# Heavy Metals in the Environment

## Immobilization of Nickel and Other Metals in Contaminated Sediments by Hydroxyapatite Addition

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#### ABSTRACT

Batch experiments were conducted to evaluate the ability of hydroxyapatite (HA) to reduce the solubility of metals, including the primary contaminants of concern, Ni and U, from contaminated sediments located on the Department of Energy's Savannah River Site, near Aiken, SC. Hydroxyapatite was added to the sediments at application rates of 0, 5, 15.8, and 50 g kg<sup>-1</sup>. After equilibrating in either 0.02 M KCl or 0.01 M CaCl<sub>2</sub>, the samples were centrifuged and the supernatants filtered prior to metal, dissolved organic C, and PO<sub>4</sub> analyses. The treated soils were then air-dried and changes in solidphase metal distribution were evaluated using sequential extractions and electron-based microanalysis techniques. Hydroxyapatite was effective at reducing the solubility of U and, to a lesser degree, Ni. Hydroxyapatite was also effective in reducing the solubility of Al, Ba, Cd, Co, Mn, and Pb. Sequential extractions indicate that HA transfers such metals from more chemically labile forms, such as the water-soluble and exchangeable fractions, by altering solid-phase speciation in favor of secondary phosphate precipitates. Hydroxyapatite effectiveness was somewhat reduced in the presence of soluble organics that likely increased contaminant metal solubility through complexation. Arsenic and Cr solubility increased with HA addition, suggesting that the increase in pH and competition from PO<sub>4</sub> reduced sorption of oxyanion contaminants. Energy dispersive x-ray (EDXA) analysis conducted in the transmission electron microscope (TEM) confirmed that HA amendment sequesters U, Ni, Pb, and possibly other contaminant metals in association with secondary Al-phosphates.

IN SITU treatment and stabilization techniques for soils and sediments are typically less expensive and disruptive to functioning, albeit contaminated, ecosystems than conventional excavation, extraction, and disposal procedures. Such techniques enhance the natural attenuation mechanisms controlling contaminant migration, bioavailability, and toxicity, and are based on a fundamental understanding of the natural geochemical processes affecting the speciation and fate of the target contaminant. Previous studies have generally focused on reducing the mobility of a specific contaminant metal, e.g., Pb or U. However, most sites consist of a mixture of various contaminants, often including both inorganic and organic contaminants displaying different chemical properties that impact their mobility and toxicity in the environment (NRC, 1994). The Tims Brach system located on the Department of Energy's Savannah River Site (SRS) near Aiken, SC, is a prime example, having been contaminated with a variety of metals.

Tims Branch, a second order stream which drains approximately 16 km<sup>2</sup> within the drainage basin of the Savannah River, was contaminated with uranium (U), nickel (Ni), lead (Pb), chromium (Cr), copper (Cu), thorium (Th), and other metals resulting from nuclear materials production on the SRS (Evans et al., 1992; Pickett, 1990). Significant deposition of contaminants and suspended sediments occurred within Steed Pond, a former farm pond on Tims Branch, due to the longer residence times and reduced flow velocities (Batson, 1994; Batson et al., 1996; Evans et al., 1992). Steed Pond sediments display elevated levels of Ni, U, and several other metals when compared with nonimpacted soils from the southeastern USA (Table 1), with much of the contamination restricted to the upper 45 cm of sediment (Pickett, 1990). The wooden dam ruptured in 1984, draining the pond and exposing the contaminated sediments (Pickett, 1990). Originally it was thought that revegetation would control erosional contaminant transport (Pickett, 1990); however, many of the most contaminated regions of the pond remain unvegetated, suggesting metal toxicity continues to limit plant growth (Batson, 1994). The relatively large affected area, approximately 5.3 ha, and the potential to drastically disturb the Upper Three Runs/Tims Branch stream system and possibly enhance contaminant transport due to erosion during conventional ex situ treatment makes in situ stabilization an attractive remediation alternative.

In situ chemical stabilization techniques typically reduce the mobility of the target contaminant by redirecting chemical speciation in favor of less soluble/labile phases. The addition of apatite minerals  $[(Ca_5(PO_4)_3X) (X = halide, hydroxyl)]$  has proven effective in stabilizing many transition and heavy metals, metalloids, and radionuclides through the formation of secondary phosphate precipitates that remain stable over a wide range of geochemical conditions (Berti and Cunningham, 1997; Laperche et al., 1997; Ma et al., 1993; Nriagu, 1974; Ruby et al., 1994; Traina and Laperche, 1999; Wright, 1990; Wright et al., 1987). Research into the use of apatite as a soil amendment has focused mainly on Pb remediation. Numerous studies have demonstrated

