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# Influence of Sediment Redox Conditions on Contaminant Stabilization by Apatite and Fe(0)

By Daniel I. Kaplan<sup>1</sup> and Anna S. Knox<sup>2</sup>

## ABSTRACT:

Efficacy of stabilizing Ce, Co, and Pb by adding apatite and zero-valent Fe (Fe(0)) to contaminated wetland sediments was quantified under oxidizing and reducing conditions. The redox status and the general water chemistry of the oxidized and reduced treatments differed greatly, yet the influences of the amendments on contaminant stabilization were quite similar; both amendments significantly ( $p \leq 0.05$ ) reduced aqueous contaminant concentrations. Based on resin sorption studies and thermodynamic calculations, Ce existed primarily as cationic and to a smaller extent, anionic species, and Co existed almost as cationic, neutral, and organically complexed species. Based on a series of varying selective extractions, almost 50 wt-% of the Co and Pb were already strongly bound to the sediment, thereby limiting the potential (and need) of affecting additional immobilization through the use of amendments. Fe(0) and combined Fe(0) & apatite additions tended to increase the *in-situ* desorption  $K_d$  values more than apatite additions.

## INTRODUCTION

The use of amendments to enhance sequestration of inorganic contaminants in sediments is gaining public acceptance as the cost of *ex situ* treatment of such sediments is rapidly rising (Smith et al. 1995). Furthermore, *ex situ* approaches involve sediment excavation (and off site treatment and disposal), potential resulting in significant ecological impact and, in some cases, additional risk to remediation workers. However, *in situ* contaminant sequestration has the distinct disadvantage that the contaminants remain in place. Consequently, in order to safely apply this remediation approach, it is necessary to quantify the extent and duration that human, ecological, and groundwater risks imposed by the contaminants are reduced.

Apatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F})_2$ , has been shown to be an extremely effective sediment amendment for immobilizing Pb and U, and somewhat less effective at immobilizing Cd, Co, Cu, Mn, Ni, Zn, and ineffective with most anions (Valsami-Jones et al. 1998, Suzuki et al. 1981, Fuller et al. 2002, Seaman et al. 2001, Knox et al., 2003, Kaplan and Knox 2004). It removes solutes from the aqueous phase through three mechanisms: cation/anion exchange, isomorphic substitution, and precipitation. An example of the removal of lead via cation exchange onto apatite is presented in Eq. 1:




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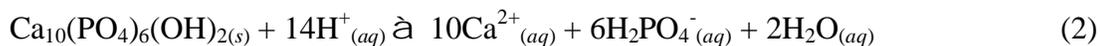
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This removal mechanism is the least desirable from the standpoint of contaminant stabilization because the bond between the contaminant and the apatite is relatively weak.

Isomorphic substitution into apatite is the contaminant substitutes for a Ca, phosphate, or hydroxide in the apatite structure. This removal mechanism is highly desirable from the standpoint of contaminant stabilization because the contaminant becomes incorporated into the apatite structure. Isomorphic substitution is common in apatite because its crystalline structure is highly flexible. Calcium exists in apatite in 7-fold and 9-fold coordination. The 7-fold coordinated Ca ions are about 10% smaller than the 9-fold coordinated ions. This difference in atomic size permits a rather large range of contaminants to substitute for Ca, including the +3 actinide series, Pb, U, Zn, Cd, Co, Ni, Hg, and Fe (Deer et al. 1975). Elements that can substitute for phosphate (0.254 nm radius) include  $\text{TcO}_4^-$  (0.268-nm) and  $\text{CO}_3^{2-}$  (0.211 nm). Finally, the hydroxyl anion (0.153-nm) can be substituted with  $\text{Br}^-$  (0.196 nm),  $\text{Cl}^-$  (0.181 nm) and  $\text{F}^-$  (0.136 nm).

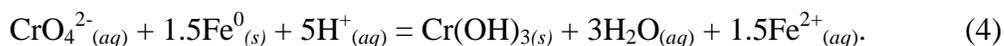
Evidence of the longevity that metals remain associated with apatite can be gleaned from the examination of apatite fossils recovered from unimpacted areas, such as the deep ocean floors (Deer et al. 1975, Wright 1987). Biogenic apatite (bones and teeth) while still associated with the living animal, has very low concentrations of transition metals, rare-earth elements (REE's), and actinides. After deposition in sediments, trace metals undergo isomorphic substitution into the apatite structure, commonly becoming enriched by many orders-of-magnitude greater than the surrounding seawater (Wright 1987). This comparison of biogenic apatite *in vivo* to biogenic apatite exposed to natural water illustrates that apatite can act as a substrate to concentrate several trace elements.

The third mechanism by which apatite removes contaminants from the aqueous phase is by first dissolving (Eq. 2), followed by forming a precipitate with a metal (Eq. 3).



where  $\text{M}^{2+}$  represents a divalent cation. Phosphate-metal precipitates have low solubilities, e.g., the solubility product ( $\log K_{sp}$ ) of  $\text{Pb}_5(\text{PO}_4)_3(\text{OH},\text{Cl})$  is -76;  $\text{Sr}_5(\text{PO}_4)_3(\text{OH})$  is -51;  $\text{Zn}_3(\text{PO}_4)_3$  is -35; and  $\text{Cd}_3(\text{PO}_4)_3$  is -24. Another important mechanism by which apatite induces precipitation of metals is through the formation of carbonate phases. As Eq. 2 shows, apatite dissolution results in an increase pH, which in turn promotes an increase in carbonate concentrations. These carbonate solutes can form precipitates with several metals. In almost all cases, carbonate precipitates are more soluble than phosphate precipitates.

