Paper 2H-13, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002.* Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2002). ISBN 1-57477-132-9, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

REMEDIATION OF METAL-CONTAMINATED SOIL AND GROUNDWATER USING APATITE

Leah J. Matheson, Ph.D. (leahm@mse-ta.com), William C. Goldberg, P.E., and
Gordon J. Huddleston (MSE Technology Applications, Inc., Butte, MT)
William D. Bostick, Ph.D. (Materials and Chemistry Laboratory, Inc., Oak Ridge, TN)

ABSTRACT: Batch and column studies have been performed by MSE to determine the efficacy of metal cation removal from aqueous solutions by an organic apatite material. Our results have shown that the Apatite II™ media rapidly removes uranium (C_0=5mg/L) from solution to below detection levels, and moderately removes cadmium. The mechanism of uranium removal appears to be by reprecipitation as the uranium phosphate autunite. Cadmium removal appears to be via several mechanisms including adsorption and phosphate mineral precipitation. Currently, a soil-mixing study is being carried out to test immobilization of metal cations in contaminated soils.

INTRODUCTION

For several years MSE Technology Applications, Inc. has studied the material ApatiteII™ (Patent Number 6,217.775; PIMS NW, Inc.; Drs James Conca and Judith Wright, developers) for the removal of metals, metalloids and radionuclides. Apatite II™ is a form of apatite that appears to have higher reactivity than natural apatite and is lower cost than commercially available bone char. To date our work has shown that ApatiteII™ is very effective in removing uranium. Several mechanisms for uranium removal by apatite are possible: uranium exchange for the calcium anions in the apatite matrix, nonspecific adsorption to the apatite material, or the dissolution of apatite will create conditions at the boundary layer that exceed the K_{sp} for autunite ($Ca(UO_2)_2(PO_4)_2 \bullet 10H_2O$) and this U-bearing crystalline phase will form. Laboratory batch studies by Bostick et al (1999) have observed the presence of meta-autunite ($Ca(UO_2)_2(PO_4)_2 \bullet 6H_2O$) within the apatite material, suggesting the formation of autunite. Meta-autunite formation was due to the drying step before analysis by X-ray Powder Diffraction.

Additionally, we have investigated the removal of soluble cadmium from synthetic and authentic contaminated groundwater. Cadmium removal by apatite is probably due to one or all of three mechanisms: ion exchange, nonspecific adsorption, and precipitation of cadmium phosphate minerals. Previous studies (Chen et al., 1997) have observed a cadmium phosphate mineral, otavite. However, the removal of cadmium only occurs at about 5 wt.% of the apatite added, as opposed to 10 to 20 wt.% in the case of uranium and lead.

Our initial studies with this material showed that uranium was rapidly removed from solution in batch shake flasks. Bacterial growth was associated with the incubation of this material at room temperature however, sterilized controls vs. unsterilized flasks did not show significant difference in the rate of uranium uptake by the apatite. Subsequently, batch studies were undertaken to determine whether surface area had an effect on uranium removal. Previous studies had used a very fine (surface area = 2.75 m^2/g) powdered apatite that would not be as easily implemented in a canister or barrier situation in the field. Various crushed sizes were tested and it was shown that for the range tested (0.425 to 4.75 mm) there was no significant difference in the rate of uranium uptake.

The object of these studies was to follow up the batch studies with column studies to determine if the apatite material could be used in permeable reactive barrier systems or canister type configurations for removal of uranium and cadmium from contaminated groundwater. Most recently we have begun studies to determine if apatite can be added in a soil-mixing scenario to remove metals from contaminated soils.

