Remediation of Uranium-contaminated Ground Water at Fry Canyon, Utah

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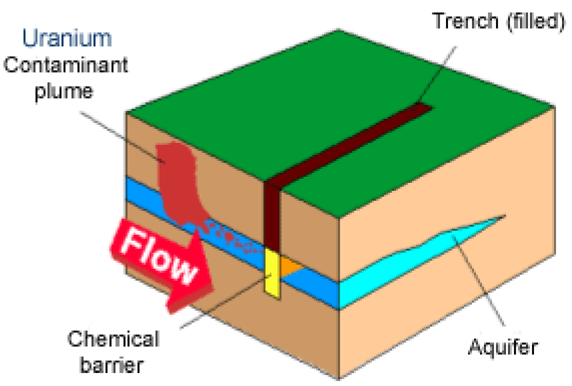
Clean up of contaminated aquifers is a difficult and expensive problem because of the inaccessibility of the subsurface and the volume of soil and ground water requiring treatment. Established technologies such as pump-and-treat and soil excavation are ineffective in most large contamination scenarios because they treat only a small fraction of the contamination or are prohibitively expensive (National Research Council, 1999). Permeable Reactive Barriers (PRBs) are a relatively new technology that offer promise to overcome these obstacles. PRBs are trenches (figure 1) or fence-like arrays of non-pumping wells emplaced in the subsurface at depths of up to 150 feet to intercept the flow of contaminated ground water (Freethey *et al.*, 2002). Fill materials contained within the PRBs react with dissolved contaminants to degrade or sequester them. Thus, in essence, PRBs act as large *in-situ* filters to clean ground water. PRB technologies offer lower operating costs, are highly energy efficient, and require no surface facilities or ground water pumping/recharge (Freethey *et al.*, 2002; Morrison and Spangler, 1992; Shoemaker *et al.*, 1995). Two commonly proposed PRB contaminant-removal mechanisms are: (a) precipitation reactions in which metal contaminants are sequestered within freshly formed mineral phases, and (b) oxidative degradation of contaminants by particulate iron metal. In order for PRBs to be cost-effective they should be effective for an economically viable period (or be replenishable). They should not be susceptible to clogging or rapid passivation by reaction products.



Schematic diagram of a reactive barrier.
(Modified from Morrison and Spangler, 1992)

Figure 1. Top: schematic diagram of a permeable reactive barrier. Bottom: installation of the apatite PRB at Fry Canyon, Utah.

The shallow alluvial aquifer at Fry Canyon, Utah, is contaminated with up to 17 mg/L uranium leached from processed tailings at an ore upgrader processing plant that was operated in the 1950s and 60s. A partnership was formed in June of 1996 between the DOE (Grand Junction Office), US EPA, Interior Department, Geological Survey (USGS), Bureau of Land Management (BLM), and the Utah

Department of Environmental Quality (UDEQ) for the purposes of demonstrating PRB *in-situ* treatment technologies for abating the ground water uranium contamination.

Commercial apatite ($Ca_5(PO_4)_3OH$), was investigated for use at Fry Canyon based on its reactivity with uranium. Apatite is soluble in ground water and slowly releases phosphate, which can react with dissolved hexavalent uranium (U(VI)) to form the mineral autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$)), which is pictured in the highlight announcement on the main page. The relatively low solubility of autunite has led some to propose that it would be an ideal inert host for *in-situ* sequestration and immobilization of U(VI). This general chemical strategy (phosphate mineral formation) has previously been shown to have a high capacity for attenuating lead- and cadmium contamination (Ma *et al.*, 1993; Valsami-Jones *et al.*, 1998).

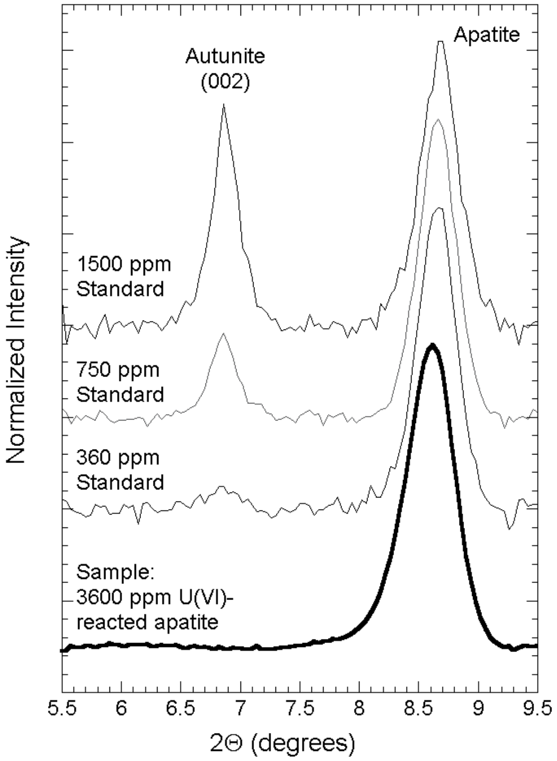


Figure 2. XRD region scans of uranium-reacted apatite contain no evidence for presence of autunite. Detection limit for autunite is 360 ppm, which is a 10-fold lower concentration than in the sample. (from Fuller *et al.*, 2002)

