

**Assessment of a Hydroxyapatite Permeable Reactive Barrier to  
Remediate Uranium at the Old Rifle Site, Colorado – 16193**

SAND2016-0995C

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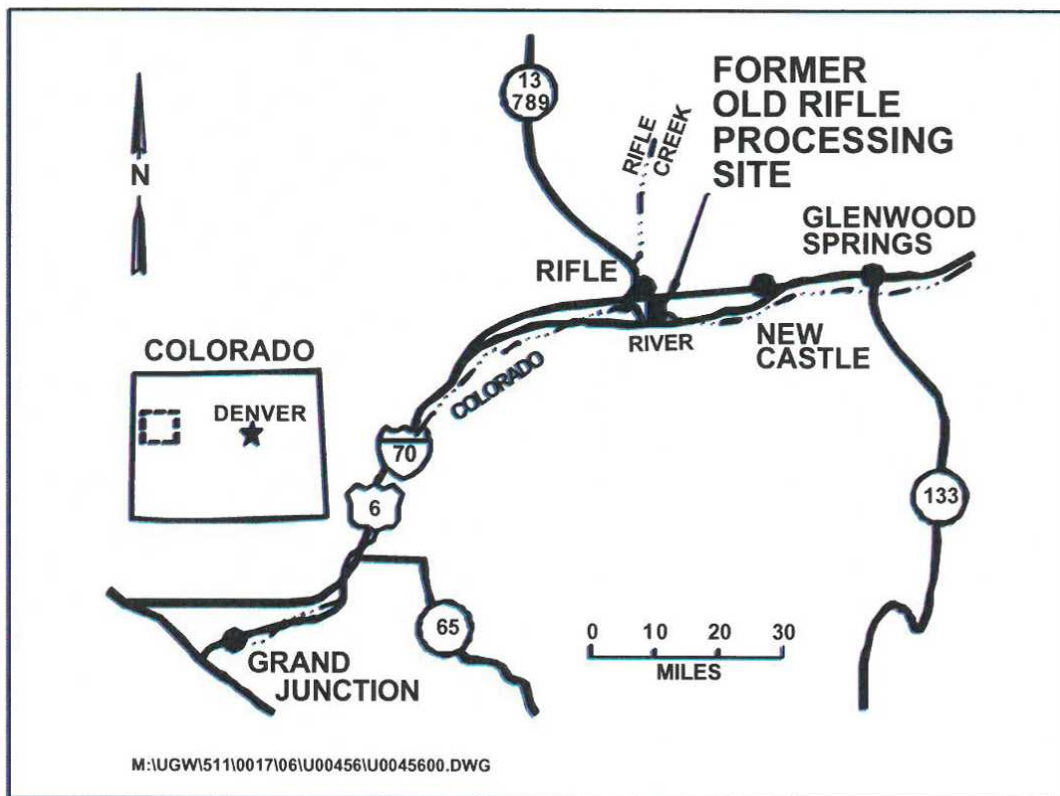
## **ABSTRACT**

We have performed an initial evaluation and testing program to assess the effectiveness of a hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) permeable reactive barrier and source area treatment to decrease uranium mobility at the Department of Energy (DOE) former Old Rifle uranium mill processing site in Rifle, western Colorado. Uranium ore was processed at the site from the 1940s to the 1970s. The mill facilities at the site as well as the uranium mill tailings previously stored there have all been removed. Groundwater in the alluvial aquifer beneath the site still contains elevated concentrations of uranium and is currently used for field tests to study uranium behavior in groundwater and investigate potential uranium remediation technologies. The technology investigated in this work is based on *in situ* formation of apatite in sediment to create a subsurface apatite PRB and also for source area treatment. The process is based on injecting a solution containing calcium citrate and sodium into the subsurface for constructing the PRB within the uranium plume. As the indigenous sediment micro-organisms biodegrade the injected citrate, the calcium is released and reacts with the phosphate to form hydroxyapatite (precipitate). This paper reports on proof-of-principle column tests with Old Rifle sediment and synthetic groundwater.