MATERIALS AND METHODS

Low Ionic Strength Column Study. This experiment consisted of four column arrays, each containing 3 columns operated in series (Figure 1). Each of the columns was constructed of clear PVC with a 2 in. OD and 18 in. length. The columns were capped with PVC cleanout fittings that were plumbed to the column series with silicon tubing. Each column was packed with Denstone™ balls on either end of an apatite/sand center "zone" approximately 10 cm long (Figure 2). The Denstone™ was used to create an even plug flow prior to meeting the apatite zone within the columns. ApatiteII™ was sieved to retain the 10 X 18 size fraction for use in the apatite zone. The apatite strengths used were 5, 10 and 100 percent by weight in silica sand. Column array 1 contained three columns in order of 0% apatite (silica sand and Denstone™), 100 wt.% apatite (no sand) and 100 wt.% apatite from influent to effluent end, respectively.

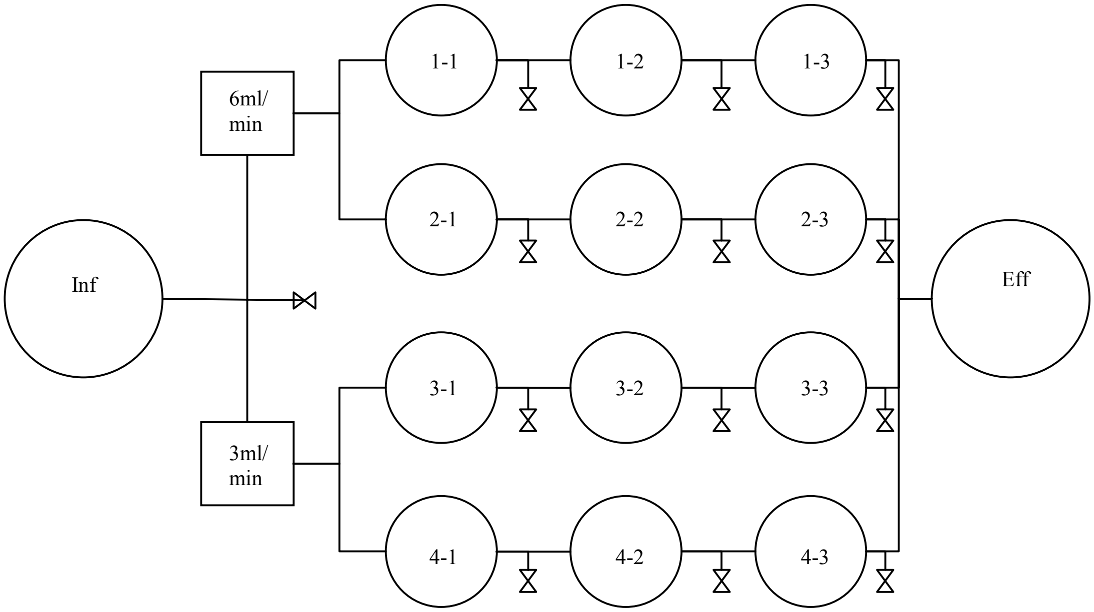

FIGURE 1. Column array diagram. Arrays are designated as 1 through 4 from top of diagram to bottom. Columns are numbered 1 through 3 from left to right. Flow is from left to right. Array 1: column 1-1=100% sand, 1-2=100% apatite, 1-3=100% apatite; Array 2: columns 2-1 through 2-3=10% apatite; Array 3: columns 3-1 through 3-3=10% apatite; Array 4: columns 4-1 through 4-3=5% apatite.

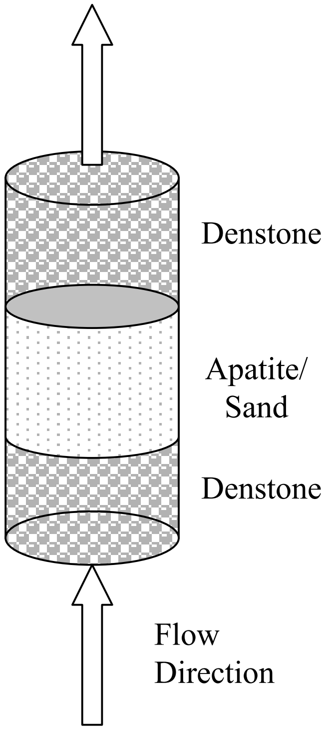

FIGURE 2. Schematic of individual column. Denstone™ is and inert ceramic material; ApatiteII™ was added as a weight percent in silica sand mixture. The apatite zone was approximately 4 inches long; total column length was approx. 18 in.

