A Comparison of Synthetic and Animal Bone Derived Apatite for Sequestering Uranium and Strontium in Soil and Groundwater

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Abstract: Apatite, $Ca_{10}(PO_4)_6(OH)_2$, is a strong sorbent for actinides, strontium, and heavy metals. Apatite may be synthetically produced, obtained from apatite ores, or made from animal bones. In this work, we compare reaction kinetics and K_d values for the reactions of synthetic hydroxyapatite, cowbone derived apatite, and fishbone derived apatite with strontium and uranium. Two methods were used for preparing apatite from fishbone: heat treatment to 700˚C and reaction with hydrogen peroxide. The apatites prepared by these two methods were compared for their effectiveness for sorption of strontium and uranium. The results indicate that U is taken up by apatite almost 3 times faster than Sr by all forms of apatite. For Sr, K_d values ranged from 128 to 307. For U, K_d values ranged from 2420 to 9240. Heat-treated apatite was more effective for strontium and uranium sorption than apatite treatment with hydrogen peroxide. The animal derived apatite that was heat-treated exhibited similar sorption characteristics as synthetic apatite.

It is well documented that apatite strongly sorbs uranium (Arey et al., 1999), strontium (Laxic and Vukovic, 1991), and other metals (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. Apatite can be produced synthetically by calcium and phosphate precipitation reactions or high temperature solid state processes (LeGeros, 1991), obtained from apatite ores, or derived from animal bones by heat treatment (Joschek et al., 2000) or treatment with hydrogen peroxide (Erts et al., 1994) to remove the organic fraction of the bone. Heat treatment has the added advantage of producing a more crystalline apatite. Although a significant amount of data on sorption exists in the literature, a comparison of the sorption properties of animal derived apatite and synthetic apatite has not been reported.

In this work, we compare reaction kinetics and K_d values for the reactions of synthetic hydroxyapatite and cowbone and fishbone derived apatites with U and Sr. Experiments were performed by placing .3 g of apatite in 30 ml of a 1 x 10^{-6} m Sr or 2.6 x 10^{-5} m U solution containing .1m KNO_3 as the background electrolyte. The pH of each solution was set to 8.0 and the solutions agitated. Samples were collected at different times and analyzed by liquid scintillation counting (LSC).

All cowbone apatite was provided by Xmax Corporation and was heat-treated at either 500, 700 or 900˚C. Fishbone apatite was treated by either heat treatment at 700˚C or by reaction with hydrogen peroxide. For hydrogen peroxide treated fishbone, the fishbone was placed in a 30%

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solution of hydrogen peroxide for 7 days. The solution was changed daily. All apatite was sized to between 60-80 mesh.

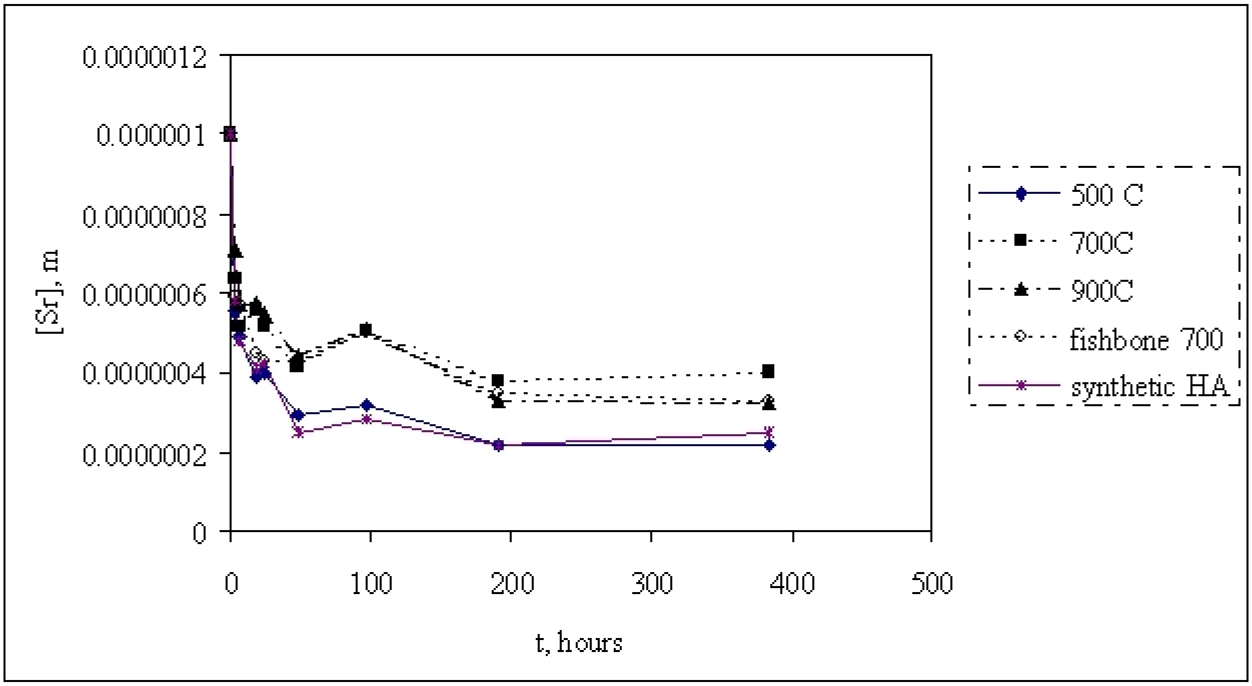

Figure 1. Plot of strontium concentration as a function of contact time with apatite. Initial strontium concentration time was 1 x 10^{-6}.