## **INTRODUCTION**

This paper reports on the evaluation of the performance potential of hydroxyapatite permeable reactive barriers (PRB) and source area treatments (SAT) deployment for uranium immobilization at the DOE Old Rifle Site. This project is a collaborative effort between Sandia National Laboratories (SNL), Pacific Northwest National Laboratory (PNNL) and URS Professional Solutions LLC (an affiliate of AECOM). Proof-of-principle experiments have been initiated in FY15 and if successful, deployment of the barrier will begin in FY16.

The Old Rifle Site, located in western Colorado (Figure 1) near to the town of Rifle and adjacent to the Colorado River, was once a vanadium and uranium ore-processing facility that operated from the 1940s through the 1970s. All the facilities for ore processing have been demolished and the uranium mill tailings stored at the site have been moved to a disposal cell. The groundwater beneath Old Rifle site is contaminated with low levels of uranium and is now a monitored natural attenuation site. In addition it is used for small-scale field testing of technologies for remediation of uranium-contaminated soil, sediments and groundwater.

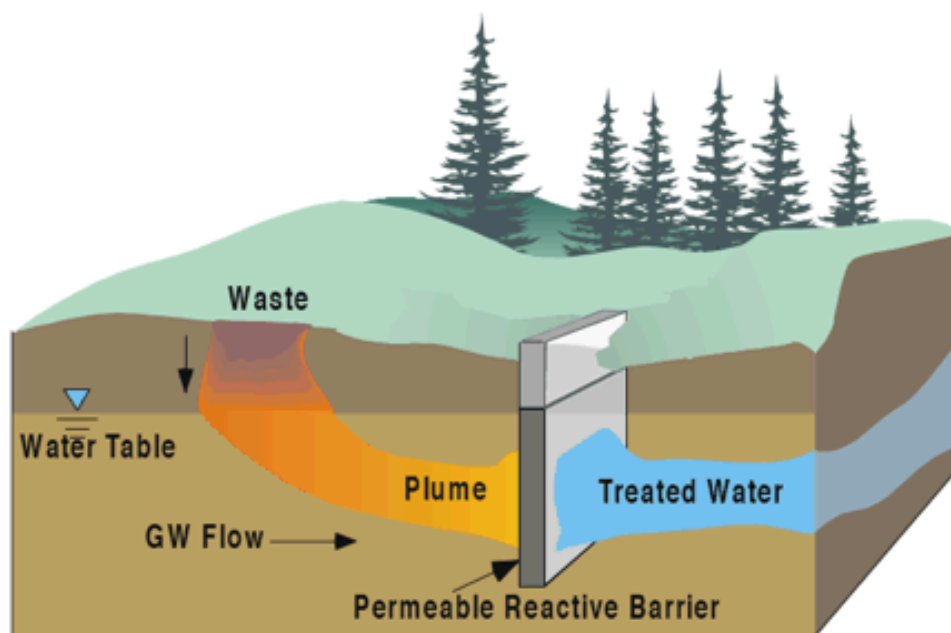


**Figure 1. Location of the Old Rifle Site in Colorado. (U.S. DOE, 1999)**

Calcium apatite or hydroxyapatite,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , is a common calcium phosphate mineral very similar to the material that makes up bone and teeth. Apatites and hydroxyapatite are mined as phosphate ore for fertilizer production of feed stock for the preparation of other chemicals. These minerals are very stable under most environmental conditions and highly insoluble in water. Apatite is host to many substitutions by cations, anions and anionic radicals that resemble its normal constituents in size and charge (McConnell, 1938). For example, the hydroxyl group in hydroxyapatite can be replaced by fluorine or chlorine through ion exchange. Minor to major amounts of Ba, Cd, Co, Cu, Fe, Mn, Mg, Ni, Pb, Sn, Sr, and Zn are known to replace calcium (Palache et al., 1951; Hughes and Rakovan, 2015). Oxyanions of carbon, including carbonate ( $\text{CO}_3^{2-}$ ), sulfur including sulfate ( $\text{SO}_4^{2-}$ ), vanadium including vanadate ( $\text{VO}_4^{3-}$ ), arsenic including arsenate ( $\text{AsO}_4^{3-}$ ), selenium including selenite ( $\text{SeO}_3^{2-}$ ), and to a lesser extent selenate ( $\text{SeO}_4^{2-}$ ), iodine including iodate ( $\text{IO}_3^-$ ), and technetium including pertechnetate ( $\text{TcO}_4^-$ ) can sorb and potentially even replace orthophosphate ( $\text{PO}_4^{3-}$ ) in the apatite structure (Palache et al., 1951; Narasaraaju and Phebe 1996; Moore et al., 2002; Duc et al., 2003; Bostick, 2003; Czerniczyniec, 2007; Lee et al., 2009; Lee, 2010; Campayo et al., 2011). The mechanisms of sorption of contaminants by apatite depends on the specific contaminant, its chemical form and oxidation state, chemical conditions of the

