

**Assessment of a Hydroxyapatite Permeable Reactive Barrier to Remediate Uranium at the Old Rifle Site, Colorado – 16193** SAND2015-9764C

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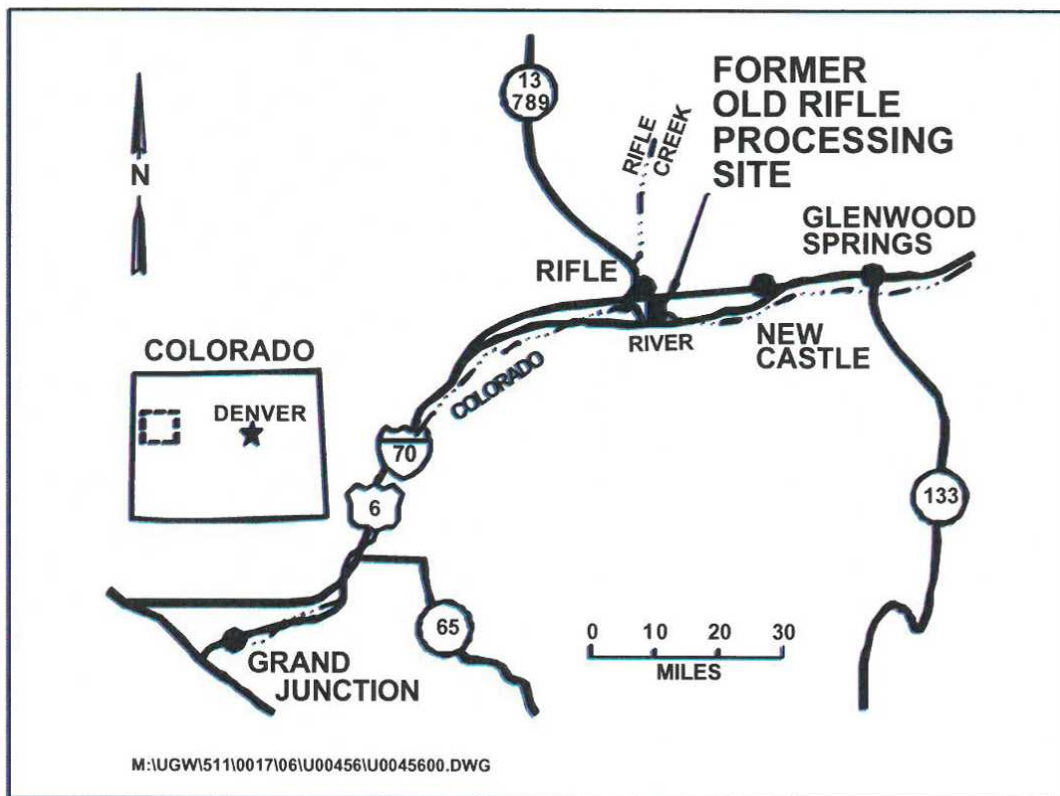
## **ABSTRACT**

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 source area treatments (SAT) and permeable reactive barrier (PRB) 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 Corp (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 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.

