positive and negative ion spectra, the reflectron mode was chosen in order to ensure high enough resolution in the isotopic patterns of the ions of interest. An HA control was prepared in 500 mL of deionized (DI) water by combining 0.800 g $\text{Pb}(\text{NO}_3)_2$ (Fisher Scientific, Fair Lawn, NJ) with 0.480 g Na_2HPO_4 (Fisher Scientific, Fair Lawn, NJ) as described by Butkus and Johnson (2011a).

2.4 *SEM -EDS*

Powder samples, described above, were analyzed by SEM-EDS. Analyses were performed on the samples using a Hitachi TM3000 Tabletop Microscope (Hitachi High Technologies America, INC. Dallas, TX) with EDS Quantax70 detector by Bruker (Bruker NanoGmbH, Berlin, Germany). Powdered solid samples were loaded onto a sample stage and placed on a mount for introduction into the vacuum chamber of the SEM. Images were made at various magnifications as indicated in the results.

2.5 *Electrophoresis*

136 Powder samples, described above, were analyzed for electrophoretic mobility as follows.
137 A suspension was prepared by combining 0.05 g of powder sample with 30 mL of 1010 mg
138 KNO_3/L , Aldrich, (St. Louis, MO). Electrophoretic mobility of each suspension was analyzed
139 with a Brookhaven Instruments Corp. (Holtsville, NY) Zeta PALS particle analyzer.
140 Electrophoretic mobility was quantified with multiple aliquots from each suspension in order to
141 minimize the effect of sample heterogeneity.

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3. Results

Trends in pH at the start and completion of sorption experiments are presented in Figure 1. Initial pH was measured approximately 20 minutes after the acidic PbNO_3 solutions were combined with both forms of Polonite and final pH was measured after the 48 hour incubation period. An increase in pH was observed in all cases. The alkalinity of the Polonite was greater than the alkalinity of the Polonite-P as indicated by the higher final pH values of the former. There appeared to be minimal buffering in the circumneutral pH range (indicated by the gap in pH measurements) for both forms of Polonite following the initial 20 minute reaction period. However, final pH values were more evenly distributed. Lead uptake as a function of pH for Polonite and Polonite-P is presented in Figure 2. Trends in the figures are comparable and both show a decrease in pH with higher Pb loadings.

Calcium release to solution as function of Pb removal from solution is presented in Figure 3(a). The axes are presented in logarithmic form to highlight data trends, which are different for each form of Polonite. More Ca was released from the Polonite suspensions at low Pb concentrations than for Polonite-P. In addition, the slope in both data sets changed at a Pb removal of approximately 8-10 μmoles . The linear regions (*cf.* coefficient of determination values) of Ca release to solution as function of Pb removal from solution is presented in Figure 3(b).

Average LDI spectra presented in Figure 4, show the ions produced from a variety of Polonite samples at a laser power (LP) of 90. A blank spectrum of the ions formed from the

stainless steel sample holder, which contribute to the overall ion population is presented in Figure 4 (red). A spectrum of Polonite (Figure 4 (blue)) depicts the complexity of this substrate via the variety of ions that were measured. This result was expected based on the composition of Polonite (Gustafsson et al., 2008). Figures 4 (green) and (orange) present spectra for Polonite-P, and Pb treated Polonite-P (3.97 mg Pb/g Polonite-P). Background peaks generated from the stainless steel are present in all four spectra. The m/z data and comparison of the isotopic peak patterns in the spectra with that calculated by the Isotope Distribution Calculator and Mass Spec Plotter (<http://www.sisweb.com/mstools/isotope.htm>) were used to propose the identity of ions of selected species associated with Ca, Pb, PO₄, and Si, from each sample (Table 1). The extent to which an ion was observed was defined as follows: small peak (sm) being a minimum of 3x the intensity of the background noise signal and average peak (X) being a minimum of 10x the intensity of the background noise signal. A sample of Pb treated Polonite at low Pb concentration (3.29×10^{-2} mg Pb/g Polonite) was also evaluated, but was not included in Table 1 because Pb species were not detected. The Pb treated Polonite-P reveals an isotopic cluster of peaks at m/z of 509, which indicates the presence of Pb₂PO₄. Additional data collected at slightly higher laser power (LP=100) resulted in an additional isotopic clusters at m/z of 733 and 1036, which indicate the presence of Pb₃O(PO₄) and Pb₄O(PO₄)₂, respectively. The increase in laser power was necessary to ionize sample components with higher molecular weights. Calcium carbonate was observed in negative mode on all surfaces, with larger peaks detected on Polonite and Pb treated Polonite-P. However, species containing both Pb and CO₃, e.g. cerussite, were not detected.