surroundings including pH and the presence of competing ions, and the morphology, surface area, and chemical composition of the apatite used.

Remarkably, there is a cornucopia of possible substitutions, in fact more than half the elements that occur as long-lived isotopes can be incorporated into the apatite structure (Hughes and Rakovan, 2015). Furthermore, a number of radioactive elements that lack stable isotopes such as U, Pu, Am, and Tc have also been shown to strongly sorb or incorporate into the apatite structure (Moore et al. 2002). Because apatite can incorporate such a large number of substituents the potential uses for apatite in environmental remediation are very broad (Rakovan and Pasteris, 2015). Apatite can potentially be used for both *ex situ* (as a sorbent for pump and treat systems) and *in situ* (as a permeable reactive barrier or source area treatment) engineered remediation systems. The current study focuses on the deployment of apatite PRB and SAT for the *in situ* remediation and immobilization of uranium in the subsurface at the Old Rifle site.

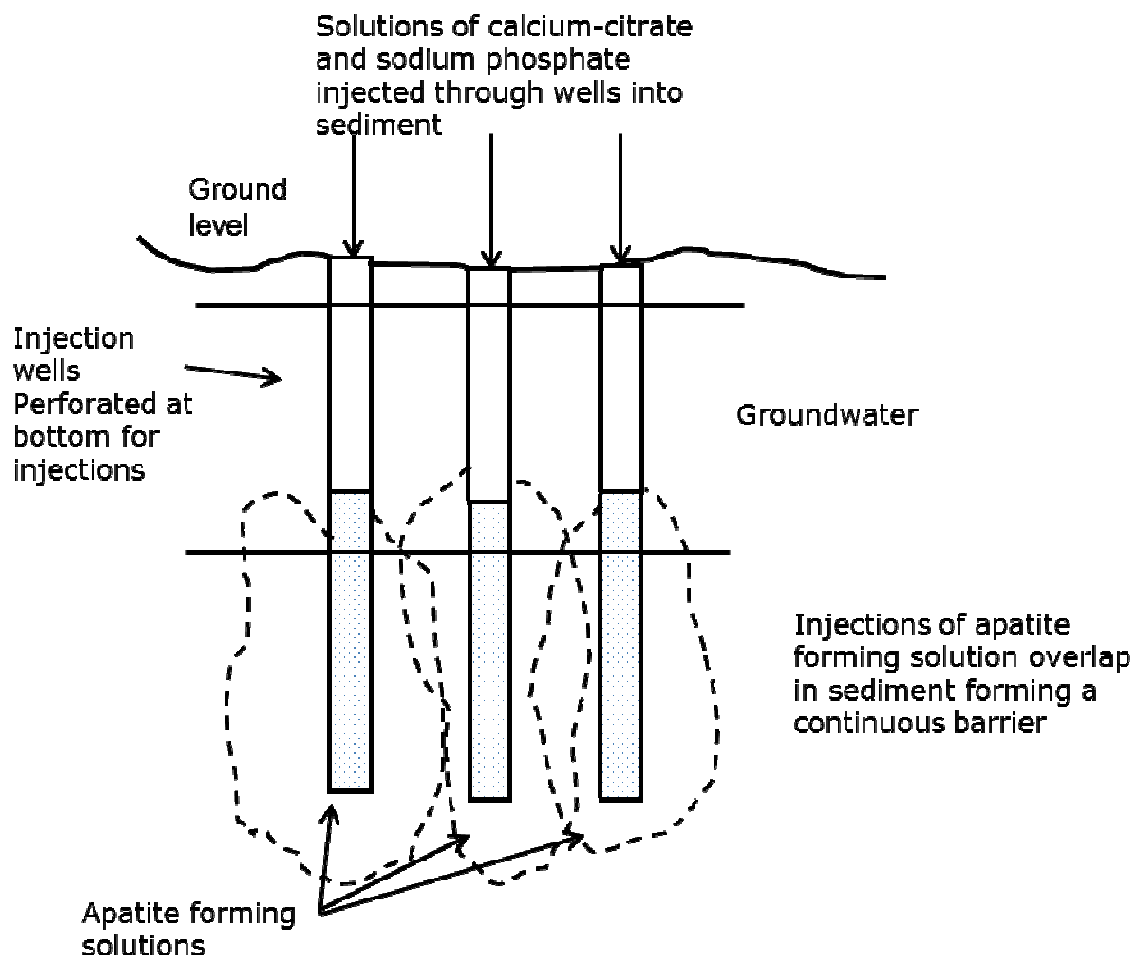


**Figure 2. Permeable reactive barrier. Contaminated groundwater flows through the reactive barrier where the reactive media removes the contaminant and treated, contaminant free groundwater exits the barrier.**

A PRB is a simple, passive treatment technology for separating and immobilizing contaminants in groundwater. Figure 2 is an illustration of a permeable reactive barrier. After determining the direction of the flow path, the reactive or sorptive media is placed perpendicular to the path of contaminated groundwater. As this groundwater passes through the barrier, the contaminants are removed. Conventional construction methods for permeable reactive barriers include trenching followed by backfilling with a

reactive media or high pressure injection of the media. An alternative barrier construction method is to form apatite *in situ* using an apatite forming aqueous solution injected into the subsurface sediments in the flow path of the contaminated groundwater.