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**Abbreviations:** CBD, citrate–dithionite–bicarbonate extraction; DOC, dissolved organic carbon; EC, electrical conductivity; EDXA, energy dispersive x-ray analysis; fel, feldspar; gibb, gibbsite; goe, goe-thite; HA, hydroxyapatite; HIV, hydroxy-interlayered vermiculite; *k*, kaolinite; *q*, quartz; SRS, Savannah River Site; TCLP, toxicity characteristic leaching procedure; TEM, transmission electron microscope; XRD, X-ray diffraction.

that apatite addition reduces the solubility, mobility, and bioavailability of Pb in controlled batch studies (Chen et al., 1997b; Ma et al., 1993, 1994a, 1994b; Takeuchi and Arai, 1990; Traina and Laperche, 1999; Wright et al., 1995; Xu and Schwartz, 1994; Xu et al., 1994; Zhang and Ryan, 1998; Zhang et al., 1997) and experiments using Pb-contaminated soils (Chen et al., 1997a, 1997b; Laperche et al., 1997; Ma et al., 1993; Wright et al., 1995).

Apatite addition has been proven effective in reducing the solubility of a wide range of contaminant metals (Arey et al., 1999; Ma et al., 1994b; Wright et al., 1995), which suggests its widespread utility in addressing sites contaminated with multiple metals, such as the high levels of U, Ni and other metals found in Steed Pond (Pickett, 1990). However, the presence of other metals can inhibit contaminant stabilization by reducing the amount and rate at which PO<sub>4</sub> becomes available for precipitation with the target contaminant, and by altering the nature of any secondary phosphate precipitates that are formed (Ma et al., 1994b; Wright et al., 1995). For example, less soluble phases such as strengite (Fe- $PO_4 \cdot 2H_2O$ ) and variscite (AlPO<sub>4</sub> \cdot 2H<sub>2</sub>O) may control solution-phase phosphate activity under acidic soil conditions (Lindsay, 1979; Nriagu, 1974).

Arey et al. (1999) demonstrated that addition of hydroxyapatite (HA),  $Ca_5(PO_4)_3OH$ , reduces U solubility in Steed Pond sediments. However, metal complexation by dissolved organic matter and the buffering capacity of the contaminated material are important factors controlling U solid-phase partitioning. Despite the potential for organic complexation to enhance solubility, HAtreated sediments were greatly undersaturated with respect to U-phosphate precipitates, namely Ca- or K-autunite. Energy dispersive x-ray (EDX) analysis of the treated sediments conducted in a transmission electron microscope (TEM) failed to identify autunite and suggested that U was sequestered primarily in poorly ordered secondary Al/Fe-phosphate phases (Arey et al., 1999).

Clearly the immobilization mechanisms occurring in contaminated soil systems may be far more complex than the simple batch analogs. However, the relatively large land area and shallow nature of the contamination make Steed Pond an ideal site for in situ immobilization techniques. Numerous studies, many of which were cited above, have verified the utility of HA in treating Pb-

Table 1. Concentration of selected metals in two Steed Pond samples compared with the average for Savannah River Site (SRS) sediments (Pickett et al., 1985).

Metals	Avg for SDS	Steed Pond samples		
	soils/sediments	<b>S1</b>	<b>S2</b>	
		— mg kg <sup>-1</sup> ———		
As		18.6	17.4	
Cd		0.5	1.1	
Со		6.4	11.0	
Cr	38	113	175	
Cu	18	52.1	76.5	
Ni	10	946	1922	
Pb	13	60.6	91.6	
U	2	1727	2260	

contaminated soils, and Arey et al. (1999) demonstrated its effectiveness for U. However, little information is available on the effectiveness of apatite in addressing Ni contamination, which can be as high as  $5300 \text{ mg kg}^{-1}$ in Steed Pond (Pickett, 1990). Additionally, few studies have evaluated the ability of HA to immobilize a range of contaminant metals in weathered systems where the contaminants have been exposed to the sediments for long time periods. The objective of the present study was to evaluate the effectiveness of HA at chemically stabilizing Ni and other contaminant metals present in Steed Pond sediments that differ in terms of organic C content, and to identify and characterize potential sorptive phases. Two background solutions, 0.02 M KCl or  $0.01 M \text{ CaCl}_2$ , were used to evaluate the impact of the common ion, i.e., Ca, on HA solubility and contaminant metal partitioning.