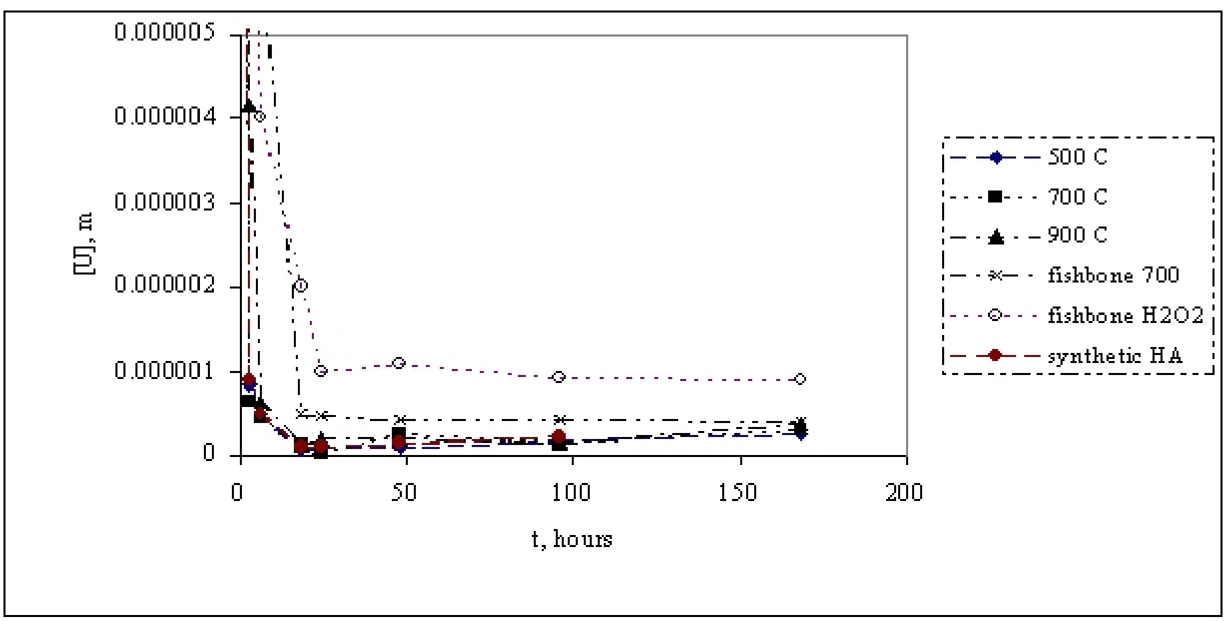

Figure 2. Plot of uranium concentration as a function of contact time with apatite. Initial uranium concentration was 2.6 x 10^{-5}. Initial value not shown on plot.

The results for Sr and U sorption are given graphically in Figures 1 and 2, respectively. The results indicate Sr uptake by apatite takes approximately 50 to 100 hours of contact time to reach equilibrium. For U, the kinetics are much faster with equilibrium being reached in approximately 24 hours. For the cowbone apatite, heat treatment at 500, 700, or 900°C made little difference in Sr or U sorption. Fishbone that was heat treated at 700°C gave similar sorption behavior as cowbone apatite processed by heat treatment. Fishbone treated by reaction with hydrogen peroxide did not uptake as much U as heat treated or synthetic apatite. Analysis of the fishbone apatite indicated 15% organics remained after hydrogen peroxide treatment whereas less that 1% remained in the fishbone after heat treatment. Wudneh and Breese (1999) have reported that fishbone apatite is less effective than synthetic apatite for removing lead from water. However, the authors do not indicate how the fishbone in their experiments was processed to remove organic components from the bone. Hydrogen peroxide treatment for longer periods of time may produce apatite with better sorption properties.

K_d values (defined as ratio of conc. in solid, in moles of Sr or U per mole of apatite, to the conc. in sol., in mol/L) were calculated for the most and least effective apatite sorbent in each case for Sr and U. For Sr, a value of 307 was determined for synthetic hydroxyapatite and a value of 128 was determined for cowbone apatite treated to 700°C. For U, a value of 9240 was calculated for synthetic and 500°C cowbone apatite and a value of 2420 was calculated for fishbone treated with hydrogen peroxide. The results indicated heat treatment of cowbone and fishbone produces apatite that has similar sorption behavior as synthetic apatite. However, synthetic apatite is approximately 100 times the cost of animal bone apatite. Therefore, animal bone apatite is much more economical to use. More work on hydrogen peroxide treatment of animal bones is needed. In all reversibility experiments less than 1% of the Sr or U was released back into solution.

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