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Containment of Uranium in the Proposed Egyptian Geologic Repository for Radioactive Waste Using Hydroxyapatite

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Abstract

Currently, the Egyptian Atomic Energy Authority is designing a shallow-land disposal facility for low-level radioactive waste. To insure containment and prevent migration of radionuclides from the site, the use of a reactive backfill material is being considered. One material under consideration is hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, which has a high affinity for the sorption of many radionuclides. Hydroxyapatite has many properties that make it an ideal material for use as a backfill including low water solubility ($K_{sp}>10^{-40}$), high stability under reducing and oxidizing conditions over a wide temperature range, availability, and low cost. However, there is often considerable variation in the properties of apatites depending on source and method of preparation. In this work, we characterized and compared a synthetic hydroxyapatite with hydroxyapatites prepared from cattle bone calcined at 500°C, 700°C, 900°C and 1100°C. The analysis indicated the synthetic hydroxyapatite was similar in morphology to 500°C prepared cattle hydroxyapatite. With increasing calcination temperature the crystallinity and crystal size of the hydroxyapatites increased and the BET surface area and carbonate concentration decreased. Batch sorption experiments were performed to determine the effectiveness of each material to sorb uranium. Sorption of U was strong regardless of apatite type indicating all apatite materials evaluated. Sixty day desorption experiments indicated desorption of uranium for each hydroxyapatite was negligible.

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1.0 Introduction

The Egyptian Atomic Energy Authority is currently designing a shallow-land disposal facility for low-level radioactive waste. To ensure that radionuclides are not released from the site, reactive barrier materials, such as radionuclide sorbents, are being evaluated for use at the facility. Among the sorbents being evaluated is hydroxyapatite. In this work, we characterized and compared hydroxyapatite made from cattle bone by calcination to high purity synthetic hydroxyapatite for sorption of uranium.

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ in its purist form, is a crystalline solid that exhibits a high stability under reducing and oxidizing conditions and very low water solubility ($K_{sp}<10^{-40}$) under alkaline conditions. The term "apatite" refers to a family of compounds with the general chemical structure $Ca_{10-n} X_n (PO_4)_{6-m} Y_m Z_2$ where X and Y are cation and anions, respectively that substitute for Ca^{2+} and PO_4^{3-} groups in the apatite structure. Typical cation substitutions include Sr^{2+}, Na^+, Pb^{2+} and Cd^{2+} while anions substitutes include HPO_4^{2-}, and CO_3^{2-}. Z is usually OH^-, F^-, Cl^-, or Br^- (LeGeros et al., (1979). Hydroxyapatite can be produced synthetically through precipitation from aqueous solutions containing calcium and phosphate (Andronescu et al., 2002), from high temperature solid-state reactions (Papargyris et al., 2002), from calcination of animal bones (Tofe, 1998) or mined (Dahanayake and Subasinghe, 1991).

Hydroxyapatite is a strong sorbent for many heavy metals (Boisson et al., 1999; Bostick et al., 1999; Da Rocha et al., 2002; Nilce at al., 2002; Seaman et al., 2001; Xu and Schwartz, 1994; Zhang et al., 1998) and radionuclides (Lazic and Vukovic, 1991; LeGeros et al., 1979; Seaman et al., 2001), including uranium (Arey et al., 1999; Fuller and Bagar, 2001; Fuller et al., 2002; Jeanjean et al., 1995; Vukovic et al., 1998). However, the mechanism of retention varies by metal species. Fuller et al. (Vukovic et al., 1998) reports the mechanism of U (VI) sorption to hydroxyapatite is concentration dependent. At low uranium concentrations (< 4700ppm), uranium(VI) phosphate solids were not detected suggesting a surface complexation mechanism. At higher concentrations (>7000ppm), crystalline uranium (VI) phosphate solids were detected. Strontium sorption by hydroxyapatite is reported by Vukovic et al. (Elless and Lee, 1998) to be a substitution reaction for calcium in the apatite structure.

There is a wide variation in hydroxyapatite crystallinity, morphology, texture, stability, and solubility depending on source and method of preparation. LeGeros et al. (LeGeros et al., 1979) reports that calcination causes strong modification of the hydroxyapatite bulk and surface structures, which in turn might affect its sorption capacity. Nilce et al. (Bostick et al., 1999) reports that synthesis temperature and pH affected hydroxyapatite stoichiometry (Ca/P), surface area, and sorption capacity for Cd^{2+}. Cation and anion substitutions are important factors that affect apatite properties. For example, the substitution of carbonate for PO_4, results in reduced crystal size, increased surface area, and increased solubility (LeGeros et al., 1979).