SEM-EDS images of Pb treated Polonite and Pb treated Polonite-P are presented in Figure 5. Lead was concentrated in regions where Ca was concentrated on Polonite (Figure 5(a)). Lead was not observed in regions where Si was predominant on Polonite. Phosphorus was concentrated in regions where Ca was present on Polonite-P (Figure 5(b)). Lead was highly concentrated in regions where P was highly concentrated on Polonite-P.

Electrophoretic mobility was used to evaluate macroscopic changes on the Polonite and Polonite-P surfaces in the alkaline pH range (Figure 6). Electrophoretic mobility of Polonite-P was significantly greater than Polonite ($P < 0.025$). A single factor ANOVA test revealed that electrophoretic mobility of Pb treated Polonite (3.9×10^{-3} mg Pb/g Polonite, 4.0 mg Pb/g Polonite, 39 mg Pb/g Polonite) were not statistically different ($P < 0.29$), which implies that the charged fraction of Polonite surfaces were mostly unaltered by Pb. However, electrophoretic mobility of Pb treated Polonite-P (3.97 g Pb/kg Polonite-P) was significantly higher than Polonite-P ($P < 1.49 \times 10^{-2}$). Electrophoretic mobility of PbCO_3 and Pb(OH)_2 were also were significantly different ($P < 3.35 \times 10^{-3}$ and $P < 4.52 \times 10^{-4}$) than Pb treated Polonite (4.0 g Pb/kg Polonite) and significantly different ($P < 2.44 \times 10^{-4}$ and $P < 3.31 \times 10^{-3}$) than Pb treated Polonite-P (4.0 g Pb/kg Polonite-P).

4. Discussion

4.1 LDI-TOF

Literature studies reveal few distinct analyses of inorganic compounds via laser desorption ionization mass spectrometry. The use of LDI-TOF analysis for investigating speciation of inorganic compounds, such as Pb, on complex media including soils and minerals has not been reported. Research is being done to establish a database of inorganic compounds in solids as a generalized approach to predict the species mass spectral behavior (Van Hamm, et al., 2004). In another study, laser microprobe mass analysis (LAMMA), which is a similar technique, was utilized to discriminate between adsorbed and co-precipitated Pb on individual calcite particles (Wouters et al., 1988). The authors concluded that the method of LAMMA was useful in determining the differences in Pb distribution at 100 mg/L and 1000 mg/L. The objective of LDI-TOF, in this work, was to aid in characterization of Pb and PO₄ precipitates and surface complexes on Polonite and Polonite-P surfaces. Analysis using LDI hinges on being able to optimize the laser power intensity to render sample ions that represent sample content and not gas phase ion-ion or ion-neutral interactions. Careful determination of the optimum laser power was carried out to enhance the production of intact molecular ions of interest. Dyson *et al.* (2004) recommended using a laser power intensity that is just above the threshold for ion production. Consequently, laser power was optimized using this recommendation. The results in Figure 4 and Table 1 demonstrate that LDI-TOF can be an effective tool for aiding in characterization of speciation on surfaces that are primarily inorganic.

4.2 *Polonite in an indifferent electrolyte*

When Polonite was suspended in an indifferent electrolyte (10 mM KNO₃) for 48 hours, pH increased to 10.45 and Ca increased to *ca.* 125 mg/L. The increase in Ca and pH was likely from dissolution of CaO (Ca(OH)₂ when exposed to H₂O), wallastonite (CaSiO₃), silicates, and CaCO₃ because these compounds have been reported to be present in Polonite (Renman et al., 2009; Kolosov, 2014) and similar ionic species were present in the LDI-TOF data (Table 1). Dissolution of CaSiO₃ can neutralize acid and increase Ca as follows (*cf.* Fernández-Caliani et al., 2008).