Zero-valent iron,  $\text{Fe}(0)$ , is commonly used to address a wide range of environmental problems because it is a strong reductant, nontoxic, inexpensive, and the reaction rates of interests are limited by mass transport (Schreier and Reinhard 1994).  $\text{Fe}(0)$  removes metals from the aqueous phase by three primary processes: reductive precipitation (via  $\text{Fe}(0)$  or  $\text{Fe}(\text{II})$ ), coprecipitation with  $\text{Fe}(\text{II}/\text{III})$ , and metal sorption by  $\text{Fe}(\text{II}/\text{III})$ -oxyhydroxides, originated from  $\text{Fe}(0)$ . Reductive precipitation involves the transfer of electrons from  $\text{Fe}(0)$  to a contaminant and transforming the contaminant to a less soluble form. Common contaminants that can be removed from the aqueous phase in this manner are Cr, Hg, Mo, Tc, and U. For example, the reductive precipitation of  $\text{Cr}(\text{VI})$  can be described by Eq. 4:



In this example,  $\text{CrO}_4^{2-}$  is both more mobile and toxic than  $\text{Cr}(\text{OH})_3$ , which is a solid phase. Equation 4 also shows that  $\text{Fe}^{2+}$  is released and acidity is consumed. Both of these changes are conducive to the formation of Fe(II/III)-oxyhydroxides. The Fe(II/III)-oxyhydroxides increases the sorption capacity of the system. Contaminant removal in this manner is the least desirable of the three Fe(0) removal mechanisms due to the weak nature of the bond between the contaminant and the Fe(II/III)-oxyhydroxide. If other metals are present, they may coprecipitate with the Fe(II/III)-oxyhydroxide. This removal or stabilization process is generally more desirable than sorption onto the newly formed Fe(II/III)-oxyhydroxides surfaces.

A pilot-scale, nuclear-research facility located on the Savannah River Site, Aiken, South Carolina, introduced more than 50 metals (including Cd, Co, Cr, Hg, and Pb) and radioactive isotopes (including  $^{228}\text{Ac}$ ,  $^{228}\text{Th}$ , and  $^{233/234/235/238}\text{U}$ ) into an unlined seepage basin during the 1960's and 1970's. Several of these contaminants have since migrated into an adjacent wetland area. The forested affected 3-ha area is within the 100-yr flood plain and is often flooded during winter and spring.

The objective of this study was to evaluate the use of Fe(0) and apatite as sediment amendments at the site as a less ecologically intrusive alternative to the baseline *ex situ* remediation approach. It is anticipated that the sediment amendments will be broadcast on the ground surface and backfilled into drilled 2-cm diameter x 30-cm deep holes positioned across the contaminated area. Because of the large number of different inorganic contaminants at the site, both sediment amendments were evaluated, potentially providing a wide range of chemical immobilization processes, as discussed above. Particular attention was directed at evaluating the efficacy of the amendments under varying redox and moisture conditions, attempting to simulate the wide range of these parameters expected at the test site. Of the wide range of possible contaminants to monitor for this study, Co, Ce, and Pb were selected. Cobalt was selected because it behaved similar to other transition divalent-metal contaminants (including Ni, Zn, Cd, and Hg; Kaplan et al. 2002). Cerium was selected because it was used as an analogue of trivalent radionuclide contaminants (e.g.,  $^{228}\text{Ac}^{3+}$ ,  $^{241}\text{Am}^{3+}$ ,  $^{242}\text{Cm}^{3+}$ , and  $^{141.144}\text{Ce}^{3+}$ ). Lead was selected because it has been documented to precipitate as a sparingly soluble phosphate phase, pyromorphite ( $\text{Pb}_5(\text{PO}_4)_3(\text{OH},\text{Cl})$ ), and as such would provide an example of this highly desirable stabilization process (Ryan et al. 2001).

## MATERIALS AND METHODS

The general approach used in this study was to collect a contaminated sediment from the impacted wetland area at the pilot-scale, nuclear-research facility located on the Savannah River Site, characterize it, amend it with apatite and Fe(0), and then equilibrate it with groundwater by two methods: saturated and wet/dry-cycling. The saturated treatment was designed to approximate flooded field (lower redox) conditions, and the wet/dry-cycled treatment was designed to approximate cyclic wetting and drying (higher redox) conditions existing in more elevated wetland areas. After the 49-day period, the leachates from the samples were chemically characterized and the treated sediments were subjected to a sequential extraction procedure to provide insight into the relative extractability of Ce, Co, and Pb. From these data, distribution coefficients ( $K_d$  values; ratio of contaminant concentrations in the solid:liquid), and the strongly

bound fraction of the sediment contaminants were calculated. The details of this procedure follow.

## Materials and Characterization

The granular cast Fe(0) used in this study was kiln fired (degreased) by the vendor, Peerless Supply (Columbus, OH). Particle size distribution of the Fe(0) by sieve analysis was as follows: 0.5 wt-% was <0.15 mm, 3.5 wt-% was 0.15 – 0.30 mm, 28 wt-% was 0.30 – 0.60 mm, 55 wt-% was 0.6 – 1.18 mm, 44.5 wt-% was 1.18 – 2.38 mm, and 0.5 wt-% was 2.38 – 4.75 mm. The apatite used in this study was mined in Aurora, NC (Texas Gulf Mining). Only the apatite size fraction that could pass through a 2.36 mm sieve and be retained by a 0.6 mm sieve was used. X-ray diffraction analysis of this apatite fraction revealed that it was more specifically a carbonate hydroxyapatite that contained trace amounts of quartz.

A sediment sample was collected from a contaminated portion of the study site. The leaf litter on the sediment surface (the O horizon) was removed prior to collecting the surface 15-cm depth in plastic tubes. The sediment sample was stored moist and in the dark at 4 °C. All characterization and subsequent equilibration tests were conducted with the sediment in the moist state to minimize experimental artifacts associated with drying the sediment, such as the oxidizing of organic matter and the altering of Fe- and Mn-oxides. The sediments were characterized for: pH in a 1:1 water-sediment slurry; particle-size distribution by the sieve and pipette method; cation-exchange capacity by the unbuffered ammonium exchange method; and free Fe by the dithionite-citrate buffer method (Sparks 1996). Organic matter was determined by the weight-loss-on-ignition method conducted at 360 °C for 2 h (Schulte et al. 1991). Mineralogy was determined by x-ray diffraction analyses of the <2- $\mu$ m fraction. X-ray diffraction was conducted on a Mg-saturated sample that was subjected to three sequential heat treatments (for mineral identification purposes): 16-h at 25 °C, 16-h at 65 °C, and then 16-h at 300 °C. Redox potential was measured using a platinum electrode that was tested before and after measurements were made in standard  $E_h$  buffers; all mV readings were corrected to the standard hydrogen electrode (SHE) by adding +210 mV (Sparks 1996).

A water sample was collected from a surface stream located in the wetland approximately 1 km upstream from the study site. The water was passed through a 0.45  $\mu$ m filter and stored at 4 °C. It was chemically characterized using standard laboratory methods. The surface water was acidic (pH of 5.1), had a low ionic strength (0.6 mM as calculated using vMINTEQA2, Version 2.15; Gustaffsson 2003), was dominated by Ca and  $\text{SO}_3^{2-}$ , and contained high dissolved organic C concentrations (6.1 mg  $\text{kg}^{-1}$ ).