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and Synchrotron-based X-Ray Diffraction (SR-XRD) measurements were performed at SSRL beam lines 4-3, 11-2, and 2-1 to characterize the chemical form of U(VI)-reacted apatite in laboratory studies and in samples recovered from the bone-char apatite PRB at Fry Canyon. SR-XRD allows the identification of crystalline phases in wet samples at very low detection limit (~360 ppm detection limit for autunite, see figure 2). This capability would be very difficult to obtain using a sealed-tube laboratory x-ray source. EXAFS spectroscopy was required to characterize the speciation of U(VI) in noncrystalline phases, including U(VI) complexes adsorbed at apatite-water interfaces. As shown in figure 2, autunite was not detected in the U(VI)-reacted materials having sorbed U(VI) concentrations of 3600 ppm (1 ppm is 1 µg of uranium per g solid sample). A similar conclusion can be drawn from the EXAFS data (figure 3). The full suite of XRD and EXAFS measurements completed in this study indicate that uranium occurs as a non-crystalline species in the samples when sorbed U(VI) concentrations are < 5,500 ppm (Fuller *et al.*, 2003). Complementary SR-XRD measurements suggested that U(VI) was not incorporated into the apatite structure, and sequential filtration experiments discounted the possibility that U(VI) occurred in (amorphous) colloidal precipitates (Fuller *et al.*, 2002). Since sorbed U(VI) concentrations lower than 1,000 ppm are most relevant to the aquifer conditions, it can be concluded that U(VI) sequestration in PRBs should not be controlled by solid-phase precipitation.

It follows from these measurements that U(VI) probably occurs in the PRBs as molecular complexes adsorbed onto the surfaces of apatite. EXAFS analyses are consistent with this conclusion. EXAFS spectra suggest that uranium occurs as the uranyl cation ($U(VI)O_2^{2+}$) bonded to apatite surfaces and complexed by carbonate groups (Fuller *et al.*, 2003). The uranium-phosphorous distance is about 3.55 Å, suggesting that U(VI) coordinates to surface phosphate groups in a monodentate geometry (figure 3). These results were obtained from laboratory samples and samples extracted from the Fry Canyon barrier after 18 months of operation. Thus, uranium sequestration in the barriers is believed to occur primarily *via* adsorption of U(VI)-carbonate complexes onto the surfaces of apatite PRB material. These results have the important implication that permeability will remain high in the apatite PRB. In contrast, clogging in zero-valent-iron-based PRBs from precipitation of corrosion products can seriously impact the longevity of the PRB. However, the barrier will require monitoring to insure that re-release of sequestered U(VI) does not occur due to changes in groundwater chemistry or if the U(VI) sorption equilibrium is reached.

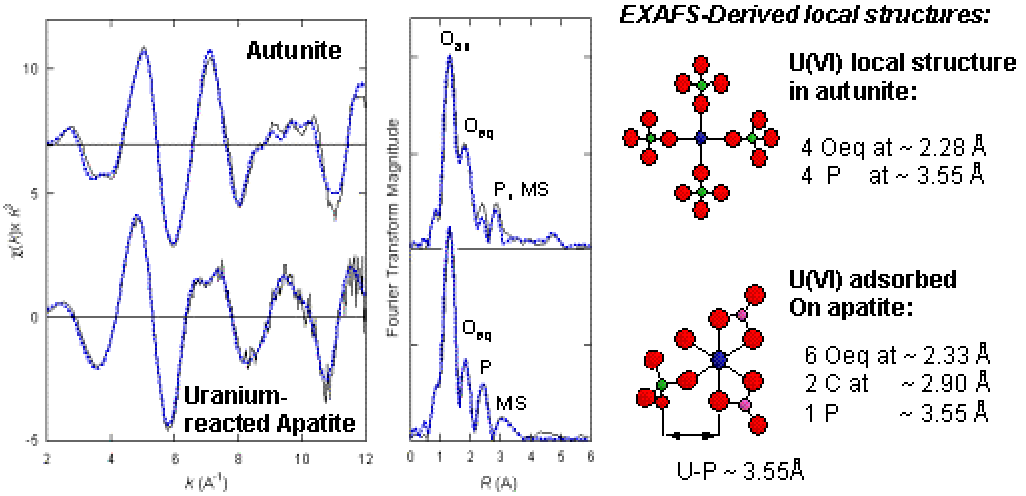


Figure 3. L_{III}-edge EXAFS and Fourier Transforms (FTs) of autunite and uranium-reacted apatite (3600 ppm sorbed U(VI)). Solid lines are data. Dotted lines are fits. Structural drawings: Blue = U(VI) (axial oxygens above and below plane of page are omitted), Red = Oxygen, Green = Phosphorous. The differences in the local structure around uranium (right hand side) give rise to the differences observed in the EXAFS and FTs.

References

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