Dissolution of CaCO₃ likely influenced pH and Ca because the final pH was near the pK_{a2} of 10.3 for the carbonate system and Polonite has been reported to contain substantial amounts of CaCO₃ (Kolosov, 2014).

4.3 *Polonite amended with PO₄ (Polonite-P)*

Calcium based filter materials, such as Polonite release Ca ions through kinetically constrained dissolution processes and precipitate calcium phosphate compounds at high pH (Gustafsson et al., 2008). Eveborn et al. (2009) reported that in column studies where Polonite

was exposed to wastewater containing PO₄ at pH 6.8, the following species were found: 14% amorphous calcium phosphate, (ACP); 31% octacalcium phosphate (Ca₈H₂(PO₄)₆·5H₂O); and 25% HA. They also reported that Polonite, used to remediate PO₄ in field samples (150 mg BOD₇/L, pH 7.8), had the following composition: 0 ACP; 61% Ca₈H₂(PO₄)₆·5H₂O; and 30% HA (Eveborn et al., 2009). Both of these systems had considerable fractions of Ca₈H₂(PO₄)₆·5H₂O. More than one form of precipitated PO₄ was expected in the Polonite-P systems studied here due to the array of ions present (Wang and Nancollas, 2008). The SEM-EDS images of Polonite-P (Figure 5(b)) indicate that PO₄ was found in regions, where Ca was present, which supports the formation of Ca₈H₂(PO₄)₆·5H₂O and other Ca-PO₄ precipitates. Reaction of phosphate with Polonite resulted in an increase of pH from *ca.* 9.6 to *ca.* 11.8. Based on this observation, PO₄ precipitates may have formed from dissolution of Ca(OH)₂ (Yin et al., 2013). Because Eveborn et al. (2009) reported significant concentrations of Ca₈H₂(PO₄)₆·5H₂O on Polonite in two distinct systems and considering the observation that Ca₈H₂(PO₄)₆·5H₂O is often formed instead of other Ca-PO₄ precipitates when CO₃ is present at alkaline pH values (Wang and Nancollas, 2008), it is likely that Ca₈H₂(PO₄)₆·5H₂O was formed with Ca(OH)₂ on Polonite as follows.

Because CaCO₃ peaks were reduced after phosphate amendment (Table 1), the following reaction for formation of Ca₈H₂(PO₄)₆·5H₂O is also plausible.

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277 Consumption of $\text{Ca}(\text{OH})_2$ and CaCO_3 resulting from PO_4 amendment (reactions 2 and 3) was
278 likely responsible for the lower alkalinity of Polonite-P shown in Figure 1. Dissolution of
279 CaSiO_3 could have also provided Ca for PO_4 precipitation. Finally, data in Figure 6 indicated
280 that there was an increase in electrophoretic mobility following phosphate amendment, which
281 implies that PO_4 likely formed surface complexes with ionized functional groups (*cf.* Butkus and
282 Johnson, 2011a).

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284 4.4 *Lead treated Polonite*

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286 Lead removal by Polonite appeared to occur by several mechanisms, which in many
287 cases, involves release of Ca. Kietlińska and Renman (2005) reported that calcium leached from
288 Polonite filter columns in amounts of up to almost twice the influent mass of Ca. At Pb
289 concentrations below 10 μmoles removed from solution with Polonite, Ca was constant and then
290 decreased slightly with increase in Pb (Figure 3(a)). (Aqueous Ca decreased from *ca.* 110 mg/L
291 to 55 mg/L in this region of Pb uptake.) The observed decrease in Ca can be attributed to the
292 formation of $\text{CaPb}_2\text{O}_2\text{H}$, which was observed in the LDI-TOF (m/z of 487, Table 1). Dissolution
293 of $\text{Ca}(\text{OH})_2$ and CaCO_3 likely contributed to formation $\text{CaPb}_2\text{O}_2\text{H}$. Increase in Pb removal above
294 10 μmoles resulted in a linear increase in aqueous Ca (Figure 3(b)).