## Desorption Study

The experiment included 24 samples: 3 replicates x 4 amendments (control/no amendment, Fe(0), apatite, and Fe(0) & apatite) x 2 moisture conditions (saturated and wet/dry-cycled). For the saturated treatments, 15 g of contaminated sediment, 0.5 g of appropriate amendment (1 g total for the Fe(0) and apatite treatment), and 25 mL of uncontaminated surface water were added to 50 mL centrifuge tubes. This corresponds to an amendment:sediment ratio of 0.032 (0.5g:15g) for treatments that received only one amendment and a ratio of 0.064 (1g:15g) when both amendments were added. The tubes were agitated on a platform shaker for 7 weeks before separating by centrifugation and 0.45- $\mu$ m filtration. The filtrates were preserved in 0.05% nitric

acid and analyzed for elemental concentration by ICP-MS and inductively coupled plasma – atomic emission spectrometry (ICP-AES). An unacidified sample was analyzed for dissolved organic and inorganic C with a carbon analyzer, which is based on pyrolysis and CO<sub>2</sub> infrared detection.

The wet/dry-cycled treatments were conducting in 12 disposable filtration units. These 150 mL polystyrene containers consisted of two chambers, separated by a 0.45- $\mu$ m cellulose nitrate membrane (Cole-Parmer Instrument Company, Vernon Hills, IL). Approximately 15 g of sediment with 0.5 g of amendment were mixed and then placed on the filter membrane. A weekly wetting followed by drying cycle was imposed on the samples. On a Friday, 25 mL of the uncontaminated surface water was added to the sediment, forming an approximate 1-cm deep layer over the sediment. The water remained above the filter until the following Monday, when it was vacuum suctioned through the filter. Once a day between Monday and Friday, the sediments were mixed with a spatula to facilitate sediment drying. Typically, the sediments were completely air dried by Wednesday. On the next Friday, the leachate in the lower chamber of the filtration unit was poured into a 25 mL graduated column and brought up to volume with the uncontaminated surface water. It typically required about 7 mL water to bring the volume to 25 mL. This 25 mL solution was then poured onto the amended sediment, starting another wetting cycle. This weekly wet/dry cycling was repeated seven times before terminating the experiment. On the day the experiment was terminated, pH, Eh, dissolved O<sub>2</sub>, and electrical conductivity (a measure of the total concentration of ions in solution) of the filtrate were measured. The solutions were then preserved and analyzed by an ICP-MS, ICP-AES, and carbon analyzer, as described above.

### **Aqueous Contaminant Charge Properties as Defined by Resin Sorption Studies and Equilibrium Speciation Modeling**

Resin sorption tests were conducted to provide insight into the charge properties of the contaminants in the leachate from the controls (unamended sediment) of the saturated treatment. The resins were used to operationally define a cationic, anionic, neutral and hydrophobic/organic fraction. Tests were conducted in triplicate and the ratio of resin to pore water was maintained at 0.03 g mL<sup>-1</sup>. The cation resin used was AG 50W-X8, H form (Bio-Rad Laboratories, Richland, CA). The anion resin used was AG2-X8, Cl form (Bio-Rad Laboratories). “Cationic” fraction was defined as the aqueous contaminant fraction that adsorbed to the cation resin. “Anionic” fraction was defined as the aqueous contaminant fraction adsorbed to the anion resin. “Neutral” fraction was defined as the aqueous contaminant fraction that did not adsorb to the mixture of cation and anion resins. Finally, the “hydrophobic/organic” fraction was defined as the aqueous contaminant fraction that partitioned to a C-18 (Rohm & Haas Co., Philadelphia, PA) or an XAD-8 resin (Rohm & Haas Co., Philadelphia, PA). This fraction would be expected to contain much of, but not the entire organically complexed contaminant fraction. Leachate was first passed through an XAD-8 resin column, and then mixed for 24 hr with a C-18 resin at a ratio of 0.03 g mL<sup>-1</sup>. The two resins have different hydrophobicities and were expected to remove slightly different organic matter fractions from the aqueous phase. The leachates from each resin contact were acidified to 0.05% nitric acid and then analyzed by ICP-MS.

### **Quantifying Contaminant Sorption to the Sediment as Defined by Selective Extractions**

At the end of the equilibration period, the amended sediments from the saturated treatments were subjected to a five-step sequential extraction procedure (modified method by Hall et al., 1995 and Miller et al. 1986). Briefly, 0.5g samples of the treated sediments were extracted by a series of solutions that targeted operationally defined contaminant fractions. The extracts were increasingly aggressive at removing contaminants. The five fractions were: 1) extractable (1.0M CH<sub>3</sub>COONa, pH 5); 2) readily reducible [0.25M (NH<sub>4</sub>)<sub>2</sub>OH·HCl in 0.25M HCl at 60°C for 30 min]; 3) less-readily reducible [1.0M (NH<sub>4</sub>)<sub>2</sub>OH·HCl in 25% CH<sub>3</sub>COOH at 90°C for 3 hr]; 4) oxidizable (30% H<sub>2</sub>O<sub>2</sub> pH 2 at 80°C for 2 hr); and 5) residual (total microwave digestion in 0.6 g solid + 10 mL HNO<sub>3</sub> + 4 mL H<sub>2</sub>SO<sub>4</sub> + 2 mL HCl). Between each extraction, the sediment was washed for 30 minutes with 0.01M CaCl<sub>2</sub>. The resulting extract solutions were characterized by ICP-MS. The amount of contaminant desorbed during the saturated and wet/dry-cycling equilibrium periods was added to the extractable fraction.

Desorption  $K_d$  values were operationally defined as:

$$K_d = \frac{C_{exch} + C_{readily\ reducible} + C_{oxid}}{C_{aq}} \quad (5)$$

where  $C$  represents concentration, and the subscripts *exch*, *readily reducible*, and *oxid*, represent the first exchangeable fraction, the second readily reducible fraction, and the fourth oxidizable fraction of the sequential extractions, respectively. The subscript *aq* represents the concentration in the aqueous phase collected from the saturated treatments at the end of the equilibration period. These fractions of the solid phase were selected because the  $K_d$  construct assumes a reversible reaction (adsorption rate is the same as the desorption rate) and these fractions most closely approach this condition. It is felt that the extremely strong reductant used to recover the fraction associated with the crystalline Fe-oxides, and the strong acids used to recover the fraction associated with the residual solids, exclude these fractions from reversible desorption.