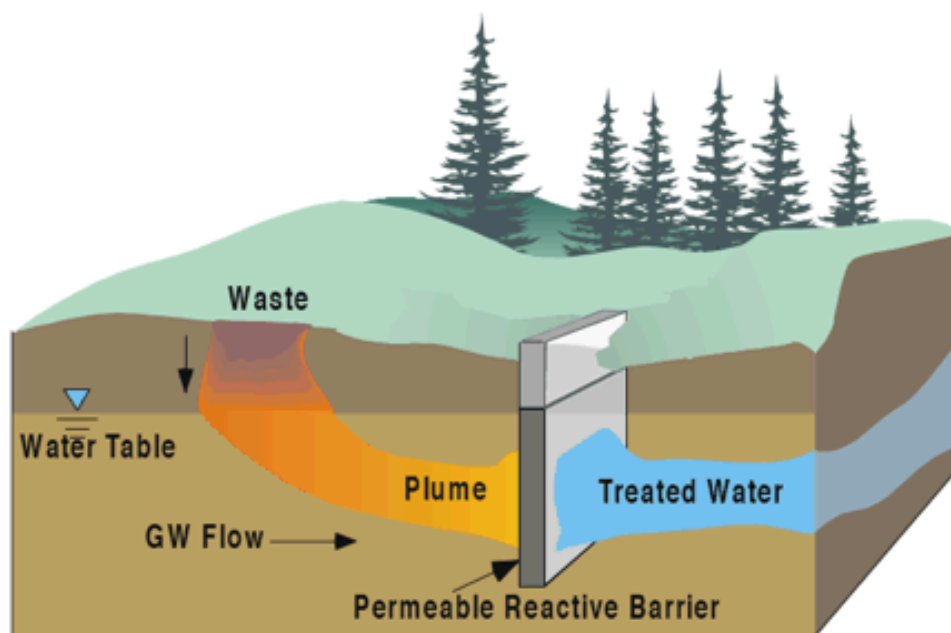


**Figure 1. Location of the Old Rifle Site in Colorado. (U.S. DOE, 1999)**

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) engineered remediation systems. The current study focuses on the deployment of apatite permeable reactive barriers for the in situ remediation and immobilization of uranium in the subsurface at the Old Rifle site.

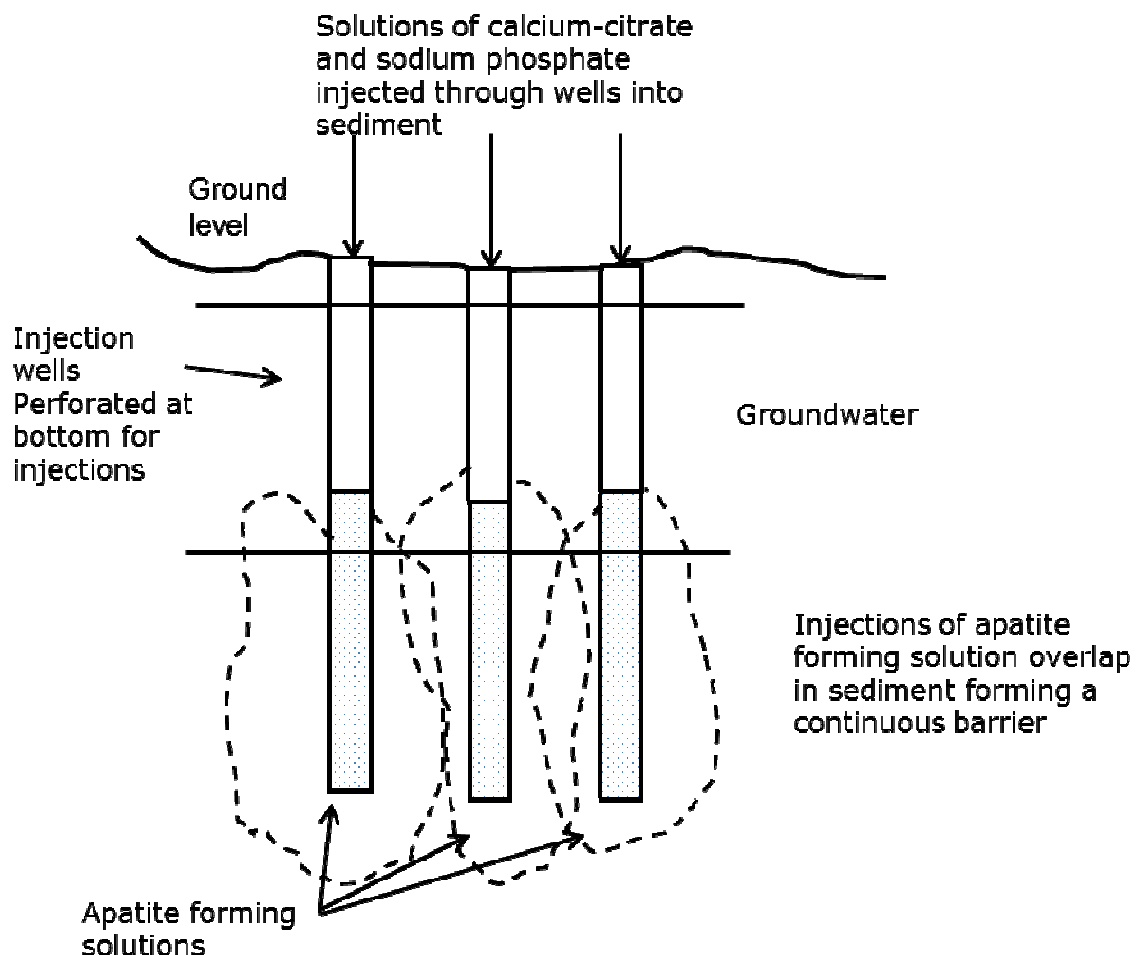


**Figure 2. Permeable reactive barrier. Contaminated groundwater flows through the reactive barrier where the reactive media removes the contaminant and treated, contaminant free groundwater exits the barrier.**