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Lead was found to be associated with pozzolanic reaction products (PbAlSi at m/z of 263) on Pb treated Polonite. Cao et al. (2008) reported that the presence of Si, Al, and Ca, which are found in Polonite, increase immobilization of Pb via the formation of Pb-cementitious hydrate products. Rose et al. (2000) reported that Pb was chemically fixed in Pb-Ca-hydrate via Pb-O-Si bonds under similar pH conditions. These reaction products are most effective at immobilization of Pb under alkaline pH conditions, similar to Portland cement (Moon et al., 2013), which is extensible to Polonite immobilization.

Reaction of Pb with Polonite resulted in the formation of Pb oxide ions (Table 1), which may have derived from surface complexes and precipitates (Kietlińska and Renman, 2005). Dissolution of $\text{Ca}(\text{OH})_2$ followed by precipitation of Pb is a potential mechanism of Pb removal and Ca release under alkaline conditions associated with Polonite as reported by Kietlińska and Renman (2005) for other metals. Elzinga and Sparks (2002) reported that Pb appeared to form a combination of coupled mononuclear and polynuclear complexes on SiO_2 . Lead complexation with amorphous Si increases with pH (Elzinga and Sparks, 2002), which also renders Polonite an effective Pb sink, since it has relatively high concentrations of Si and it tends to buffer aqueous systems at alkaline pH values. However, based on the LDI-TOF data and SEM-EDS images, this mechanism was expected to have a minor influence on overall Pb immobilization by Polonite. Also, because Polonite contains 4% Al_2O_3 and 2% Fe_2O_3 (Renman et al., 2009), Pb could have formed inner sphere complexes with Al oxides (Chisholm-Brause, 1990) and Fe oxides (Roe et al., 1991) on Polonite. Lead carbonate species were not observed in the LDI-TOF data. Based on this observation and differences in electrophoretic mobility between Pb treated Polonite and PbCO_3 , precipitates of Pb and CO_3 were considered negligible.

4.5 *Lead treated Polonite-P*

Mavropoulous et al. (2002) reported that uptake of Pb and release of Ca could be used as a means of discerning the mechanism of lead uptake on HA. A similar approach was used here because Polonite has a substantial quantity of Ca and Polonite-P likely contains precipitates of Ca and PO_4 . Using this approach, Pb removal by Polonite-P appeared to occur by several mechanisms as indicated by the changes in Polonite-P slope in Figure 4(a). At values below *ca.* 10 μmole Pb removed from the aqueous phase, Ca increases gradually with Pb removal. The slope of the line increases substantially above *ca.* 10 μmole Pb removed. The LDI-TOF data was collected with Pb treated Polonite-P samples with an average final mass ratio of 3.97 mg Pb/g Polonite-P. This point is located in Figure 4(a) where the slope has transitioned into the linear region (77 μmoles Pb removed from solution). Consequently, the LDI-TOF data should represent Pb species derived from most mechanisms of Pb removal. Because LDI-TOF identified PbAlSi on the surface of Pb treated Polonite-P (m/z of 263, Table 1), Pb was chemically fixed in Ca-Si-hydrate as discussed above. The LDI-TOF data (Table 1) also identified the presence of Pb and PO_4 ions and precipitates including Pb_2PO_4 , $\text{Pb}_3\text{O}(\text{PO}_4)$, and $\text{Pb}_4\text{O}(\text{PO}_4)_2$ on the surface of Pb treated Polonite-P. Species on the surface of the Pb- PO_4 control included Pb_2PO_4 and $\text{Pb}_3\text{O}(\text{PO}_4)$. Using X-ray Diffraction (XRD), Butkus and Johnson (2011a) reported that a similar control material was comprised of pyromorphite ($\text{Pb}_5(\text{PO}_4)_3(\text{OH})$). Pyromorphite could not be confirmed for any samples with LDI-TOF, because of noise in the m/z range of 1337. However, $\text{Pb}_4\text{O}(\text{PO}_4)_2$ was not observed on the control. This implies that differences in the form of Pb- PO_4 species existed between the control and Polonite-P. (XRD was