The sequential extraction data was also used to calculate the Strongly Bound Fraction:

$$\text{Strongly Bound Fraction} = \left[ \frac{C_{less-readily\ reducible} + C_{residual}}{C_{exch} + C_{readily\ reducible} + C_{oxid} + C_{less-readily\ reducible} + C_{residual}} \right] \times 100 \quad (6)$$

where  $C$  represents concentration, and the subscripts *less-readily reducible* and *residual*, represent the third less-readily reducible fraction and the final residual fraction of the sequential extractions, respectively. This construct provides an estimate of the percentage of a contaminant in the contaminated sediment that was resistant to leaching, i.e., the contaminant fraction not likely to be part of the source term in subsequent risk modeling. This construct likely underestimates the actual effectiveness of the amendments to immobilize the contaminants because the laboratory experiments were conducted over a relatively short period, 49 days, thereby limiting the duration that the contaminants could desorb from the sediment and resorb onto or into the amendments. Stated differently, the contaminants that desorbed from the sediment did not likely have sufficient time to age with the amendments and transition to more strongly bound forms.

## RESULTS AND DISCUSSION

### Sediment, Apatite, and Fe(0) Characterization

The contaminated sediment did not differ greatly from a nearby background sediment, except of course, it contained high contaminant concentrations (Table 1). Both sediments had a loamy sand texture and near identical pH levels, cation exchange capacities, and mineralogy. Cerium, cobalt and lead concentrations were approximately an order of magnitude greater in the contaminated sediment than in the background sediment. The apatite had comparable Ce, Co, and Pb concentrations as the background sediment. The Fe(0) had appreciably higher Co, but lower Ce, and Pb concentrations than the background sediment. The potential introduction of Co to the study site through the addition of Fe(0) may require additional evaluation.

### Desorption Study

The general chemistry of the wet/dry-cycled and saturated treatments differed greatly (Table 2). Comparing the Controls, the wet/dry-cycled and saturated treatments had significantly different ( $p \leq 0.05$ ) Eh, pH, total organic carbon, Ca, and Fe concentrations. Not surprisingly, the Eh of the saturated control treatment was appreciably lower than the wet/dry control treatment. This difference, in turn, resulted in the well documented sediment response of increased pH, the result of  $e^-$  and  $H^+$  maintaining charge neutrality, and increased aqueous Fe concentrations, the result of Fe-oxyhydroxide reductive dissolution (Baas-Becking et al. 1960). Contaminant (and Ca and total organic C) concentrations were also higher in the saturated control samples, which is likely the result of greater water and sediment contact time, promoting contaminant desorption.

The influence of the amendments on contaminant retention by the solid phase was quite similar in the wet/dry-cycled and saturated treatments (Table 2). Generally, the differences between the treatment means were greater in the saturated systems because the range of contaminant concentrations were greater than in the wet/dry-cycled systems. In the wet/dry cycled treatments, the Fe(0) and the Fe(0) & apatite amendments significantly lowered leachate Ce and Co concentrations compared to the control (Table 2). All amendments significantly reduced Pb porewater concentrations compared to the control. In the saturated treatments, all three amendments significantly reduced Ce, Co, and Pb porewater concentrations with respect to the control leachate concentrations.

The speciation of contaminants is important because it directly affects the appropriate chemical method to employ for contaminant stabilization. For example, if a contaminant is strongly complexed to natural organic matter, it may not readily precipitate as a phosphate phase in a contaminated sediment system treated with apatite. Sorption studies were conducted with well characterized resins to provide insight into the charge properties of the contaminants. Thermodynamic equilibrium calculations were also conducted to provide additional insight. Based on the resin studies, 84% of the porewater Ce existed as a cation, 23% as an anion, 4% as a neutral species, and 6% as a hydrophobic/organic species (Table 3). The sum of these percentages is 127%, indicating that the resins did not sorb mutually exclusive fractions. This is not surprising, since, for example, many natural organic matter-metal complexes would be expected to sorb to the hydrophobic, cation, and anion resins. Similarly, a cation resin may adsorb anionic species, albeit very weakly. Thermodynamic equilibrium calculation results of

the porewater largely support the resin data, indicating that most of the Ce existed as cations ( $\text{CeOH}^{2+}$  and  $\text{CeCO}_3^+$ ) and anions [ $\text{Ce}(\text{CO}_3)_2^-$ ], and very little, if any, existed as neutral or hydrophobic/organic species (Table 3).

According to the resin data, most of the Co existed as cationic species, with appreciably less existing as neutral or hydrophobic/organic species (Table 3). Results from the equilibrium calculations were remarkably similar to those of the resin study. The equilibrium calculations indicated that the cationic species were  $\text{Co}^{2+}$ ,  $\text{CoOH}^+$ , and  $\text{CoH}(\text{CO}_3)^+$ , whereas the neutral species were  $\text{Co}(\text{OH})_2^0$  and  $\text{CaCO}_3^0$ . Also, a Co-dissolved organic matter (DOM) complex was predicted to form.

The sorption characteristics of Pb could not be measured in the resin studies because of interference and detection limit problems. The equilibrium calculations indicated that aqueous Pb existed almost exclusively as a Pb-DOM complex. This is consistent with the laboratory observations that Pb and DOM form exceptionally strong complexes (Stevenson 1976).

Saturation Index is a thermodynamic construct used to estimate the degree to which a particular compound exceeds saturation at equilibrium. It is the logarithmic ratio of the ion-activity products (*IAP*; the sum of each ion activity raised to the power of its mass balance stoichiometry) and the corresponding solubility constant ( $K_{sp}$ ):

$$\text{Saturation Index} = \log \frac{IAP}{K_{sp}} \quad (7)$$

If the saturation index for a particular mineral is negative, the system is undersaturated with respect to that mineral. If the index is positive, the solution is supersaturated with respect to that mineral and precipitation is theoretically expected to occur (provided the system is truly in equilibrium and not kinetically hindered). In the control saturated aqueous system, all minerals had negative saturation indices except  $\text{PbAl}(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$  (plumbgummite),  $\text{Ce}(\text{PO}_4)$ , and  $\text{Co}(\text{OH})_3$ , which had saturation indices of +1.83, +6.30 and +8.56, respectively. The first two positive values suggest that the system can not hold any more phosphate in solution, without precipitating Pb and Ce solid phases. Thus, the reason that no increase in solution P was measured in the apatite-amended system is because the P likely precipitated (and/or adsorbed) from solution (Table 2; saturated control sample). A second equilibrium calculation was conducted to estimate what phases may have precipitated out of solution once the P dissolved from the apatite entered into the aqueous phase. In this calculation, the P concentration,  $9.488 \text{ mg L}^{-1}$ , was based on a separate solubility measurement of P aqueous concentrations in a simple water and apatite system. This concentration provides a first approximation of the concentration that may have existed in the absence of the contaminated sediment and does not account for a number of competing reactions, such as P sediment adsorption. With the additional aqueous P included in the calculations, no new phases were identified as having positive saturation indices, instead the Saturation Indices increased for the already identified phases. The Saturated Index for  $\text{PbAl}(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$  (plumbgummite) increased to 3.33 and  $\text{Ce}(\text{PO}_4)$  increased to +7.147.