The sand-only column served as a control for uranium removal by sand and/or Denstone™. Column array 2 and column array 3 each consisted of three columns, all packed identically with 10 wt.% apatite. Column array 4 consisted of three columns each packed with 5 wt.% apatite. Arrays 1 and 2 were fed 5 mg/L uranium (as uranyl nitrate in dI water) at 6 ml/min., and arrays 3 & 4 were fed 5 mg/L uranium at 3 ml/min. Sample ports were located downstream of each column and unfiltered samples were analyzed for total uranium by ICP-MS. When the column study was terminated samples were removed from the columns in sections, dried, packaged and sent for mineralogical analyses including XRD, SEM-EDS, TCLP, and X-ray Fluorescence.

High Ionic Strength Column Studies. These experiments consisted of three column arrays, with individual columns (as described above, Figure 2) operated in series similar to those shown in Figure 1. The apatite strengths used in these experiments varied from 10% to 50% by weight in sand. The first set of column experiments were designated "non-SPLP" and were fed a synthetic groundwater medium (Table 1) at 6 ml/min that was spiked with 5mg/L uranium (as uranyl nitrate). A second column array (designated "SPLP") was fed the high ionic strength uranium-containing medium for 45 days and then the Synthetically Prepared Leachate Procedure (SPLP) was initiated. The purpose of this procedure is to determine if the contaminant, once sorbed, can be desorbed by the acid leachate under longer leaching durations, simulating acid rain conditions. As in the low ionic strength studies, the columns were sectioned, dried and sent for mineralogical analyses. A third column array was fed the high ionic strength medium spiked with 5 mg/L cadmium (as cadmium chloride).

TABLE 1. Supplement to Butte, MT tapwater for high ionic strength synthetic column feed.

Supplement	Concentration (g/L)
$Ca(NO_3)_2{\cdot}4H_2O$	5.0
$Mg(NO_3)_2{\cdot}6H_2O$	4.2
$NaNO_3$	0.85
NaCl	0.43
$Na(SO_4){\cdot}7H_2O$	0.21
$NaHCO_3$	0.03

Lower Ionic Strength Column Study. Another column study was performed with lower ionic strength feed and cadmium. This consisted of the Butte, MT tapwater spiked with 1 mg/L cadmium. The column array consisted of two columns in series loaded as before with an apatite strength of 50% by weight.

RESULTS AND DISCUSSION

Low Ionic Strength Column Studies. The four column arrays in this study operated for three months, treating a total of 2400 L of 5mg/L uranium (Figure 3). Individually, the 6ml/min columns treated approximately 1500 pore volumes and the 3ml/min columns treated 750 pore volumes. Column arrays 1 through 3 were shut off after 92 days. During this time >99% uranium was removed by the first apatite-containing column of each array. Operation of column array 4 continued until uranium breakthrough was observed after the first column (Figure 3; Array 4, port 1). This array removed uranium at greater than 90% for 4 months by the 5% apatite/sand mixture, before breakthrough began. No breakthrough was observed in the higher percentage apatite columns and the higher uranium feed rates. The pH of the unbuffered influent was ca. 4 and increased to ca. 7 after the first apatite column. Bacterial activity was indicated by biopolymer (slime) at the upstream interface of the apatite/sand material of the first apatite columns. No significant slime layers were observed in any of the apatite zones of the subsequent columns in each array. The heaviest biopolymer was observed in the 100% apatite column. No plugging occurred that could be directly attributed to the slime layers. Uranium removal is not attributed to biological activity based on our previous laboratory batch studies with sterilized and unsterilized systems (not shown). Mineralogical analyses showed that uranium was precipitated as the stable uranium phosphate mineral autunite (XRD, not shown). SEM-EDS images show large amounts of uranium precipitate (Figure 4). An SEM-EDS image from the high ionic strength column studies reported below (Figure 5) is very similar to the crystalline uranium-rich images from low ionic strength columns. It shows uranium-rich plate-like crystalline structures similar to autunite. TCLP analyses revealed that uranium precipitant was stable since no uranium was desorbed during this assay.