unable to reveal Pb-PO₄ species on Polonite and Polonite-P due to the relatively low concentrations of these compounds in the complex Polonite matrices; data not shown). Transition from Pb₄O(PO₄)₂ to Pb₅(PO₄)₃(OH), on Pb treated Polonite-P, would be expected at pH below 9.5 (Michalowska-Kaczmarczyk and Michalowski, 2014). The control and Pb treated Polonite-P both contained Pb oxides at m/z of 430 and 448. It is uncertain if these oxides were derived from a species comprised of Pb and PO₄ prior to exposure to LDI. It is also uncertain if Pb₂PO₄ and Pb₃O(PO₄) were formed from Pb-PO₄ precipitates during LDI or if they were derived from surface complexes during LDI. The observed increase in electrophoretic mobility of Pb treated Polonite-P (Figure 6) offers limited support for the latter. Dissolution of Ca₈H₂(PO₄)₆·5H₂O followed by formation of Pb₄O(PO₄)₂ and Pb₂PO₄ (if it existed prior to LDI) are proposed mechanisms of Pb removal by Polonite-P as follows.

The ratio of Ca release to Pb removal is 0.66 in both cases, which corresponds to the slope of the data for Pb treated Polonite-P shown in Figure 4(b). The ratio of Ca release to Pb removal for Ca₈H₂(PO₄)₆·5H₂O and Pb forming Pb₅(PO₄)₃(OH) is 0.8. The ratio of Ca release to Pb removal for Ca₈H₂(PO₄)₆·5H₂O and Pb forming Pb₃O(PO₄) is 0.44. These ratios are not consistent with the data in Figure 4(b). Cao et al. (2004) reported a slope of 0.92 for Ca release, as a function of

Pb removal, when using PO₄ rock as a substrate. Mavropoulos et al. (2002) reported that the molar ratio of Ca release to Pb removal decreased from 0.92 to 0.65 as a function of initial aqueous Pb concentration (from 581 mg Pb/L to 1770 mg Pb/L) on HA, which they attributed to surface immobilization. The release of H⁺, in reactions (4) and (5), suggests that pH should decrease with increase in Pb removal and this was observed at pH < 10.3 in the Polonite-P sorption edge shown in Figure 2. Further, the pH point (5.4, 10) where final pH begins to decrease substantially in the Polonite-P data (Figure 1) corresponds to the same Pb removal (77 µmoles of Pb removed from the aqueous phase in Figure 4(a)), where the Ca released data begins to increase linearly at a slope of 0.66.

Surface complexation of Pb with HA surface functional groups could be modeled with ion exchange reactions including the following (Mavropoulos et al. (2002)).

Similar processes are plausible for the surface of Polonite-P based on the observed increase in electrophoretic mobility (Figure 6) and the Pb oxides observed in the LDI-TOF data (Table 1). Lead surface complexes with Al oxides (Chisholm-Brause, 1990) and Fe oxides (Roe et al., 1991) are also possible as discussed above. Species comprised of Pb and CO₃ and Pb and OH will not form in appreciable concentrations at equilibrium when PO₄ is available, due to lower solubility limits (Nriagu, 1974; Traina and Laperche, 1999). Because of this and differences in electrophoretic mobility discussed above, PbCO₃ and Pb(OH)₂, two more soluble forms of Pb

solids, were not expected to be present in an appreciable concentration on the surface of Polonite-P.