The barrier is deployed (U.S. Patents 6,416,252 and 6,592,294) when a solution mixture of calcium citrate and sodium phosphate is injected into the sediment in the path of the contaminated groundwater. Indigenous microorganisms present in the subsurface soil and sediment biodegrade the citrate and release the calcium in a chemical form that allows it to react rapidly with the phosphate to form apatite *in situ*. The apatite precipitates in pores and void space within the sediments finely and evenly coating the surfaces of indigenous mineral grains without plugging the pore space.



**Figure 3. View of apatite deployed through injections wells into groundwater to form an apatite permeable reactive barrier and provide source area treatment to the contaminated sediments.**

Overlapping injections of the apatite forming solution follow the preliminary injection to form a continuous permeable reactive barrier that is able to sorb

and immobilize radionuclide contaminants from groundwater that passes through the barrier (Figure 3).

Using this process an apatite PRB has been deployed along a 300-foot-long stretch of the Columbia River to prevent radioactive strontium from reaching the river (Vermuel et al., 2014). After six years, monitoring wells drilled between the barrier and the Columbia River indicated that the barrier sequestered more than 95 percent of the strontium before it could reach the river.

In addition to forming a permeable reactive barrier this same process of solution injection described above can also serve as a source area treatment (SAT) where a contaminant is as a precipitate or sorbed to mineral surfaces (Wellman et al., 2008). As the solutions deployed and spread through the subsurface, apatite precipitates on the surface of pores and coats mineral surfaces. The precipitated apatite can thereby encapsulate and isolate uranium that is sorbed or precipitated from the accessible environment and prevent it from being remobilized in ground water.