In most of the studies reported in the literature on radionuclide sorption by hydroxyapatite, synthetic apatites, which are very expensive, were used. For use as a backfill material in a nuclear waste repository or any other application requiring large amounts of hydroxyapatite, an economical alternative is the use of hydroxyapatite made from animal bones. The objective of this work was to characterize and compare the physical and chemical properties of bovine derived apatites to synthetic hydroxyapatite and evaluate their potential to sorb and retain U.

2.0 Experimental

2.1 Materials

Water was purified using a Barstead Nanopure Water Filtration System. All chemicals were reagent grade (Fisher Scientific). Synthetic hydroxyapatite (HA SYN) was purchased from BioRad Laboratories (Hercules, CA). The material is chromatography grade and guaranteed 99.9% pure. It was washed with DI water prior to use. Cattle bone hydroxyapatite was prepared by grinding bone to approximately 0.5 mm diameter followed by calcination at 500°C (HA 500), 700°C (HA 700), 900°C (HA 900) and 1100°C (HA 1100) in the presence of oxygen for 48 hours followed by washing with DI water. All apatite materials were sieved prior to use and only the fraction between 10 nm and 100 nm was used in these experiments. ^{236}U was purchased as U_3O_8 from Isotope Products, Valencia, CA. This material was certified >99% pure (ISO 9001 certified). The powder was dissolved in 4M HNO_3, neutralized to pH 8.0 using NaOH, and then oxidized to U(VI) with hydrogen peroxide. Excess peroxide was destroyed by exposure of the solution to UV light for several days.

2.2 Apatite characterization

The apatites were characterized using BET surface area analysis, Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray Diffraction (XRD), and Fourier Transform-Infrared Spectroscopy (FT-IR). Samples for TEM were prepared by depositing apatite-bearing water on a holey-carbon coated copper grid. TEM and EDS were carried out with a JEOL JEM-2010 high-resolution TEM (HRTEM) and an Oxford Link ISIS EDS system. Point-to-point resolution of the HRTEM is 1.9 Å. FT-IR was performed using a Perkin Elmer Spectrum GX FT-IR System and X-ray Diffraction (XRD) using a Bruker D8 Advance X-Ray Diffraction System with a Kevex model 2005-212 detector with a 0.125 mm window. Ca/P ratios of each material were determined by dissolving a gram of material in 2M HCl and measuring the Ca and P concentrations by inductively coupled plasma-mass spectroscopy (ICP-MS) and ion chromatography (IC). The solubility of each hydroxyapatite was determined by mixing 1 g of material in 10 mL of DI water and equilibrating on a rotary shaker for 1 month. Ca and PO_4 concentrations were determined by ICP-MS and IC. Surface areas of the hydroxyapatites were measured by BET.

2.3 U Sorption studies

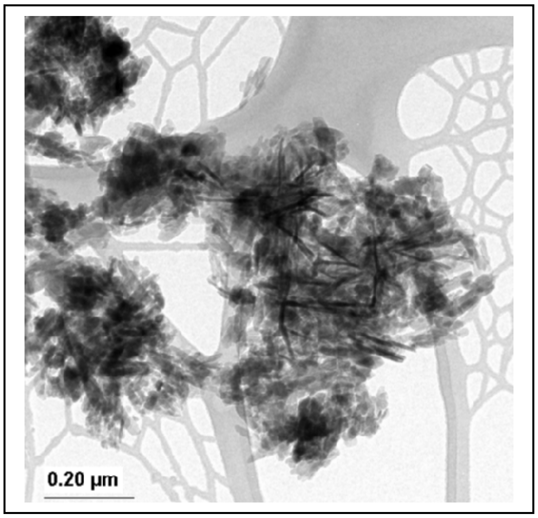
Batch sorption experiments were performed in polycarbonate Oak Ridge Centrifuge Tubes (Fisher Scientific). Hydroxyapatites were weighed at 0.1 g and were equilibrated with 25 mL of 0.1M KNO_3 solution, the background electrolyte, at various pH (6 to11). All samples were duplicated and the pH was adjusted daily, with HNO_3 or NaOH. pH was measured using a 250A-plus Thermo Orion pH meter. U(VI) was added to each sample to achieve an initial concentration of 5.1×10^{-4} M U(VI) and the samples placed on a reciprocating shaker for 30 days at 10 oscillations/min. The solution phase was analyzed radiometrically for U (VI) after removing a 1.0 mL supernatant for counting using a Tri-Carb Liquid Scintillation Analyzer. The samples were filtered through 0.2 μm syringe filter (Whatman). To close the mass balance U(VI) sorbed to the hydroxyapatite and bone apatites was also analyzed radiometrically. U(VI) in the solution phase and that sorbed to the solid summed to 96 to 99 % of that introduced into the sample polycarbonate tubes. The calculated uncertainty in each value was 4 to 11%.