## **MATERIALS AND METHODS**

Steed Pond sediments are characteristic of the highly weathered soils/sediments of the Atlantic Coastal Plain. The sediments tend to be acidic (pH 4.0–4.5) with the clay fraction dominated by kaolinite with lesser amounts of illite, hydroxyinterlayered vermiculite (HIV), gibbsite, and goethite (Batson, 1994). For the present study, two distinct contaminated strata differing in organic matter content, hereafter referred to as S1 and S2, were collected at depth intervals from 2 to 7 and 7 to 22 cm, respectively, at the same coring site in Steed Pond (Table 2). The samples were stored in a field-moist state at 4°C. Both sediments have similar properties with respect to mineralogy, pH, and texture, but vary greatly with respect to organic C content.

#### **Batch Equilibrations**

Five g (dry wt.) of field-moist sediment were placed in 50mL centrifuge tubes with three replicates for each treatment. Four levels of reagent-grade HA were added to each sediment, 0, 5, 15.8, and 50 g kg<sup>-1</sup>, which correspond to 0, 0.5, 1.58, and 5.0% by weight, with 25 mL of 0.02 *M* KCl or 0.01 *M* CaCl<sub>2</sub>. After equilibrating on a reciprocating shaker for 42 h at 25°C, the sediment suspensions were allowed to settle for at least 2 h before measuring the supernatant pH and electrical conductivity (EC). For comparison, sediment-free centrifuge

Table 2. Physical and chemical characteristics of two contaminated sediment strata from Steed Pond.

		Sediment zone	
Characteristics	<b>S1</b>	<b>S2</b>	
Depth, cm		2–7	7–22
pH <sup>+</sup>		4.4	4.1
CDB Ext. Fe, g kg <sup>-1</sup> ‡		2.9	3.2
Organic C, g kg <sup>-1</sup> §		123	49
Particle-size distribution¶	Mineralogy		
Sand, %	$\mathbf{#q} >> \mathbf{fel}$	25.7	19.2
Silt, %	q > k >> fel	35.8	45.2
Clay, %	$\hat{\mathbf{k}} >> \mathbf{HIV} > \mathbf{gibb} >$	38.5	35.6

† 2:1 solution/soil ratio in deionized water.

‡ CDB, citrate-dithionite-bicarbonate extraction (Jackson et al., 1986).

§ Total organic C, dry combustion method (Nelson and Sommers, 1982).

¶ Micro-pipette method (Miller and Miller, 1987).

# Mineralogy determined by x-ray diffraction; fel = feldspar, k = kaolinite, HIV = hydroxy-interlayered vermiculite, gibb = gibbsite, q = quartz, goe = goethite. tubes were used to evaluate HA dissolution in the two background solutions, 0.02 M KCl or 0.01 M CaCl<sub>2</sub>, under pH conditions similar to that of the sediment treatments. Selected treatments were also replicated with batch reaction times of 136 h to determine if equilibrium had been reached with respect to metal immobilization. The suspensions were then centrifuged at 10 000 rpm (11 952 g) for 30 min using a Sorvall RC2-B supercentrifuge and passed through a polycarbonate membrane filter (0.22-µm pore size). A fraction of the filtered supernatant was immediately analyzed for DOC using a Shimadzu TOC-500 organic C analyzer and for soluble orthophosphate using the molybdate ascorbic acid colorimetric method (Olsen and Sommers, 1982). Sulfate  $(SO_4^{2-})$ , chloride  $(Cl^{-})$ , and nitrate  $(NO_3^-)$  contents in the same supernatant fraction were determined by ion chromatography (USEPA Method 300.0, 1993). The remaining supernatants were acidified (1% nitric acid) and analyzed for metals by inductively coupled plasma-mass spectrometry (ICP-MS) (Elan 6000, Perkin-Elmer Corp., Norwalk, CT). The residual-treated soils were air-dried and changes in solid-phase metal distribution were evaluated using sequential extractions and TEM microanalysis techniques.

## Toxicity Characteristic Leaching Procedure and Sequential Extraction

A subsample from two of the equilibration replicates of each treatment was extracted using the USEPA standardized Toxicity Characteristic Leaching Procedure (TCLP; USEPA, 1992). The TCLP leaching solution is comprised of 0.1 *M* glacial acetic acid and 0.0643 *M* NaOH, with a final pH of 4.93. Fifty g of leaching solution were added to 2.5 g of treated sediment, the mixture was agitated on a reciprocating shaker for 18 h at 25°C, and then centrifuged as described above. After centrifugation, supernatants were filtered through 0.22- $\mu$ m pore-size polycarbonate filters, acidified to 2% HNO<sub>3</sub>, and analyzed for metals using ICP-MS.