## METHODS

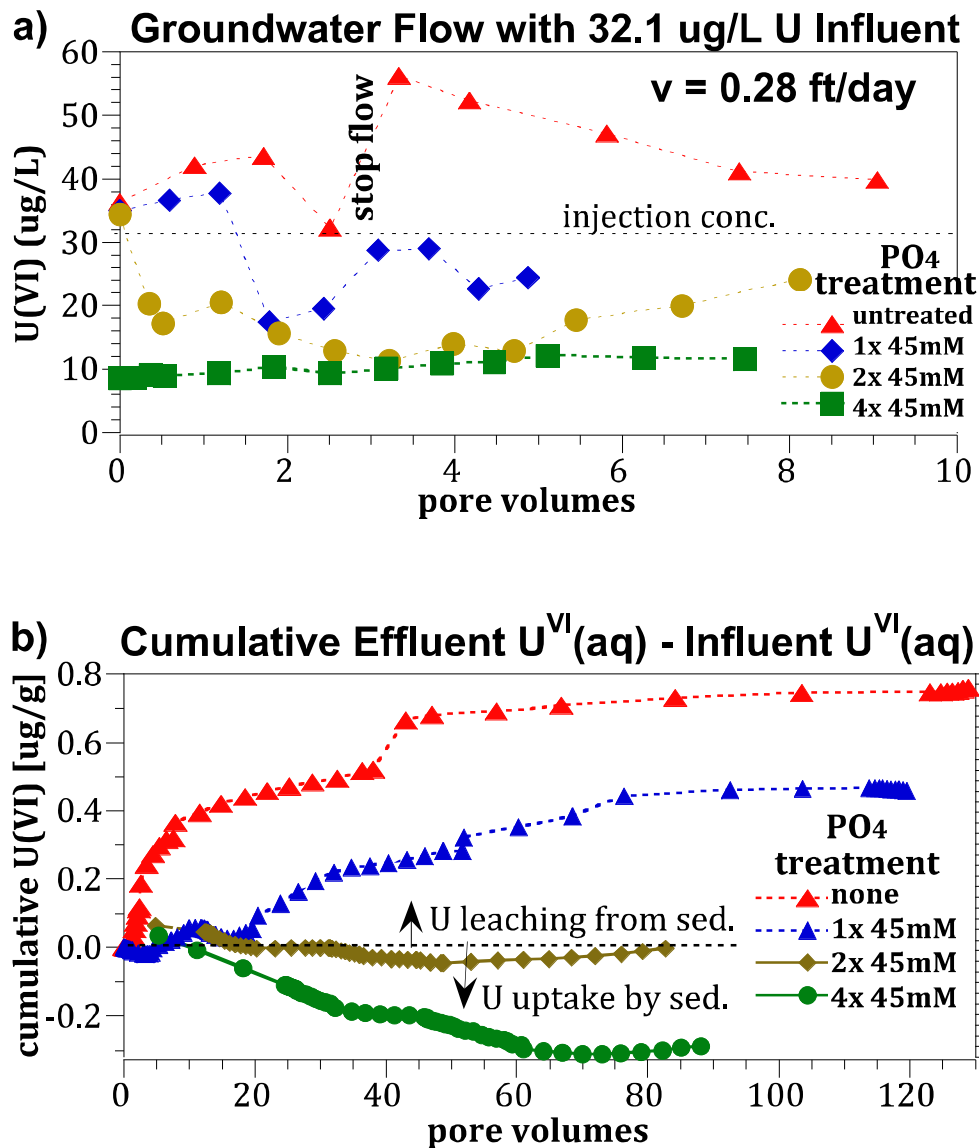
The use of Ca-citrate-phosphate to precipitate apatite as both a permeable reactive barrier (PRB) and a source area treatment (SAT) was evaluated in laboratory experiments to control uranium leaching from Rifle sediments. The Ca-citrate-PO<sub>4</sub> treatment for both PRB and SAT column testing consisted of 45 mM PO<sub>4</sub><sup>-3</sup>, 4.0 mM Ca<sup>2+</sup>, and 10.1 mM citrate (pH 7.5) mixed in Rifle groundwater. Two columns received 10 pore volumes of this solution (1x Ca-cit-PO<sub>4</sub>), one column received 12 pore volumes in two 6-pore volume doses separated by 300 h of no flow, and one column received 24 pore volumes in four 6-pore volume doses separated by 300 h of no flow. An additional two columns were untreated to provide a basis for evaluating treatment effectiveness.

