

Formation of *In situ* Apatite Barriers Using Water Soluble Reagents for Sequestering Uranium and Strontium

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Abstract: *In situ* reactive barriers show great promise for groundwater and soil remediation. However, conventional construction techniques require extensive excavation or jet grouting to place the reactive material. In this work, a new *in situ* technique for placement of apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{X})_2$, where X is monovalent anion such as OH^- , Cl^- or F^- is described. It is well documented that apatite is a strong sorbent for radionuclides and heavy metals. The new placement process is based on injecting a solution of calcium citrate and sodium phosphate into soil. As the citrate is biodegraded, calcium is gradually released and immediately reacts with the phosphate to form insoluble calcium phosphates that transform into apatite. In this work, apatite was formed in soil by adding a solution containing sodium citrate, calcium chloride, sodium phosphate, ammonium nitrate, and sodium fluoride at a pH of 8. The apatite precipitated on the soil particle surfaces was analyzed by X-ray diffraction (XRD) and closely matched the pattern of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Batch sorption studies using soil in which apatite was formed indicated that strontium and uranium are irreversibly sorbed to the apatite. The new *in situ* process can be used where conventional techniques are impractical or not possible.

It is well documented that apatite strongly sorbs uranium, plutonium, strontium, lead and other contaminants (Arey et al., 1999; Laxic, S. and Z. Vukovic, 1991; Gauglitz et al., 1992). Apatite is an ideal material for long-term containment of contaminants because of its high sorption capacity for actinides and heavy metals, low water solubility ($K_{sp} > 10^{-40}$), high stability under reducing and oxidizing conditions, availability, and low cost (LeGeros, 1991). However, placement of solid apatite into soil to form a barrier relies on extensive excavation or high pressure injection, both of which expose workers to safety hazards and are very costly (Blows et al., 2000). In this work, we describe a novel technique for placement of apatite barriers for sequestering radionuclides and heavy metals. The process is based on injecting a solution of calcium citrate and sodium phosphate into soil, and apatite is expected to form as a thin film on the soil particles. Because citrate forms strong complexes with calcium (Smith and Martel, 1977) it prevents the calcium from immediately reacting with the phosphate before it can be injected into the soil. However once injected, citrate is easily metabolized by microorganisms (Francis et al, 1992). As the citrate is biodegraded, calcium is gradually released and reacts with phosphate to form insoluble calcium phosphates. At pH between 7 to 9 and in the presence of fluoride, conditions are most favorable for the reaction of calcium and phosphate to form apatite. Once in place, the apatite will sequester radioactive and heavy metal contaminants. Figure 1 is an example of an *in situ* formed apatite barrier under a leaking waste tank.

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Apatite was formed in soil by adding a solution containing 100 mM sodium citrate, 50 mM calcium chloride, 30 mM sodium phosphate, 10 mM ammonium nitrate, and 20mM sodium fluoride at a pH of 8.0. The precipitate was separated from the soil and analyzed by XRD. The XRD pattern is given in figure 2 and matches well with crystalline hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

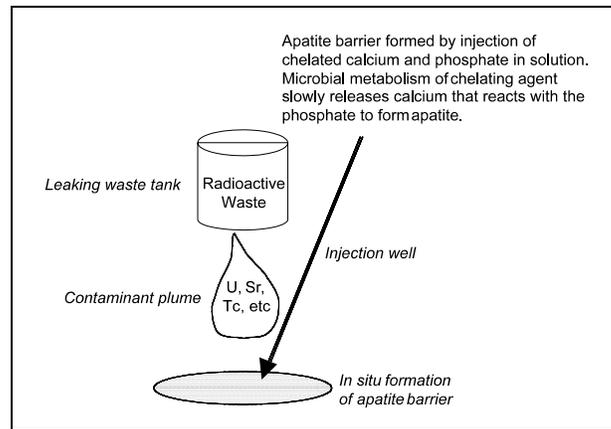


Figure 1. *In situ* apatite barrier formed under leaking waste tank by injection of calcium citrate, sodium phosphate, sodium fluoride and microbial nutrients.