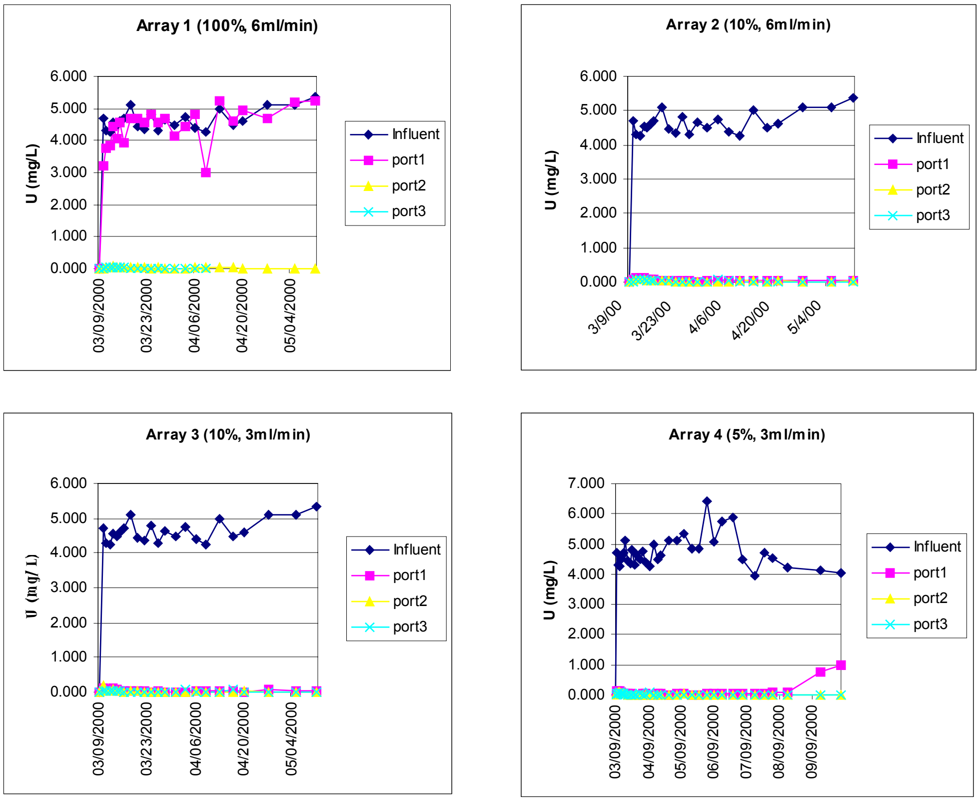

FIGURE 3. Uranium data for the four low ionic strength column arrays. Uranium is measured as total U in unfiltered samples by ICP-MS. Port 1 of Array 1 is located after the control, 100% sand/0% apatite column.

