Use of Biogenic Apatite for Stabilization of Subsurface Metal Contaminants*

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Biogenic apatite (Apatite II) is evaluated as a "sorbent" for the removal of select priority metals in aqueous solution (synthetic DOE Y-12 Plant groundwater and authentic legacy waste), and other media (including contaminated soil). The high reactivity of Apatite II relative to other phosphate reagents comes from the unusual structure of the solid. Most of the material is porous amorphous hydroxyapatite (calcium phosphate). The amorphous structure is relatively reactive and is sufficiently soluble to provide phosphate ion to solution, locally exceeding the solubility limit of many metal-phosphate phases and resulting in precipitation reactions. At the same time, the random nanocrystals within Apatite II provide the structure for nucleating the precipitates to form crystallites on the host material surface. The apatite surface itself is an excellent sorbent or ion exchange medium for many cations; for example, uranium (as the uranyl ion) is first sorbed to the surface, then at higher loading (several weight percent metal), crystalline phases begin to appear as U replaces Ca in the host material.

Three types of substitutions that can occur in apatite structures:

- Cations, e.g., Pb^{2+} , Sr^{2+} , Zn^{2+} , Mn^{+2} , Ce^{3+} , etc., can substitute for Ca^{2+} ;
- Oxyanions, e.g., $AsO_4^{3^-}$, $VO_4^{3^-}$, $CO_3^{2^-}$, $SO_4^{2^-}$ can replace structural $PO_4^{3^-}$;
- Anions F⁻, Cl⁻ can exchange with OH⁻. (fluoroapatite is the least soluble)

In our investigations, the affinity for priority cationic contaminants on Apatite II follows the approximate series (ranked by decreasing magnitude of the contaminant distribution coefficient, Kd, at lowest solution phase residual concentration evaluated in batch tests):

$$UO_2^{+2} > Pb^{+2} \ge Th^{+4} > Cd^{+2} > Mn^{+2} \sim Zn^{+2} > Cu^{+2} \sim SbO^+ \sim Hg^{+2} > Ni^{+2} > Sr^{+2} > Ba^{+2}$$

Removal of contaminant oxyanions to pre-existing apatite phase in short-term batch tests was less successful; the approximate order of preference for sorption is:

$$VO_4^{-3} > MoO_4^{-2} > SeO_3^{-2} > AsO_4^{-3} > CrO_4^{-2} > TcO_4^{-2}$$

Results will be presented for treatment of aqueous DOE legacy waste, containing U, Cd, and Zn as the priority metals, and also a series of soil column studies to demonstrate enhanced retention of metals.

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