Sequential extraction was performed in triplicate for each of the sediment treatments using the modified procedure from Miller et al. 1986, which is more appropriate for highly weathered soils than many of the other commonly used sequential extraction schemes. Each extraction step and the target phase are listed in procedural order from least to most chemically aggressive:

- 1. Deionized water = Water soluble.
- 2. 0.5 M Ca(NO<sub>3</sub>)<sub>2</sub> = Exchangeable.
- 3. 0.44 *M* Glacial acetic acid + 0.1 *M*  $Ca(NO_3)_2 = Acid soluble.$
- 4. 0.01 M NH<sub>2</sub>OH-HCl + 0.1 M HNO<sub>3</sub> = Mn occluded.
- 5. 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>-10H<sub>2</sub>O = Organically bound.
- 6. 0.175 M (NH<sub>4</sub>) 2C<sub>2</sub>O<sub>2</sub>-H<sub>2</sub>O, 0.1 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in the dark = Amorphous Fe oxides.
- 7. Reduction with 0.5 g Na-dithionite in 0.15 M Na<sub>3</sub>-H<sub>5</sub>C<sub>6</sub>O<sub>7</sub> + 0.05 M H<sub>8</sub>C<sub>6</sub>O<sub>7</sub> (sodium-citrate buffer) = Crystalline Fe oxides.
- 8. 6 mL of HF and 5 mL of  $HNO_3$  and heated at 880 kPa (120 psi) in a digestion microwave for 30-min intervals until residual digestion was complete = Residual fraction.

Extracted metals in each fraction were quantified by ICP-MS. For comparison with sequential extraction results, total metals for the original unamended soils were determined using an HF/HNO<sub>3</sub>-based, microwave-assisted digestion method (USEPA Method 3052) followed by ICP-MS analysis.

#### **Analytical Electron Microscopy**

Analytical electron microscopy was used to identify solid phases that may influence contaminant metal solubility. A small fraction of each HA-treated soil and the control samples was embedded in a low viscosity fixative (Embed 812) and cured overnight. The samples were then cut into thin sections ( $\approx$ 70 nm) using an ultramicrotome equipped with a diamond knife. The thin sections were then placed onto TEM grids and analyzed using a JEOL 2010 transmission electron microscope (TEM) equipped with a thin-window detector for EDX analysis of lighter elements ( $Z \ge 6$ ).

## **Thermodynamic Modeling**

Equilibrium modeling was conducted using the USEPA's MINTEQA2 geochemical code (v. 3.11) to compare the batch results with various secondary precipitates that may control metal and PO<sub>4</sub> solubility (USEPA, 1997). The database was updated with the Nuclear Energy Agency's thermodynamic data set for U minerals (Turner et al., 1993; USEPA, 1997). Solution conditions (i.e., metal and PO<sub>4</sub> concentrations and pH) were based on results from the initial HA/soil equilibrations for the 50 g kg<sup>-1</sup> amendment treatment level in each of the background equilibrating solutions, 0.01 *M* CaCl<sub>2</sub> or 0.02 *M* KCl. The degree of saturation with respect to a specific solid phase ( $\Omega$ ) is defined as

## $\Omega = IAP/K_{so}$

where IAP is the ion activity product and  $K_{so}$  is the solubility product. To readily compare the degree of saturation for a set of potential solid phases, the saturation index (SI) is then defined as the log $\Omega$ . If SI < 0 (i.e., negative value), the solution is undersaturated, whereas if SI > 0, the solution is supersaturated with respect to a specified solid phase. If SI = 0, the solution is in equilibrium with a given solid. The saturation indices with respect to HA were determined without including an initial solid phase. To calculate the saturation indices for Ni [Ni(OH)<sub>2</sub>, Ni<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>], Al (varascite), and U (autunite), however, HA was added as an infinite solid without allowing secondary phases to precipitate that would alter the observed solution chemistry.

## **RESULTS AND DISCUSSION**

Steed Pond sediments display elevated levels of U, Ni, Cr, Cu, and Pb that are several times higher than the reported values for nonimpacted soils on the SRS (Pickett, 1990; Pickett et al., 1985; Zeigler et al., 1986). In fact, the levels of U and Ni are several hundred times higher than normal, and apparently limit revegetation in localized areas (Table 1). Hydroxyapatite addition decreased Ni and U solubility and increased soluble PO<sub>4</sub> and solution pH (Fig. 1). However, the soluble Ni concentrations in the HA-amended sediments were still >1 mg L<sup>-1</sup>, much higher than the soluble U concentrations (<50 µg L<sup>-1</sup>) at the same amendment levels (Arey et al., 1999).

In the presence of  $CaCl_2$ , the levels of soluble  $PO_4$ for each sediment at a given HA treatment level were consistently less than the KCl treatments, and the soluble Ni and U levels were higher as well. This suggests that HA solubility, available  $PO_4$ , and the subsequent impact on contaminant metal immobilization were in part reduced due to the common ion effect of  $Ca^{2+}$  on



Fig. 1. Effect of hydroxyapatite (HA) amendment on (A) Ni, (B) U (redrawn from Arey et al., 1999; Fig. 1), (C) PO<sub>4</sub>, and (D) pH for two sediments equilibrated in 0.02 M KCl or 0.01 M CaCl<sub>2</sub>.