## DISCUSSION AND RESULTS

**Table 1.** Leaching Study Results of Phosphate Treatment of Rifle Sediments.

treatment	injection U conc.	peak U effluent <sup>s</sup>	U leach rate*	for permeable reactive barrier			for source area treatment			sed. PO <sub>4</sub> (mg/g)
	(ug/L)	(ug/L)	(ug/Kg/d)	Q (ft/day)	effluent U (ug/L)	% immobilized	pore volumes	mobilized sed. U (ug/g)	% immobilized	
none	32.1	564.6	2.80	0.37	43.5	--	134	0.675	--	--
1x Ca-cit-PO <sub>4</sub>	32.1	106.7	-0.78	0.28	20.8	52.2	120	0.399	40.9	1.54
2x Ca-cit-PO <sub>4</sub>	32.1	34.3	-2.70	0.32	16.9	61.1	42.1	< 0.01	100	2.53
4x Ca-cit-PO <sub>4</sub>	32.1	37.0	-4.25	0.30	10.1	76.8	55.7	< 0.01	100	5.62

<sup>s</sup> with 32.1 ug/L U influent \* + is U release from sed., - is U uptake by sed.



**Figure 4.** Comparison of uranium leaching in untreated and Ca-citrate-phosphate treated Rifle sediment columns shows uranium immobilization by: a) a decrease in effluent uranium concentration; and b) a decrease in accumulated uranium mass in effluent minus influent.

#### Evaluation of Apatite as a PRB

A qualitative comparison shows higher phosphate dose results in lower effluent uranium concentration (Figure 4a), with effluent values lower than influent. The cumulative effluent uranium mass minus influent (Figure 4b) shows substantially less uranium leaching with higher phosphate treatment and that there is uptake by the phosphate-laden sediment with effluent averaging 20.8 ug/L (single 45 mM PO<sub>4</sub> treatment), 16.9 ug/L (two treatments), and 10.1 ug/L (four treatments). The fraction uranium removed was 53% (single treatment), 61% (two treatments), and 77% (four treatments, Table 1, column 7). The mass of phosphate in the sediment (Table 1, last column) was higher for sediments that received multiple treatments.

## **Evaluation of Apatite for SAT**

Performance as a source area treatment showed 41% to 100% less uranium mass leached from the treated sediment compared to the untreated sediment (Table 1, green section). The two columns that had higher phosphate loading (Table 1, last column) were the most effective. This reduction in leached uranium mass is relatively long term, as 40 to 134 pore volumes of groundwater had been injected through sediments. Treated sediments actively removed aqueous U at a slow rate (Table 1, fifth column), as U concentrations after stop flow events were lower. In contrast, uranium continued to leach from untreated sediments as shown by higher effluent U concentration compared to influent and higher U concentration after stop flow events in columns. Uranium extractions conducted on sediments pre- and post-leach show most mobile phases are advected out of the column (not shown). Cumulative leached uranium mass in excess of influent uranium mass (Figure 4b) shows higher phosphate loading results in no net leaching from the sediment and that influent uranium is being removed (i.e., values < 0.0).

## **CONCLUSIONS**

Initial testing indicates that Ca-citrate-phosphate treatment showed good effectiveness as a source area treatment to stabilize uranium in sediments and decrease leaching, and good effectiveness as a permeable reactive barrier at low groundwater velocities. The uranium removal mechanism is likely one or more of the following: (1) adsorption to the apatite; (2) precipitation of U-phosphate surface phases; or (3) phosphate precipitates coating uranium surface phases. It should be noted that more than one of these mechanisms may be operating in these experiments. In fact, previous studies have shown that Ca-citrate-phosphate treated sediments contained significantly less mobile uranium surface phases that were the result of incorporation into apatite or precipitate coatings.