4.6 *Potential use of Polonite-P as a stabilization agent*

The accepted practice of using HA for Pb stabilization under low to neutral pH conditions requires substantial incubation times and can lead to inadvertent transport of Pb complexes (Butkus and Johnson, 2011a and 2011b). Polonite-P could be a suitable replacement for HA and other PO₄ sources, which require low pH as a stabilization amendment for the following reasons:

- it is an alkaline material, which will increase soil pH and provide buffering in unbuffered soils;
- colloidal Pb species tend to be less mobile under alkaline pH conditions (Chen et al., 2002; Butkus and Johnson, 2011b);
- it promotes formation of Pb-PO₄ precipitates (Nriagu, 1974) and Pb-cementitious hydrate products (Cao et al., 2008), which are desirable forms of stabilized lead;
- Polonite has been evaluated and recommended for further study as a multicomponent fertilizer (*cf.* Cucarella et al, 2008); and
- PO₄ amendment could be accomplished by reusing Polonite that was first used to capture PO₄ in wastewater applications (Renman and Renman, 2010).

Field studies could further elucidate the efficacy of Polonite-P as a Pb stabilization agent.

5. **Conclusions**

406 This study evaluated the ability and mechanism of Polonite and Polonite-P to remove Pb
407 from aqueous systems. Both Polonite and Polonite-P were capable of forming Pb-cementitious
408 hydrate products, which are desirable forms of stabilized Pb. However, the results suggest that
409 PO₄, on Polonite-P, could also be released to form desirable Pb-PO₄ precipitates that are known
410 to have low solubility. For these reasons, Polonite-P should be further evaluated as a
411 replacement for current PO₄ sources as a Pb stabilization agent.

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References

- Butkus, M.A., Johnson, M.C., 2011a. Reevaluation of phosphate as a means of retarding lead transport from sandy firing ranges, *Soil Sediment Contam.* 20 (2), 172-187.
- Butkus, M.A., Johnson, M.C., 2011b. Influence of Phosphate on the Transport Properties of Lead in Sand, *J. Haz. Mat.* 185 (1), 275-280.
- Cao, X., Dermatas, D., Xu, X., Shen, G., 2008. Immobilization of lead in shooting range soils by means of cement, quicklime, and phosphate amendments, *Env. Sci. Pollut. Res.* 15 (2), 120-127.
- Cao, X., Ma, L.Q., Rhue, D.R., Appel, C.S., 2004. Mechanisms of lead, copper, and zinc retention by phosphate rock, *Environ. Pollut.* 131 (3), 435-444.
- Chen, M., Daroub, S.H., Ma, L.Q., Harris, W.G., Cao, X., 2002. Characterization of lead in soils of a rifle/pistol shooting range in central Florida, USA, *Soil Sediment Contam.* 11 (1), 1-17.
- Chrysochoou, M., Dermatas, D., Grubb, D.G., 2007. Phosphate application to firing range soils for Pb immobilization: the unclear role of phosphate, *J. Haz. Mat.* 144 (1-2), 1-14.
- Cucarella, V., Zaleski, T., Mazurek, R., Renman, G. 2008. Effect of reactive substrates used for the removal of phosphorus from wastewater on the fertility of acid soils, *Bioresource Technol.* 99 (10), 4308-4314.
- Cucarella, V., Renman, G., 2009. Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments—a comparative study, *J. Environ. Qual.* 38 (2), 381-392.
- Dyson, P. J., Hearley, A. K., Johnson, B. F., Langridge-Smith, P. R., McIndoe, J. S., 2004. Analysis of low oxidation state transition metal clusters by laser desorption/ionization time-of-flight mass spectrometry. *Inorg. Chem.* 43 (16), 4962-4973.
- Elzinga, E. J., Sparks, D. L., 2002. X-ray absorption spectroscopy study of the effects of pH and ionic strength on Pb (II) sorption to amorphous silica, *Environ. Sci. Technol.* 36 (20), 4352-4357.
- Eveborn, D., Gustafsson, J. P., Hesterberg, D., Hillier, S., 2009. XANES speciation of P in environmental samples: An assessment of filter media for on-site wastewater treatment, *Environ. Sci. Technol.* 43 (17), 6515-6521.
- Fernández-Caliani, J. C., Barba-Brioso, C., Pérez-López, R., 2008. Long-term interaction of wollastonite with acid mine water and effects on arsenic and metal removal, *Appl. Geochem.* 23 (5), 1288-1298.
- Hashimoto, Y., Sato, T., 2007. Removal of aqueous lead by poorly-crystalline hydroxyapatites. *Chemosphere* 69 (11), 1775-1782.