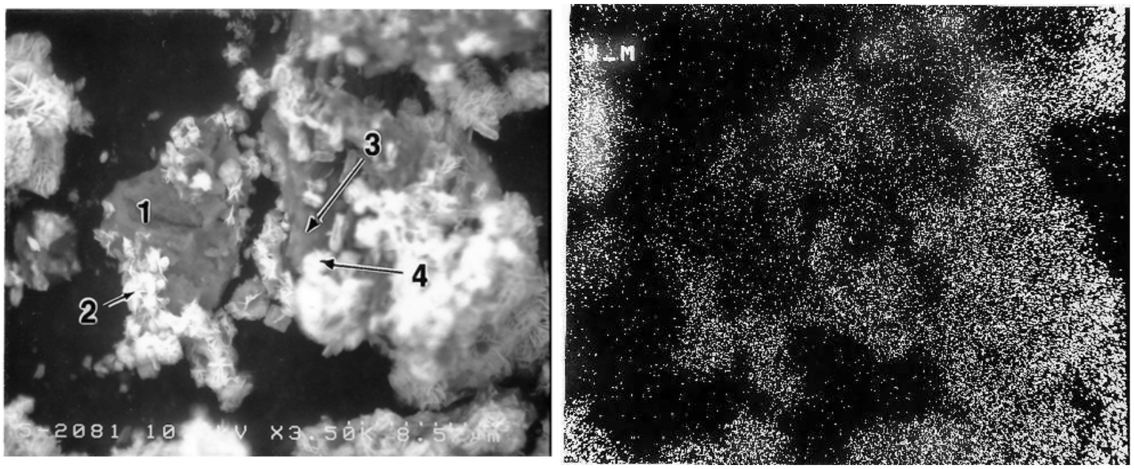

FIGURE 4. Left: SEM-BES image of apatite region of the low ionic strength column study Array 1, Column 2 (c.f. Figure 1, column 1-2). Brighter images reflect higher density of heavy atoms (e.g. uranium). Numbered arrows point to selected spots at which elemental composition was determined. Right: Relative uranium distribution (element-selective "dot-map" image) for the same sample.

FIGURE 5. Examination of a uranium-rich area on an apatite grain from the high ionic strength column

High Ionic Strength Columns. Flow to the column studies was shut off after they had operated for 4 months. The arrays treated a total of 3g of either uranium or cadmium. The results of the uranium SPLP column study are shown in Figure 6. The non-SPLP uranium column results are not shown but are similar to the uranium-SPLP results. The uranium and cadmium influent concentrations were doubled after 15 days because the concentrations of these elements were initially added at half the desired strength in error. The influent pH values were ca. 5.5 and effluent pH values were ca. 7. Both uranium column arrays were effective in removing uranium under the high ionic strength conditions. An average of 99% of the uranium concentration was removed before breakthrough occurred after approximately 70 days in the non-SPLP columns. In the SPLP-uranium array, no uranium was leached off the columns after switching the high ionic strength influent to the SPLP solution. Uranium was detected in the apatite section of the first 10 wt.% non-SPLP column and by SEM-EDS was found to contain uranium in plate-like crystalline structures characteristic of autunite (Figure 5). However, autunite was not confirmed by XRD. The SPLP column material was also analyzed by SEM-EDS and found to contain uranium. By XRD a good pattern match for sodium autunite was observed but sodium was not found in the SEM. It is possible that the sodium component of this form of autunite is too low to be detected by SEM. Cadmium was not removed as well as uranium by the apatite in the high ionic strength study (not shown). Breakthrough of cadmium was seen from the outset with less than 50% cadmium removal after the first 10% apatite column. The second column, containing 50% apatite, removed the cadmium breaking through the first column (about 0.75 mg/L) for about 18 days. Subsequently the influent concentration was increased and breakthrough after both columns increased accordingly. The results of the mineralogical analyses showed that 1% cadmium by apatite weight was found on the apatite material from the first 10 wt.% apatite column in the array. It is not known if this is a cadmium phosphate mineral precipitate (e.g. otavite) since it is in an amorphous form and cannot be identified by XRD.

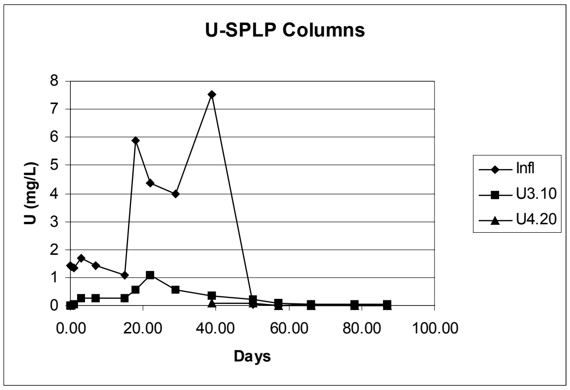

FIGURE 6. Aqueous phase total U concentrations in the uranium high ionic strength SPLP columns. Symbols: Diamonds=Influent total U concentration in mg/L; Squares=total U concentrations after the first 10 wt.% apatite column; Triangles=total U concentrations after the second 20 wt.% apatite column in series. Note: high ionic strength uranium influent replaced with SPLP solution at 45 days.