### Solid Phase Characterization

The objective of the sequential extraction measurements was to measure how desorption of Ce, Co, and Pb changed when apatite and Fe(0) was added. Sequential extraction methods have been criticized for their lack of selectivity, operational nature, and potential to create

experimental artifacts that fail to preserve the *in situ* chemistry of the sample (Nirel and Morel 1990; Scheckel et al. 2003). They have also been shown not to be suitable for some metals, including Pb in phosphate-amended sediments (Scheckel et al. 2003). In the contaminated sediment, almost 80 wt-% of the Ce existed in the two least-strongly bound fractions and only 17 wt-% of the Ce existed in the residual fraction (Fig. 1). This indicates that there is a large potential to increase the stability of the Ce through the use of amendments. Regarding the apatite source material, essentially all the Ce (93 wt-%) existed in the residual fraction. After adding apatite to the sediment, there were no significant ( $p \leq 0.05$ ,  $n = 2$ ) changes in the Ce fractionation. After adding Fe(0), the residual fraction significantly increased with respect to the control. This suggests that the Fe(0), but not the apatite, produced the desired affect of converting the Ce into a more strongly bound species. The mechanism by which the Fe(0) accomplished this is not know. Sediment Ce exists in its lowest redox state, +3, therefore reductive precipitation is not the mechanism. Perhaps the Ce coprecipitated to form the solid solution  $(\text{Fe}^{\text{III}}, \text{Ce}^{\text{III}})(\text{OH})_{3(s)}$  in an analogous manner as  $(\text{Fe}^{\text{III}}, \text{Cr}^{\text{III}})(\text{OH})_{3(s)}$  is formed (Sass and Rai 1987).

Cobalt concentrations in the apatite,  $781 \mu\text{g kg}^{-1}$ , were about the same as those in the background sediment,  $663 \mu\text{g kg}^{-1}$  (Table 1). In the sediment, only 35 wt-% of the Co existed in the residual fraction and 30 wt-% existed in the exchangeable or less-readily reducible fraction (Fig. 1). Thus, unlike Ce, there was appreciably less potential of affecting a positive transformation of the Co from weakly bound fractions to more strongly bound fractions. In the apatite source material, 60 wt-% Co existed in the residual fraction. Apatite and Fe(0) additions to the sediment produced similar shifts in Co distribution as was observed for Ce, namely, apatite promoted a shift from the readily reducible to the less-readily reducible fraction; Fe(0) additions promoted a shift from the reducible to the less-readily reducible and residual fractions. Again, the Fe(0), but not the apatite accomplished the desired shift in Co fractionation.

Lead concentration in the sediment and apatite were similar  $12.2$  and  $17.6 \text{ mg kg}^{-1}$ , respectively (Table 1). In the sediment, Pb was primarily in the residual (42 wt-%), readily reducible (26 wt-%), and exchangeable (20 wt-%) fractions (Fig. 1). This indicates that much of the lead is already strongly bound to the sediment and that the amendments may enhance stabilization of only about half of the Pb in sediment. In the apatite source material, most of the Pb (73 wt-%) was in the residual fraction. Upon adding apatite to the sediment, there was little change in the Pb desorption fractionation. There was no significant ( $p \leq 0.05$ ,  $n = 2$ ) difference in the residual fractions of the control and apatite amended samples. This is surprising in light of the strong evidence that in the presence of halides and apatite, Pb forms the sparingly soluble phase, pyromorphite  $(\text{Pb}_{10}(\text{PO}_4)_6\text{X}_2)$ , where X can be F, Cl, or Br (Ma et al. 1993, Cao et al. 2002); Ryan et al. 2001, Lower et al. 1998). Apparently, what little Pb that was sorbed from the porewater before or after desorption from the sediment, partitioned to the readily reducible fraction, but did not have sufficient time during the 49-day equilibration period to transition (“age”) into the residual fraction. Fe(0) additions by themselves or together with apatite did not produce the desired shift in Pb fractionation: exchangeable and residual fractions significantly ( $p \leq 0.05$ ) decreased, while the readily reducible fraction significantly increased with respect to the controls.

Equation 5 was used to calculate desorption  $K_d$  values (Fig. 2) using the data in Fig. 1 and the porewater contaminant concentrations reported in Table 2. In order to detect an increased  $K_d$  value in the amended treatments, the contaminant sorbed to the sediment must first desorb and then re-(ad)sorb either by precipitation or inner-sphere adsorption into the sediment amendment.

It is likely that steady state conditions implicitly assumed in the operation definition of  $K_d$  (Eq. 5) were not achieved during the 49 day study. Three reactions are known to be very slow, they are 1) reductive dissolution of Fe-oxyhydroxides, leading to the release of some sorbed contaminants (applicable to Fe(0) treatments; Vepraskas 1996), 2) diffusion of adsorbed contaminants into strongly sorbing (high energy) sites, leading to contaminant incorporation into the mineral structure through isomorphic substitution (applicable to apatite treatments), 3) desorption of polyvalent ions is generally a kinetically hindered reaction that often takes weeks to months to come to steady state (Stumm and Morgan 1996), and 4) formation of pyromorphite in an apatite amended sediment (Cao et al. 2002).  $K_d$  values based on a system that has not reached steady state would be lower than those based on a system that had reached steady state.

Cerium  $K_d$  values significantly ( $p \leq 0.05$ ) increased only when apatite and Fe(0) were added to the sediment. Cobalt and lead  $K_d$  values significantly increased only when Fe(0) was added, either alone or together with apatite. The increased  $K_d$  values indicate that more contaminant were bound to the solid phase.