HA dissolution. However,  $Ca^{2+}$  competition for sorption sites may have also enhanced soluble Ni levels. Soluble PO<sub>4</sub> increased almost linearly as a function of HA addition in sediment-free background solutions (data not shown), and displayed a similar trend in the



Fig. 2. Aqueous PO<sub>4</sub> as related to (A) DOC concentration, (B) pH, and (C) Ni concentration in hydroxyapatite (HA)-amended sediments.

presence of Steed Pond sediments (Fig. 1C). Soluble PO<sub>4</sub> levels in sediment-free CaCl<sub>2</sub> solution with HA were comparable to those observed in the presence of HA-treated sediments. However, the concentration of soluble PO<sub>4</sub> levels was much higher for the sediment-free KCl solutions, demonstrating the impact of both the sediment components and the background solution (i.e., Ca<sup>2+</sup>) in controlling HA dissolution. The increase in soluble PO<sub>4</sub> with treatment level for all the solution and sediment treatments suggests that HA dissolution may have been kinetically limited during the batch experiments. However, the final aqueous phase concentra-



Fig. 3. Effect of hydroxyapatite (HA) amendment on soluble (A) Ba, (B) Cd, (C) Co, and (D) Pb for two sediments equilibrated in 0.02 M KCl or 0.01 M CaCl<sub>2</sub>. Bars represent the standard deviation of the treatment means.

tions of Ni, U, and other contaminant metals were very similar for samples equilibrated for 42 or 136 h.

Similar levels of soluble Ni were observed for both sediments despite more than twofold differences in total Ni content, i.e., 946 vs. 1922 mg kg<sup>-1</sup> (Table 1). Previous studies have clearly demonstrated the role of organics in controlling metal partitioning in Steed Pond sediments (Arey et al., 1999; Batson et al., 1996). As observed for U (Arey et al., 1999), the enhanced metal solubility may reflect the impact of complexation by native soluble humic substances. When the treatments are plotted as a



Fig. 4. Effect of hydroxyapatite (HA) amendment on soluble (A) As and (B) Cr concentration for two sediments equilibrated in 0.02 M KCl or 0.01 M CaCl<sub>2</sub>. Bars represent the standard deviation of the treatment means.

function of PO<sub>4</sub> concentration, dissolved organic carbon (DOC) and suspension pH increased, while soluble Ni decreased with increasing soluble  $PO_4$  (Fig. 2). Each sediment apparently displays a clearly distinct trend with respect to DOC, pH, and Ni as a function of PO<sub>4</sub> levels. Treatments in the CaCl<sub>2</sub> background solution display consistently lower soluble PO4 for a given HA treatment level, again suggesting that the CaCl<sub>2</sub> solution reduces HA solubility due to the common ion effect. The increased solubilization of organic matter with HA addition may have resulted from PO<sub>4</sub> competition with anionic organic acids and humic substances for sorption sites, the enhanced solubility of humics with increasing pH, or the precipitation of metals with PO<sub>4</sub> that would otherwise act to coagulate soluble organics (Bhatti et al., 1998; Lopez-Hernandez et al., 1986; Violante et al., 1991; Yuan, 1980). At a given soluble PO<sub>4</sub> concentration, however, sediment S1 displayed consistently higher DOC and Ni levels (Fig. 2), indicating that humics enhanced metal solubility by lowering the free-ion activity product for the metal being complexed.

In addition to Ni and U, HA reduced the solubility of aluminum (Al; data not shown), barium (Ba), cadmium (Cd), cobalt (Co), manganese (Mn; data not shown), and lead (Pb) during batch equilibration (Fig. 3), dem-



Fig. 5. Transmission electron microscope (TEM) micrographs of (A) fine-grained secondary Al/Fe-phosphate precipitates (40K magnification), (B) fine-grained, lath-shaped residual hydroxyapatite (HA) (50K magnification), and (C) typical energy dispersive x-ray (EDXA) spectrum of Ni- and U-rich secondary Al/Fe-phosphate precipitates in sediment S1 amended with 50 g kg<sup>-1</sup> HA.

onstrating the potential efficacy of HA in addressing soils/sediments with multiple contaminant metals. In contrast, however, HA noticeably increased the solubility of As, and to a lesser degree Cr (Fig. 4). This is likely due to the increased sorption competition between  $PO_4$  and possibly humics with the oxyanion species of As

(arsenate and arsenite) and Cr (James and Bartlett, 1983; Peryea, 1991), demonstrating that HA would not be effective for remediating such oxyanion contaminants.