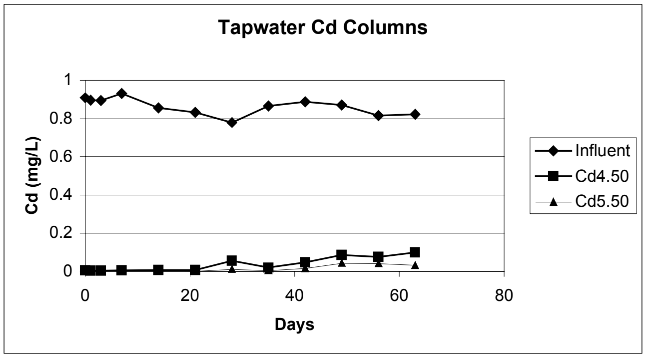

FIGURE 7. Aqueous total cadmium concentrations in mg/L for the low ionic strength column studies. Symbols: Diamonds=Influent total cadmium concentrations; Squares=total cadmium concentrations after the first 50 wt.% apatite column; Triangles=total cadmium concentrations after the second 50 wt.% apatite column in the series.

Lower Ionic Strength Columns. Due to the breakthrough observed in the high ionic strength experiment the lower ionic strength cadmium columns were initiated. The results are shown in Figure 7. Cadmium was removed in these tapwater based experiments at a much greater extent than the high ionic strength array. These results show that the removal mechanism for cadmium appears to be adsorption, either nonspecific or ion exchange, and that competing ions can prevent adsorption of cadmium. With the number of competing ions removed in the lower ionic strength experiment, cadmium was removed to a much greater degree. Cadmium breakthrough did begin to occur in these experiments but to a much lesser degree and at a much more gradual rate than under high ionic strength conditions. It appears that the cadmium breaking through the first 50 wt.% apatite column also broke through the second 50 wt.% apatite column in the series. This result indicates that this cadmium may have been in a very mobile form that was not labile to adsorption by the apatite.

CONCLUSIONS

The column studies reported here show that ApatiteII™ is an effective agent for the removal of uranium from contaminated groundwater. The uranium forms a stable phosphate mineral, autunite, in the presence of this material. However, cadmium removal by this material may be less effective since it is apparently due to adsorption/ion exchange mechanisms. A pilot-scale apatite field reactor was installed at the Y-12 plant site in Oak Ridge, TN to investigate cadmium and uranium removal. The reactor operated for approximately one year but was hampered by equipment complications and changes in the site water geochemistry. Currently we are testing the apatite material for use in soil mixing applications at metal contaminated sites.

ACKNOWLEDGMENTS

Work was conducted through the DOE National Energy Technology Laboratory at the Western Environmental Technology Office under DOE Contract Number DE-AC22-96EW96405.

REFERENCES

Bostick, W.D., R.J. Stevenson, R.J. Jarabek, and J.L. Conca. 1999. “Use of Apatite and Bone Char for the Removal of Soluble Radionuclides in Authentic and Simulated DOE Groundwater.” *Advances in Environmental Research*. 3(4):488-498.

Chen, X.-B., J. V. Wright, J. L. Conca, and L. M. Peurrung, 1997. “Evaluation of Heavy Metal Remediation Using Mineral Apatite”, *Water, Air and Soil Pollution,* vol. 98, p. 57-78.

Conca, J. L. 1997, “Phosphate-Induced Metal Stabilization (PIMS),” *Final Report to the U.S. Environmental Protection Agency*, #68D60023.