Equation 6 was used to calculate the strongly bound or immobilized fraction (Fig. 3). There was no significant increase in the percent Ce in the strongly bound fraction upon the addition of any of the amendments. The addition of apatite significantly lowered the percent Co in the immobilize fraction. Conversely, the Fe(0) and the apatite & Fe(0) treatments significantly increased the percent Co in the immobilized fraction. Finally, the Fe(0) and the apatite & Fe(0) treatments significantly lowered the percent Co in the immobilized fraction. Perhaps the most important point of this data is that even though the amendments generally increase the capacity of the sediment to sorb the contaminants, i.e., their  $K_d$  values increased, they do not necessarily increase the proportion of the sorbed contaminant in the immobilized fraction. Again, this may in part be attributed to the relatively short duration of the study.

## CONCLUSIONS

The redox status and the general water chemistry of the wet/dry-cycled and saturated treatments varied greatly, yet the influence of the amendments on contaminant stabilization were quite similar; namely, apatite and Fe(0), added by themselves or together, significantly reduced aqueous Ce, Co and Pb concentrations. There were fewer significant differences in the wet/dry cycled treatments than in the saturated treatments because less desorption occurred in the former. One anticipated advantage of adding the two amendments, as compared to only one, was that it would provide more sequestering mechanisms to immobile the wide range of contaminants at the study site, >50 metals, metalloids, and radioisotopes. Furthermore, if both amendments immobilize the contaminants, than there would be two quite different mechanisms controlling contaminant desorption into the mobile aqueous phase. This would diminish the tendency of the amended sediments from releasing the contaminants all at one time in response to a drastic environmental change, such as a redox, saturation, or vegetation change induced by nature or man. Much of the potential groundwater risk (as compared, for example, to residential risk) imposed by a contaminant site is dictated by the maximum contaminant concentration released by the site. Having more than one stabilizing process acting on a contaminant in a sediment would increase the chance of a gradual and lower concentration contaminant release.

One of the objectives of this study was to produce geochemical input values for a model to evaluate risk reduction achieved through the use of these amendments.  $K_d$  values and the percent of strongly bound contaminant were estimated through the use of operationally defined selective

extraction tests.  $K_d$  values of the Fe(0) or Fe(0) & apatite, but not apatite alone, treatments were significantly increased compared to the unamended sediment. Although the amended sediments generally sorbed more contaminants than the unamended sediments, the contaminant fraction likely to enter the mobile phase, the source term in the risk model, occasionally increased. This seemingly contradictory result is likely the result of the newly bound contaminants sorbed to the amendments not having sufficient time to partition to the more strongly bound fractions (i.e., insufficient time for the contaminants to “age” with the solids). Based on theoretical considerations and empirical observations, it is anticipated that this weakly bound fraction will become more strongly bound as contact time increases (Ruby et al. 1994, Ryan et al. 2001, Cao et al. 2002, Byrne et al. 1996).

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## APPENDIX I. REFERENCES

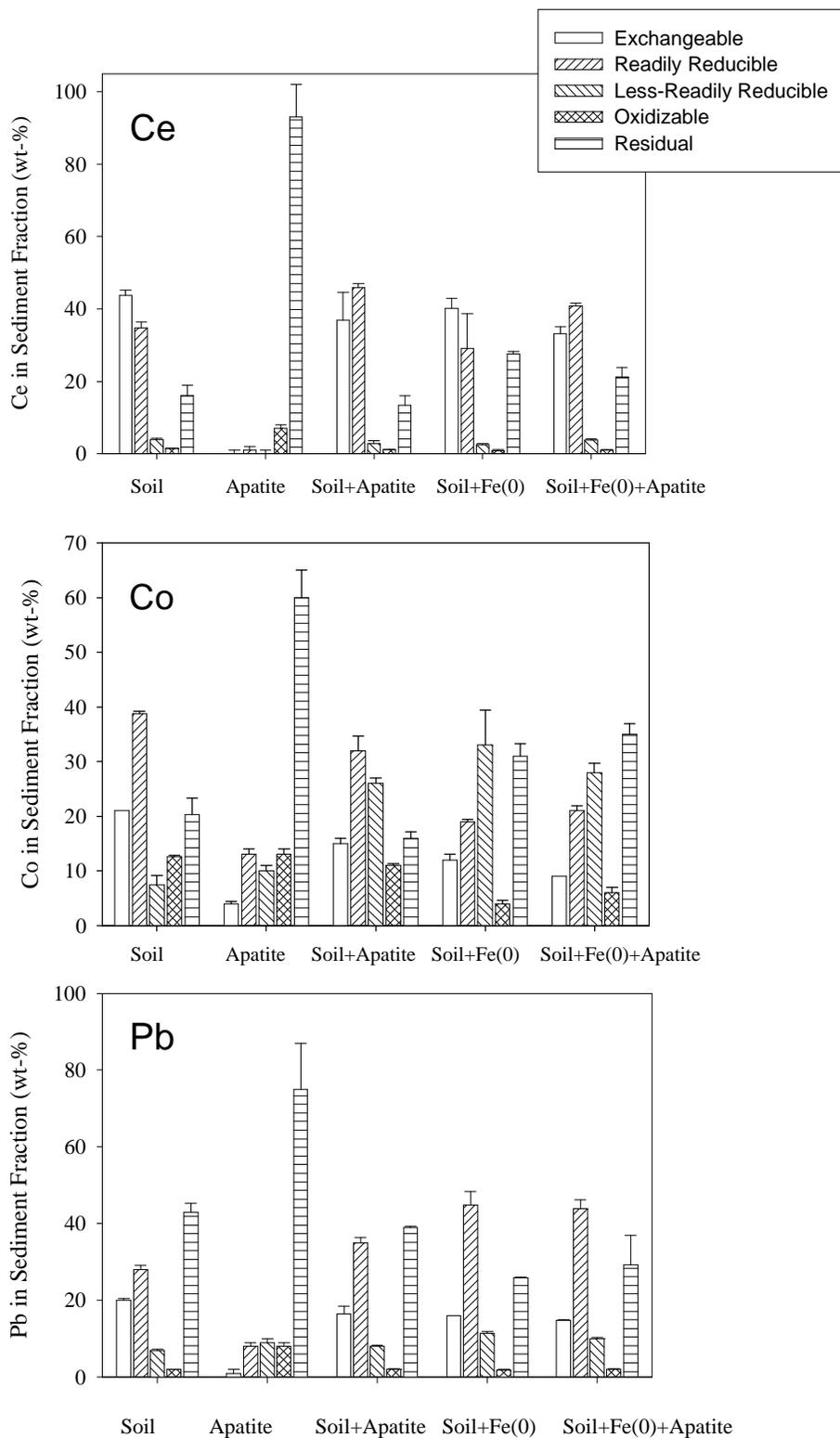
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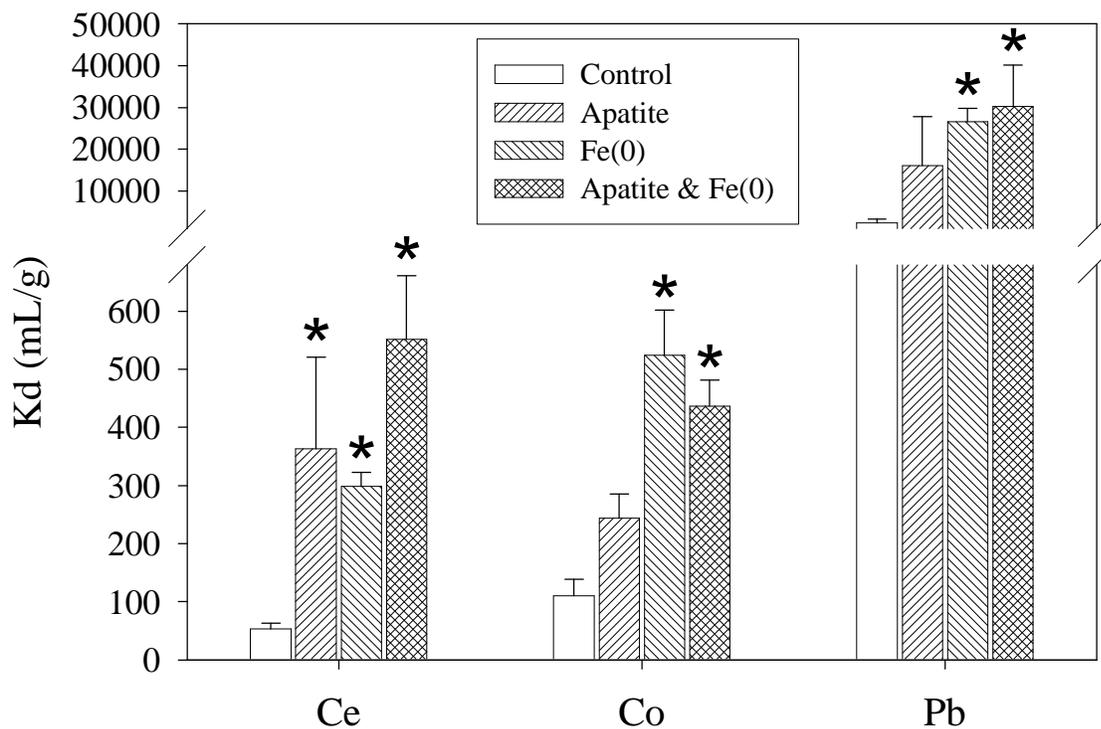
**APPENDIX II. NOTATION**