## **REFERENCES**

- Bostick, W.D., "Use of Apatite for Chemical Stabilization of Subsurface Contaminants", Final Report under contract DE-AC26-01NT41306. US Dept. of Energy, National Energy Technology Laboratory. 2003
- Campayo, L., A. Grandjean, A. Coulon, R. Delorme, D. Vantelon, and D. Laurencin Incorporation of iodates into hydroxyapatites a new approach for the Confinement of Radioactive Iodine, *Journal of Materials Chemistry*, 21, 2011, pp.17609-17611.
- Czerniczyniec, M., S. Farias, J. Magallanes, and D. Cicerone, Arsenic (V) adsorption onto biogenic hydroxyapatite: solution composition effects. *Water Air Soil Pollution*, 180, 2007, pp.75-82.
- Duc, M., G. Lefevre, M. Fedoroff, J. Jeanjean, J.C. Rouchaud, F. Montiel-Rivera, J. Dumonceau, and S Milonjic, Sorption of selenium anionic species on apatites and iron oxides from aqueous solutions. *J. Env. Radioact.* 70, 2003, pp. 61-72.
- Hughes, J.M. and J.F. Rakovan, Structurally Robust, Chemically Diverse Apatite and Apatite Supergroup Minerals, *Elements*, 11, 2015, pp.165-170.
- Hyun, S. P., P. M. Fox, J. A. Davis, K.M. Campbell, K. F. Hayes, and P. E. Long , "Surface Complexation Modeling of U(VI) Adsorption by Aquifer Sediments from a Former Mill Tailings Site at Rifle, Colorado", *Environmental Science and Technology*, 43(24), 2009 pp.9368–9373.
- Jeanjean, J., J.C. Rouchaud and L Tran "Sorption of Uranium and Other Heavy Metals on Hydroxyapatite." *Journal of Radioanalytical and Nuclear Chemistry – Letters* 201(6) 1995 pp. 529-539
- Lee, Y.J., P.W. Stephens, Y. Tang, W. Li, B.L. Phillips, J.B. Parise, and R.J. Reeder, Arsenate Substitution in Hydroxylapatite: Structural Characterization of the  $\text{Ca}_5(\text{PxAs}_{1-x}\text{O}_4)_3\text{OH}$  Solid Solution" *American Mineralogist*, 94, 2009, pp. 666-675.
- Lee, Y.J., "Spectroscopic Investigation of Arsenate and Selenate Incorporation into Hydroxylapatite." *Current Applied Physics*, 10, 2010, pp.158-163.
- McConnell, D. "A Structure Investigation of Isomorphism of the Apatite Group" *American Mineralogist* 23(1) 1938 pp. 1-19
- Moore, R.C., K. Holt, C. Sanchez, H. Zhao, F. Salas, A. Hasan, and D. Lucero "*In Situ* Formation of Apatite in Soil and Groundwater for Containment of Radionuclides and Heavy Metals" SAND2002-3642 November 2002
- Moore, R.C. "*In Situ* Formation of Apatite for Sequestering Radionuclides and Heavy Metals" "U.S. Patent 6,416,252 2002



## **WM2016 Conference, March 6 – 10, 2016, Phoenix, Arizona, USA**

Moore, R.C. "Hydroxyapatite Barriers for Radionuclide Containment" U.S. Patent 6,592,294 2003

Narasaraju, T.S.B. and D.E. Phebe "Some Physico-Chemical Aspects of Hydroxyapatite." Journal of Materials Science 31(1) 1996 pp. 1-21

Palache, C., B., H. Berman and C. Fondel " Dana's System of Mineralogy" 27<sup>th</sup> ed.: New York, Wiley and Sons 1951 pp. 1224

Rakovan, J.F and J.D. Pasteris, "A technological Gem: Materials, Medical, and Environmental Mineralogy of Apatite." Element 11(3) 2015 pp. 195-200

U.S. DOE "Final Site Observational Work Plan for the UMTRA Project Old Rifle Site" Document number U0042501, GJO-99-88-TAR Rev. 1 August, 1999

Vermuel, V., J. Szecsody, B. Fritz, M. Williams, J Fruchter, and R.C. Moore "Injectable Apatite Permeable Reactive Barrier for in situ Sr-90 Immobilization" Groundwater Monitoring and Remediation, 24(2), pp. 14-28.

Wellman, D.M., J.N. Glovack, K.E. Parker, E.L. Richards, and E.M. Pierce "Sequestration and Retention of Uranium (VI) in the Presence of Hydroxylapatite under Dynamic Geochemical Condition "Environmental Chemistry 5(1) 2008 pp. 40-5

### **ACKNOWLEDGEMENTS**

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.