A permeable reactive barrier 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 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. Microorganisms present in the 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. Overlapping injections of the apatite forming solution follow the preliminary injection to form a continuous permeable reactive barrier that is able to sorb and hold radionuclide contaminants from groundwater that passes through the barrier (Figure 3).



**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.**

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 Rifle sediment used (Rifle BH-2-1-13 < 4.75 mm) contained  $2.23 \pm 0.15$  ug U/g, with ~15% aqueous/adsorbed (i.e., highly mobile) and ~50% associated with carbonates (potentially mobile). Treatment effectiveness was evaluated by comparing uranium leaching and surface phase changes between treated and untreated sediment. Sequential uranium extractions before and after leaching were used to characterize which uranium surface phases were mobilized. The Ca-citrate- $\text{PO}_4$  treatment for both PRB and SAT column testing consisted of 45 mM  $\text{PO}_4^{-3}$ , 4.0 mM  $\text{Ca}^{2+}$ , and 10.1 mM citrate (pH 7.5) mixed in Rifle groundwater.

## **DISCUSSION AND RESULTS**

### **Evaluation of Apatite as a PRB**

Performance as a permeable reactive barrier was evaluated by characterizing the concentration and rate of aqueous uranium uptake as Rifle groundwater with 32.1 or 178 or 383 ug/L uranium was injected into the treated sediment. Flow rates used bracketed groundwater velocities that occur at the Rifle site (0.25 to 3.2 ft/day). Column studies showed that untreated sediments leached significant uranium with a peak concentration of 564 ug/L (Table 1, third column), in contrast to Ca-citrate-phosphate treated sediments with significantly lower uranium leaching (peak concentration 138 ug/L). Performance as a permeable reactive barrier at low (~0.3 ft/day) groundwater flow rate showed treated sediments with 17.4 to 24.3 ug/L effluent uranium (44 to 60% less) compared to the untreated sediment in which effluent averaged 43.5 ug/L (blue section in Table 1). Higher uranium influent (383 ug/L) resulted in less removal (0 to 12%).

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

treatment	injection U conc.	peak U effluent <sup>§</sup>	U leach rate*	for permeable reactive barrier			for source area treatment		
	(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	34.3 - 56.3 <sup>#</sup>	--	134	0.675	--
Ca-cit-PO <sub>4</sub>	32.1	106.7	-0.78	0.28	17.4 - 24.3	44.1 - 60.0	120	0.399	40.9
none	383	472.9	1.01	0.38	323 - 380 <sup>^</sup>	--	137	0.554	--
Ca-cit-PO <sub>4</sub>	383	138.2	-0.65	0.26	318 - 384	0.0 - 12.1	99.4	0.166	70.0

<sup>§</sup> with 32.1 ug/L U influent \* + is U release from sed., - is U uptake by sed. <sup>#</sup> average 43.5 ug/L <sup>^</sup> average 361 ug/L

### Evaluation of Apatite for SAT

SAT was evaluated by the change in uranium surface phases as a result of leaching between treated versus untreated sediment. Performance as a source area treatment showed 40.9% to 70.0% less uranium mass leached from the treated sediment compared to the untreated sediment (Table 1, green section). This reduction in leached uranium mass is relatively long term, as 100 to 137 pore volumes of groundwater had been injected through sediments. Uranium sequential extractions will be conducted after leaching studies are completed to identify changes in uranium surface phases. 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.

### CONCLUSIONS

Overall, 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 velocity. 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.

It is anticipated that increasing apatite loading in future column experiments will improve both PRB and SAT performance. Hence, additional experiments have been initiated with higher (i.e., 2x and 4x) phosphate loading in the sediment to evaluate the extent of increase in uranium uptake mass and rate.

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