*The following symbols are used in this manuscript:*

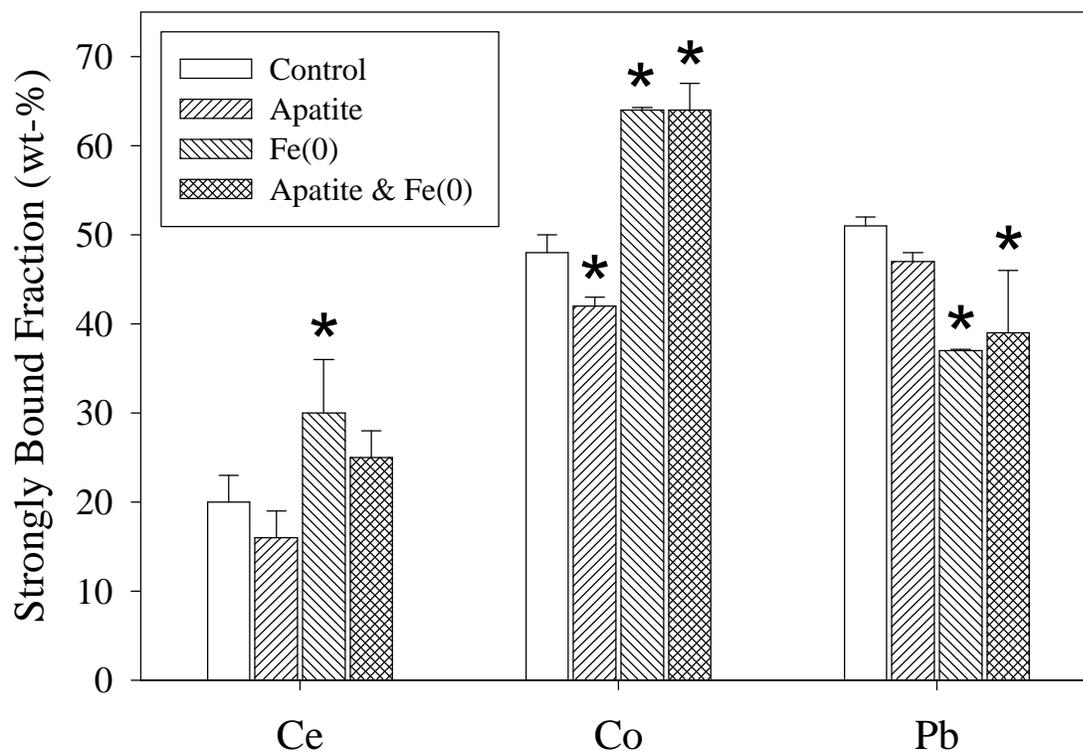
- $C_{exch}$  = contaminant concentration in the exchangeable fraction of the sequential extractions;
- $C_{readily\ reducible}$  = contaminant concentration in the amorphous Fe-oxide fraction of the sequential extractions;
- $C_{oxid}$  = contaminant concentration in the organic/sulfide fraction of the sequential extractions;
- $C_{less-readily\ reducible}$  = contaminant concentration in the crystalline Fe-oxide fraction of the sequential extractions;
- $C_{residual}$  = contaminant concentration in the residual fraction of the sequential extractions;
- $C_{aq}$  = contaminant concentration in the leachate of the flooded treatment;
- $K_d$  = distribution coefficient;
- $IAP$  = ion activity product; and
- $K_{sp}$  = solubility constant.