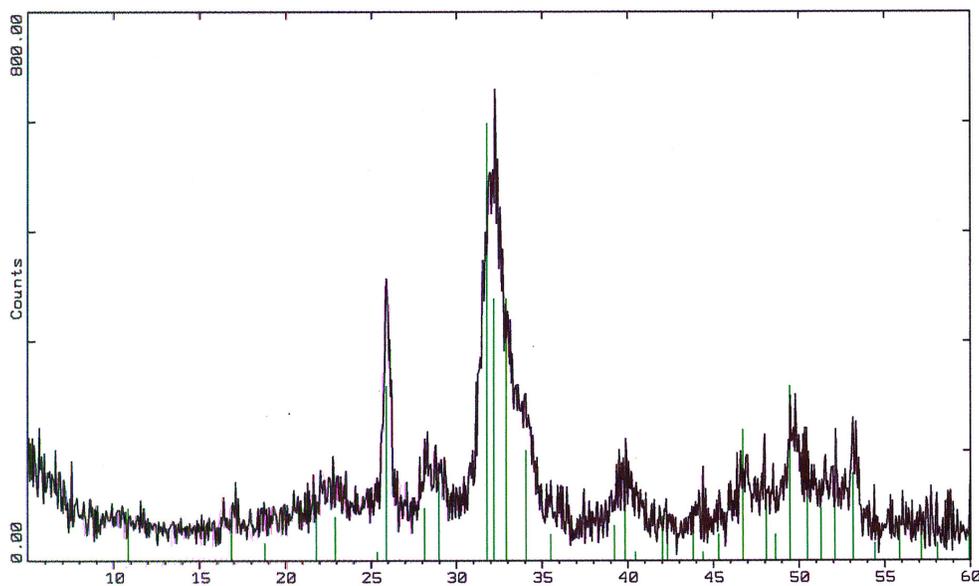


Figure 2. XRD pattern for apatitic material formed *in situ* using calcium citrate, sodium phosphate, ammonium nitrate and sodium fluoride at a pH of 8.0. Reaction time was 2 weeks. The vertical lines represent peaks for hydroxyapatite.

Soil treated with the *in situ* formed apatite was used in batch sorption experiments for uranium and strontium. 1-2 g of untreated and treated soil was contacted with 25 ml. of solution, shaken for 24 hours and analyzed by liquid scintillation counting (LSC). Reversibility studies were

conducted by removing the liquid phase and adding fresh .1M potassium nitrate solution to each sample and shaking for 3 days. The results are given in table 1. The results indicate the apatite treated soil irreversibly sorbs more uranium and strontium than untreated soil. In the case of uranium the treated soil did not release any uranium in reversibility experiments. Multiple treatment of the soil with more apatite forming solution would increase the capacity of the soil for strontium and uranium sorption.

Table 1. Sorption of Strontium and Uranium on *in situ* Formed Apatite in Soil.

Strontium				
Soil	[Sr], m	[Sr], m	% sorbed	% desorbed
	initial	after 24 Hrs.	on soil	from soil after 72 Hrs.
1.0 g. untreated	1.00E-06	7.40E-07	26%	43%
2.0 g. untreated	1.00E-06	5.90E-07	41%	35%
1.0 g treated	1.00E-06	5.30E-07	47%	23%
1.0 g treated	1.00E-06	4.00E-08	60%	17%

Uranium				
Soil	[U], m	[U], m	% sorbed	% desorbed
	initial	after 24 Hrs.	on soil	from soil after 72 Hrs.
1.0 g untreated	1.00E-06	3.80E-07	62%	33%
2.0 g untreated	1.00E-06	2.60E-07	74%	31%
1.0 g treated	1.00E-06	1.10E-07	89%	0%
1.0 g treated	1.00E-06	7.10E-08	93%	0%

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