Mechanistic interpretation of batch equilibration data is somewhat difficult because of the inability to discrimi-

Table 3. MinteqA2 input parameters based on the batch equilibration data for sediment S1 and S2 amended with 50 kg<sup>-1</sup> HA in either a 0.01 *M* CaCl<sub>2</sub> or 0.02 *M* KCl background solution.

	pН	Ca	K	Cl	PO <sub>4</sub>	Ni	Al†	U
			—— mg l	L <sup>-1</sup>			– μg L <sup>–1</sup>	
S1			-					
KCI	5.17	164	782	709	14.8	869	246	29.83
CaCl <sub>2</sub>	5.00	401	3.76	709	10.7	1604	39	25.33
S2								
KCl	5.46	154	782	709	6.7	943	1.0	9.02
CaCl <sub>2</sub>	5.24	401	0.80	709	5.0	1774	1.0	7.76

 $\dagger$  Total soluble Al was entered as 1.0  $\mu g~L^{-1}$  for S2, although the actual analytical total was < 1.0  $\mu g~L^{-1}$ .

nate between various chemical changes resulting from HA addition. Reductions in metal solubility can result from a number of distinct mechanisms, including surface adsorption, ion exchange, substitution, and precipitation. Controlled batch experiments clearly demonstrate that Pb immobilization occurs through HA dissolution followed by rapid precipitation of sparingly soluble Pbphosphates, such as hydroxypyromorphite and chloropyromorphite, with most of the Pb precipitated within minutes (Ma et al., 1993, 1994a, 1994b; Wright et al., 1995; Xu and Schwartz, 1994). However, the mechanisms responsible for HA induced immobilization of other metals, such as Zn and Cd, may be more complex and highly dependent on factors such as solution pH and the presence of competitive species when compared with Pb (Wright et al., 1995; Xu et al., 1994). For example, changes in soil pH can alter sorption equilibria with respect to various native sorptive minerals, such as Ni sorption by goethite and other hydrous oxides, which generally increases with pH (Dzombak and Morel, 1990). In addition to the formation of secondary phosphate precipitates or sorption to the HA and phosphate precipitates, metal stabilization may result from the precipitation of metal oxyhydroxides due to the buffering capacity of HA (Wright et al., 1995).

## **Electron Microscopy**

As observed by Arey et al. (1999) for U in unamended Steed Pond sediments, Ni appeared to be widely dispersed without the presence of an obvious enriched sorptive phase. Secondary Al/Fe phosphates, nanocrystalline in nature and containing only trace amounts of residual  $Ca^{2+}$ , were observed in the HA-treated sediments (Fig. 5). A portion of the Fe detected by EDXA was identified by electron diffraction as goethite crystals, which were often closely associated with the poorly ordered phosphate precipitates, making it difficult to differentiate Fe associated with the secondary precipitate. Phosphate and metals sorbed to goethite can act as a precursor for secondary phosphate precipitation below the solubility threshold for a given phase (Sato et al., 1997), i.e., surface facilitated precipitation. Uranium, Ni, and in some cases Pb were associated with the secondary Al/Fe–PO<sub>4</sub> precipitates (Fig. 5C). In contrast, residual HA grains in the treated sediments contained an appropriate Ca/P ratio, and were much larger and more crystalline than the secondary precipitates, with little or no detectable U, Ni, or Pb (Fig. 5B).

## **Thermodynamic Modeling**

MinteqA2 model input parameters were based on the 50 g kg<sup>-1</sup> HA treatment level because residual HA was observed during TEM analysis for both materials at this treatment level (Table 3). The degree of saturation with respect to residual HA was based solely on the solution composition. However, HA was entered as an infinite solid for computing the degree of saturation with respect to Ni, U, and Al mineral phases. Despite the observed presence of residual HA observed during EM analysis, the solutions were undersaturated with respect to HA (Table 4). The saturation indices for variscite (Al- $PO_4 \cdot 2H_2O$ ), an Al phosphate phase thought to control PO<sub>4</sub> activity under acidic soil conditions (Lindsay, 1979; Nriagu, 1974), were close to 0, especially for the S2 sediment that had less dissolved organic matter, which apparently enhanced metal solubility for the S1 sediment. In fact, the two saturation values for the S2 sediment treatments are likely to be closer to variscite because Al was below the detection limit and, thus, was entered as 1  $\mu$ g L<sup>-1</sup>. Entering the higher conservative estimate increases the degree of supersaturation (i.e.,  $\log \Omega$ . > 0) above the actual value. Despite the high levels of soluble Ni in the HA-treated sediments, the solutions were still undersaturated (i.e., SI < 0) with respect to  $Ni(OH)_2$  and  $Ni_3(PO_4)_2$ . The levels of U were also well below the predicted saturation point for the autunite minerals. Since complexation by DOC that would lower the free ion activity for U and Ni was not considered in the MinteqA2 calculations, the solutions are likely to be even more undersaturated with respect to the reported solid phases. The high degree of undersaturation observed for the U and Ni solid phases indicates that an alternate phase, possibly an Al phosphate as suggested by the EM results, controls Ni, U, and even Al solubility in the amended soils.