**Fig. 1. Sequential Extractions of Contaminated Sediment Amended with Apatite and Fe(0): Mean of Three Replicates from the Saturated Treatments.**



**Fig. 2. Influence of Amendments on Ce, Co, and Pb Distribution Coefficients (Kd values; Equation 1; \* = significant difference between the Control mean and the treatment mean according to Dunnett's Test for Comparing Means to a Control ( $p \leq 0.05$ ,  $n = 3$ )).**



**Fig. 3. Strongly Bound Fraction (Equation 2; \* = Significant Difference Between the Control Mean and the Treatment Mean According to Dunnett's Test for Comparing Means to a Control ( $p \leq 0.05$ ,  $n = 3$ )).**

**Table 1. Properties of Sediments and Amendments**

Parameter (1)	Units (2)	Background Wetland Sediment (3)	Contaminated Wetland Sediment (4)	Mined Apatite (5)	Fe(0) (6)
Ce	$\mu\text{g kg}^{-1}$	NA	4,850	NA	209
Co	$\mu\text{g kg}^{-1}$	663	3,664	897	3,459
Pb	$\mu\text{g kg}^{-1}$	12,191	35,338	17,644	1,292
pH		4.2	4.5	7.9	6.2
Sand-silt-clay	wt-%	80-14-6	82-13-5	98-2-0	99-1-0
Organic C	wt-%	0.140	0.143	<0.2	<0.2
C.E.C. <sup>a</sup>	$\text{cmol}_{(+)} \text{kg}^{-1}$	4.8	7.3	NA	NA
Mineralogy <sup>b</sup>		$\text{K}^1\text{H}^1\text{G}^3\text{Q}^2$	$\text{K}^1\text{H}^1\text{G}^3\text{Q}^2$	Quartz, Carbonate- hydroxyapatite	Amorphous

<sup>a</sup> C.E.C. = cation exchange capacity; NA = not available.

<sup>b</sup> Relative amounts as determined by x-ray diffraction of <2 $\mu\text{m}$  fraction of kaolinite (K), hydroxyl-interlayered vermiculite (H), gibbsite (G), and quartz (Q), ranging from most (1) to least (4) abundant.

**Table 2. Aqueous Chemical Properties from Sediments Treated with Apatite and Fe(0)**

Experiment <sup>a</sup> (1)	Amendment (2)	Eh – SHE (mV) (3)	pH (4)	TIC (mg L <sup>-1</sup> ) (5)	TOC (mg L <sup>-1</sup> ) (6)	Ca (mg L <sup>-1</sup> ) (7)	P (mg L <sup>-1</sup> ) (8)	Fe (mg L <sup>-1</sup> ) (9)	Ce (µg L <sup>-1</sup> ) (10)	Co (µg L <sup>-1</sup> ) (11)	Pb (µg L <sup>-1</sup> ) (12)
Wet/Dry	Control	497 a <sup>b</sup>	4.46 b	9.83 a	118 b	4.02 b	0.45 b	4.11 b	17.53 b	8.70 b	1.78 b
	Apatite	424*	5.20*	10.19	228*	39.35*	1.00*	1.20*	13.88	4.19	0.86*
	Fe(0)	440	5.29*	10.51	115	2.27	0.45	1.26*	2.94*	2.46*	0.57*
	Apatite&Fe(0)	403*	5.67*	10.19	143	15.90	0.64	1.34*	3.58*	0.97*	0.87*
Saturated	Control	65 b	5.79 a	11.61 a	240 a	12.44 a	1.42 a	177.1 a	49.43 a	20.69 a	7.39 a
	Apatite	34*	6.63*	12.83	166*	75.51*	1.23	118.0*	9.60*	9.53*	1.47*
	Fe(0)	37*	6.29*	10.41	254	15.08	1.34	171.8	10.22*	6.22*	0.76*
	Apatite&Fe(0)	24*	6.69*	10.80	248	63.72	1.22	125.8*	5.43*	6.96*	0.67*

<sup>a</sup> “Wet/Dry” is the last (seventh) leachate recovered from the sediments that received the weekly wet/dry cycled treatment.

“Saturated” is the final equilibrated solution recovered from the saturated treatment after 70-days.

<sup>b</sup> Control means within a column sharing the same letter do not differ significantly according to Student’s two-tailed *t*-test ( $p \leq 0.05$ ,  $n = 3$ ).

\* = a significant difference between the Control mean and the treatment mean within an experiment according to Dunnett’s Test for Comparing Means to a Control ( $p \leq 0.05$ ,  $n = 3$ ).

**Table 3. Ce and Co Charge Properties as Defined by Resin Sorption Tests and Equilibrium Calculations: Saturated Control Leachate**

Solute Charge (1)	Resin <sup>a</sup>				Computed <sup>c</sup>					
	Operational Definition (2)	Ce (wt-%) (3)	Co (wt-%) (4)	Pb <sup>b</sup> (wt-%) (5)	Ce		Co		Pb	
					(wt-%) (6)	Dominant Species (7)	(wt-%) (8)	Dominant Species (9)	(wt-%) (10)	Dominant Species (11)
Cationic	Adsorbed to a cation resin	94 ± 0.3	93 ± 0.9	BD	57	CeOH <sup>2+</sup> , CeCO <sub>3</sub> <sup>+</sup>	77	Co <sup>2+</sup> , CoOH <sup>+</sup> , CoH(CO <sub>3</sub> ) <sup>+</sup>	0	
Anionic	Adsorbed to an anion resin	23 ± 2.5	0 ± 5.3	BD	44	Ce(CO <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	0	None	0	
Neutral	Did not adsorb to cation or anion resin	4 ± 0.6	8 ± 0.7	BD	0	None	14	Co(OH) <sub>2</sub> <sup>0</sup> , CoCO <sub>3</sub> <sup>0</sup>	0	
Hydrophobic/ Organic	Partitioned to C-18 or XAD-8 resins	6	7	BD	0	None	9	Co-DOM	100	Pb-DOM
Total		127 ± 3	108 ± 6		100		100		100	

<sup>a</sup> All resin tests were conducted in triplicate, except the Hydrophobic/Organic test, which was not replicated.

<sup>b</sup> Pb concentrations from the resin sorption study were below detection limit.

<sup>c</sup> Calculated speciation using Visual MINTEQA2 (Version 2.15) (Gustafsson 2003). The Gaussian Ce-DOM log K was estimated to be 5.2 ± 1. The Gaussian Co-DOM log K was estimated to be 3.5 with a range of ± 0.5. All other thermodynamic equilibrium constants were those included in the Visual MINTEQA2 database.