- Herrmann, I., Nordqvist, K., Hedström, A., Viklander, M., 2014. Effect of temperature on the performance of laboratory-scale phosphorus-removing filter beds in on-site wastewater treatment, *Chemosphere*, 117, 360-366.
- Jørgensen, S.S., Willems, M., 1987. The fate of lead in soils: the transformation of lead pellets in shooting-range soils. *Ambio*. 16 (1), 11-15.
- Kietlińska, A., Renman, G., 2005. An evaluation of reactive filter media for treating landfill leachate, *Chemosphere* 61 (7), 933-940.
- Kilgour, D.W., Moseley, R.B., Barnett, M.O., Savage, K.S., Jardine, P.M., 2008. Potential Negative Consequences of Adding Phosphorous-Based Fertilizers to Immobilize Lead in Soil. *J. Environ. Qual.* 37 (5), 1733-1740.
- Mavropoulos, E., Rossi, A.M., Costa, A.M., Perez, C.A.C., Moreira, J.C., Saldanha, M., 2002. Studies on the mechanisms of lead immobilization by hydroxyapatite, *Environ. Sci. Technol.* 36 (7), 1625-1629.
- Michałowska-Kaczmarczyk, A. M., Michałowski, T., 2014. Evaluation of Transition Points between Different Solid Phases in Aqueous Media, *J. Analytical Sciences, Methods and Instrumentation*, 4 (03), 87-94.
- Moon, D.H., Park, J.W., Chang, Y.Y., Ok, Y.S., Lee, S.S., Ahmad, M., Koutsospyros, K., Park, J.H., Back, K. 2013. Immobilization of lead in contaminated firing range soil using biochar. *Environ. Sci. Pollut. Res.* 20 (12), 8464-8471.
- Park, J. H., Bolan, N., Megharaj, M., Naidu, R., 2011. Comparative value of phosphate sources on the immobilization of lead, and leaching of lead and phosphorus in lead contaminated soils, *Sci. Total Environ.* 409 (4), 853-860.
- Rose, J., Moulin, I., Hazemann, J.L., Masion, A., Bertsch, P.L., Bottero, J.Y., Mosnier, F., Haehnel, C., 2000. X-ray absorption spectroscopy study of immobilization processes for heavy metals in calcium silicate hydrates: 1. case of lead, *Langmuir* 16 (25), 9900-9906.
- Renman, A., Renman, G., Gustafsson, J.P., Hylander, L., 2009. Metal removal by bed filter materials used in domestic wastewater treatment. *J. Haz. Mat.* 166 (2-3), 734-739.
- Renman, A., Renman, G., 2010. Long-term phosphate removal by the calcium–silicate material Polonite in wastewater filtration systems. *Chemosphere* 79 (6), 659-664.
- Sugiyama, S., Ichii, T., Hayashi, H., Tomida, T., 2002. Lead immobilization by non-apatite-type calcium phosphates in aqueous solutions. *Inorg. Chem. Comm.* 5 (2), 156-158.
- Suzuki, T., Ishigaki, K., Miyake M., 1984. Synthetic hydroxyapatites as inorganic cation exchangers Part 3. Exchange characteristics of lead ions (Pb^{2+}). *J. Chem. Soc. Faraday Trans.* 1 80 (11), 3157-3165.