Batch experiments have demonstrated the ability of HA to induce solid-phase Pb redistribution from Pbsulfide, -sulfate (angelsite), and -carbonate minerals, as well as surface sorbed Pb (Ma et al., 1993; Zhang and Ryan, 1998; Zhang et al., 1997). The rate of such solid

Table 4. MinteqA2 calculated saturation indices for select Al, Ni, and U (uranyl) phases based on the batch equilibration data for sediment S1 and S2 amended with 50 g kg<sup>-1</sup> HA in either a 0.01 *M* CaCl<sub>2</sub> or 0.02 *M* KCl background solution.

0 0				8		
HA	Variscite	Ni(OH) <sub>2</sub>	Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Autunite	H-autunite	K-autunite
-3.346	2.597	-5.60	-8.58	-4.70	-6.45	-1.40
-3.149	1.751	-5.68	-8.66	-4.87	-6.58	-6.50
-2.492	0.473	-4.97	-8.26	-5.32	-7.55	-1.90
-2.477	0.125	-5.14	-8.55	-5.48	-7.64	-8.41
	HA -3.346 -3.149 -2.492 -2.477	HA         Variscite           -3.346         2.597           -3.149         1.751           -2.492         0.473           -2.477         0.125	HA         Variscite         Ni(OH) <sub>2</sub> $-3.346$ $2.597$ $-5.60$ $-3.149$ $1.751$ $-5.68$ $-2.492$ $0.473$ $-4.97$ $-2.477$ $0.125$ $-5.14$	HA         Variscite         Ni(OH)2         Ni3(PO4)2           -3.346         2.597         -5.60         -8.58           -3.149         1.751         -5.68         -8.66           -2.492         0.473         -4.97         -8.26           -2.477         0.125         -5.14         -8.55	HA         Variscite         Ni(OH) <sub>2</sub> Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Autunite $-3.346$ $2.597$ $-5.60$ $-8.58$ $-4.70$ $-3.149$ $1.751$ $-5.68$ $-8.66$ $-4.87$ $-2.492$ $0.473$ $-4.97$ $-8.26$ $-5.32$ $-2.477$ $0.125$ $-5.14$ $-8.55$ $-5.48$	HA         Variscite         Ni(OH) <sub>2</sub> Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Autunite         H-autunite $-3.346$ $2.597$ $-5.60$ $-8.58$ $-4.70$ $-6.45$ $-3.149$ $1.751$ $-5.68$ $-8.66$ $-4.87$ $-6.58$ $-2.492$ $0.473$ $-4.97$ $-8.26$ $-5.32$ $-7.55$ $-2.477$ $0.125$ $-5.14$ $-8.55$ $-5.48$ $-7.64$



Fig. 6. Toxicity Characteristic Leaching Procedure (TCLP) extractable Ni in HA-amended sediments (mg Ni kg<sup>-1</sup> sediment). The TCLP values corrected for Ni extracted during initial equilibrations are included for comparison. Dashed line represents TCLP extractable Ni for nonamended sediments that were not subjected to the initial amendment equilibrations.

phase transfer is far more sensitive to pH and other solution conditions than the rapid precipitation of an aqueous-phase metal when exposed to HA (Zhang et al., 1997). High levels of soluble native metals commonly encountered in soil systems, such as Al in the present study, or contaminant metals such as Cu, can effectively reduce Pb precipitation and pyromorphite formation, although the level of inhibition may not necessarily coincide with precipitation of the confounding metals (Ma et al., 1994b). In studies of binary metal systems (i.e., Al and Pb, Cu and Pb, etc.), pyromorphite formation was inhibited despite sufficient Pb precipitation. Alternate secondary crystalline Fe(II) and Al phases were not evident from XRD, which suggests the formation of poorly crystalline, mixed metal phosphates (Ma et al., 1994b). The transfer of Ni and U to poorly ordered secondary Al/Fe-phosphate phases in the current study is similar to the observations of Ma et al. (1994a, 1994b) for Pb precipitation in binary metal systems. In this case, however, the solubility of the resulting phase is less than that of the idealized phosphate precipitate for Ni or U (Arey et al., 1999).