- 513
514 Traina, S.J., Laperche, V., 1999. Contaminant bioavailability in soils, sediments, and aquatic
515 environments, *Proc. Natl. Acad. Sci. USA* 96 (7), 3365-3371.
516
517 Van Ham, R., Van Vaeck, L., Adams, F. C., Adriaens, A. 2004. Systematization of the mass
518 spectra for speciation of inorganic salts with static secondary ion mass spectrometry, *Analytical*
519 *chemistry*, 76 (9), 2609-2617.
520
521 Wang, L., Nancollas, G. H., 2008. Calcium orthophosphates: crystallization and dissolution,
522 *Chem. Rev.* 108 (11), 4628-4669.
523
524 Wouters, L. C., Van Grieken, R. E., Linton, R. W., Bauer, C. F., 1988. Discrimination between
525 coprecipitated and adsorbed lead on individual calcite particles using laser microprobe mass
526 analysis, *Anal. Chem.* 60 (20), 2218-2220.
527
528 Yin, H., Kong, M., Fan, F., 2013. Batch investigations on P immobilization from wastewaters
529 and sediment using natural calcium rich sepiolite as a reactive material. *Wat. Res.* 47 (13), 4247-
530 42-58.
531
532

Figure 2. Lead sorption edges for suspensions that were formed by combining 20%, by weight, of Polonite or Polonite-P with various concentrations of Pb. Suspensions were incubated under constant shaking, 200 RPM, at 25 °C for 48 hours.

Figure 3. (a) Calcium release to solution as function of Pb removal. Pb and Ca were measured following a 48 hour incubation period. (b) Linear region of Ca release to solution as function of Pb removal.

Figure 4. Comparison LDI of spectra: stainless steel background (red); Polonite (blue); Polonite-P (green); and, Pb treated Polonite-P (orange). Spectra are normalized to the Polonite spectram. Spectra are an average of 3000 laser shots.

(a)

(b)

Figure 5. (a) SEM-EDS image of Polonite treated with Pb: Ca (yellow), Si (blue), and Pb (red) are mapped on the surface. This image was detected at an 8000x magnification of the sample. (b) SEM-EDS images of Polonite-P treated with Pb: Ca (yellow), P (green), and Pb (red) are mapped at the same location on the surface. This image was detected at a 2000x magnification of the sample.

Figure 6. Electrophoretic mobility of suspensions at 25 °C in 1 mM KNO₃. Error bars represent one standard deviation.

Table 1. Proposed species observed with laser desorption ionization mass spectrometry with time of flight detection (LDI-TOF). The extent to which an ion was observed was defined as follows: small peak (sm) being a minimum of 3x the intensity of the background noise signal and average peak (X) being a minimum of 10x the intensity of the background noise signal.

Proposed Positive Ion	Mass	Lead Phosphate control	Plain Polonite	Amended Polonite	Polonite Treated with Pb^a	Polonite-P Treated with Pb^b
SiO ₂ H ₂ O	78			X	X	X
HPO ₄	96	sm	X	X	X	X
AlSiO ₃	103			X	X	X
Ca ₂ O ₂	112		X	X	X	X
Ca ₂ O ₃	128	sm	X	X	X	X
Ca ₂ O ₃ Mg	152		X	X	X	X
K ₂ PO ₃	157			X	X	sm
Pb	208	X			X	X
PbNaO	247	X				
PbAlSi	263				X	X
PbPO ₃	287	X				
Pb ₂	415	X			X	X
Pb ₂ O	430	X			X	X
Pb ₂ OOH	448	X			X	sm
CaPb ₂ O ₂ H	487				X	
Pb ₂ PO ₄	509	X				X
Pb ₃	622	sm			sm	X
Pb ₃ O ₂	655	X			X	sm ^c
Pb ₃ O ₃	671				X	
Pb ₃ O ₄ Mg	710				X	
Pb ₃ O(PO ₄)	733	X ^c				X ^c
Pb ₄	830	sm				X
Pb ₄ O ₃	878				X	
Pb ₄ O ₃ OH	895				X	
Pb ₄ O(PO ₄) ₂	1036					X ^c
Proposed Negative Ion	Mass	Lead Phosphate control	Plain Polonite	Amended Polonite	Polonite Treated with Pb^a	Polonite-P Treated with Pb^b
CaCO ₃	100		X	sm	sm	X
Pb ₃ O ₂ (OH) ₂	688				X	

Table 1. Footnotes

a. 19.6 mg Pb/g Polonite

b. 3.97 mg Pb/g Polonite-P

c. These species were observed at higher laser power.