## Toxicity Characteristic Leaching Procedure and Sequential Extractions

Less U, Al, Pb, and Cd were extracted by TCLP with increasing HA addition (data not shown). However, the results for Ni extraction were extremely variable without a clear discernable trend as a function of amendment level (Fig. 6). A significant portion of the total Ni, and certainly a much higher fraction of the readily labile Ni (soluble, exchangeable, etc.), was extracted from the control and lower HA treatment levels during the initial batch equilibrations, leaving less Ni present for the subsequent extraction by TCLP or the sequential extractants. To account for such a bias, the amount of Ni removed during the initial equilibration was added to the TCLP data. After the correction, a clear trend of decreasing Ni extraction with increasing HA treatment level becomes apparent (Fig. 6). Although this approach seems reasonable, it overestimates the effectiveness of HA since the sum of TCLP–extractable Ni and soluble Ni in soils equilibrated without HA is considerably greater than TCLP extractable Ni for materials that had not been subjected to the initial equilibration experiment. Increased Ni solubility due to the physical agitation associated with the initial 42-h equilibration step may account for such a discrepancy.

The average mass recovery for Ni in sequential extractions was 91.4% ( $\pm$  4.8%) when Ni removed in the initial batch equilibration was included. As might be expected, the same trends with respect to HA addition observed during the initial equilibrations were repeated in the water-soluble extraction data, despite the bias against the nonamended sediment resulting from metal extraction during the initial equilibration step. Hydroxyapatite was effective in reducing water-soluble Al, Ba, Cd, Co, Mn, Ni, Pb, and U for both sediments, but As increased in the water-soluble fraction with HA addition.

In general, a transfer from the water-soluble, exchangeable, and dilute acid-soluble fractions to the Mnoccluded fraction was observed for most of the metals for which HA was most effective, i.e., Al, Pb, and U. Trends with respect to other metals were less conclusive, likely due to the lower amounts of those metals present



Fig. 7. Nickel extracted in the Mn-occluded fraction for sediment (A) S1 and (B) S2 amended with various hydroxyapatite (HA) treatment levels and equilibrated in 0.02 M KCl or 0.01 M CaCl<sub>2</sub>.

in the sediments. Exchangeable and dilute acid-soluble Ni increased somewhat with HA addition, but to a lesser degree than observed for the Mn-occluded fraction (Fig. 7). As discussed above for TCLP, the results for the water-soluble, exchangeable, and possibly even more resistant fractions have been somewhat biased against the positive influence of HA (i.e., reduction in metal extractability with increasing HA) by the initial batch equilibrations. Metal partitioning to the Mn-occluded fraction is consistent with the previous observations of Arey et al. (1999) with respect to U in these sediments and demonstrates the operational nature of such extraction methods. In fact, the sediments in question have only minor amounts of Mn oxides, and more U and Ni compared with Mn was extracted during the Mnoccluded extraction procedure. This suggests that HA transfers such metals to secondary phosphate precipitates, which were more readily solubilized at the lower pH of the Mn-occluded extract (pH  $\approx$  1.26) compared to the acid soluble extract (0.44 M glacial acetic acid,pH ≈ 2.55).

## SUMMARY AND CONCLUSIONS

Hydroxyapatite addition lowered the solubility of several contaminant and native soil metals in two highly weathered containment pond sediments, demonstrating the utility of HA for remediating a wide range of metalcontaminated sites. However, HA was less effective in reducing the solubility and lability of Ni compared with U (Arey et al., 1999), the two primary contaminants of concern in Steed Pond. Even at high HA treatment levels, soluble Ni in the batch equilibrations exceeded 1 mg L<sup>-1</sup>. The moderate effectiveness of HA with respect to Ni compared to U, suggests that such a treatment may be a means of reducing plant uptake of U and increasing survival in a phytoextraction scheme targeting Ni so that the Ni-enriched plant materials are not considered a mixed waste, i.e., metals and radionuclides.

A comparison of similar sediments that differ in organic matter content suggests that complexation by DOC increases solubility of complexed metals such as Ni and U. Initial batch data and micro-analysis of the treated soils suggests that metals such as U, Ni, Al, and Pb are transferred from readily labile fractions, such as the water-soluble and exchangeable fractions, to more resistant secondary phosphates that were solubilized by the Mn-occluded extract due to the acidic pH of the extractant solution. The difference in particle size, morphology, and degree of crystallinity observed for contaminant-rich Al-phosphate precipitates compared with the residual HA support the formation of secondary precipitates rather than metal sorption by weathered HA grains. Although elevated levels of Ni were clearly associated with the secondary Al-phosphate precipitates, subsequent extraction results suggest that the degree/strength of Ni sorption with such phases is much less than observed for U, Al, and Pb.

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