Batch reversibility experiments were performed with each sample. The hydroxyapatite was separated from the liquid by centrifugation. The supernatant was decanted and 25 mL of fresh 0.1M $KNO_{3,}$ at the appropriate pH level, was added to each tube. The samples were gently shaken for 60 days with the pH adjusted daily. Samples of the supernatants were collected and analyzed as previously described. Experiments with no added hydroxyapatite indicated there was negligible sorption by the polycarbonate centrifuge tubes, syringes, syringe filters or transfer pipettes.

3.0 Results and Discussion

3.1 Hydroxyapatite characterization

TEM analysis revealed a significant amount of information about the synthetic and cattle bone prepared hydroxyapatite (Figure 1 a-f). TEM of the synthetic hydroxyapatite indicated the material was comprised of small (30 to 50 nm) fibrous crystals. The TEM of the HA 500 indicated it was similar in morphology to the synthetic hydroxyapatite. The HA 500 was unsintered, and comprised of small (40 to 50 nm) fibrous crystallites with no minor phases. But, EDS analysis shows the apatite phase contains Ca, P, O and Si, modest amounts of C, and low levels of Na and Mg. The apatite phase of HA 700 is slightly sintered but remains porous and fine-grained. EDS analysis shows that HA 700 contains a minor phase rich in Mg and O which may include MgO and/or $Mg(OH)_2$. The apatite phase of HA 900 is well-sintered with a grain size in the 0.25-0.5 um range. EDS analysis of apatite crystals detected only Ca, P, O, and a low concentration of C.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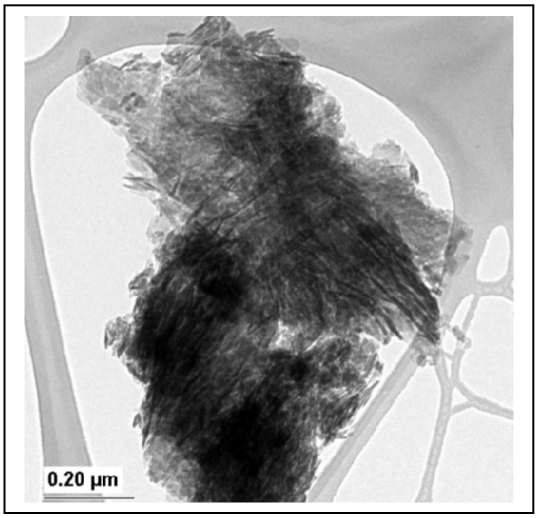
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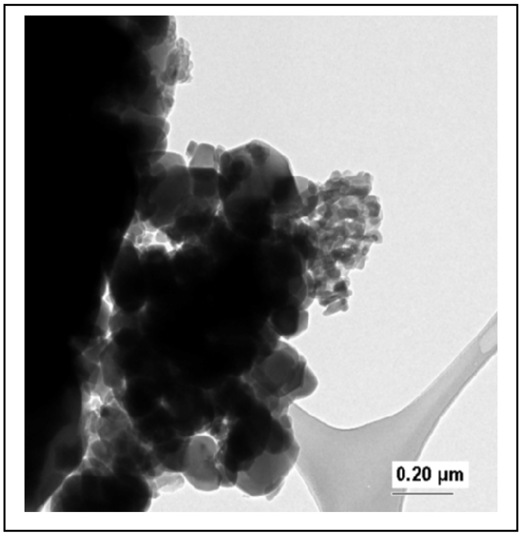
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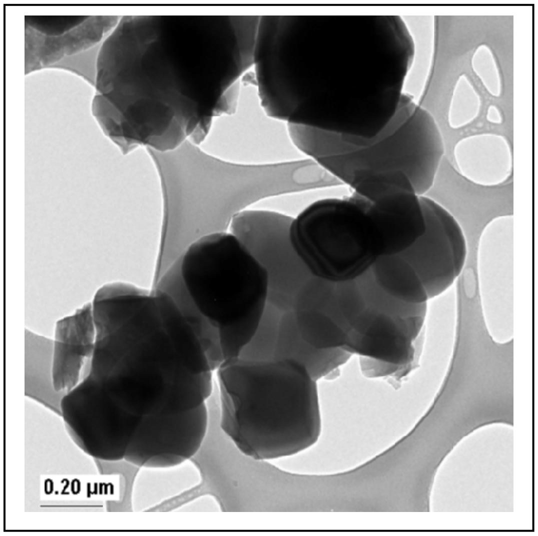
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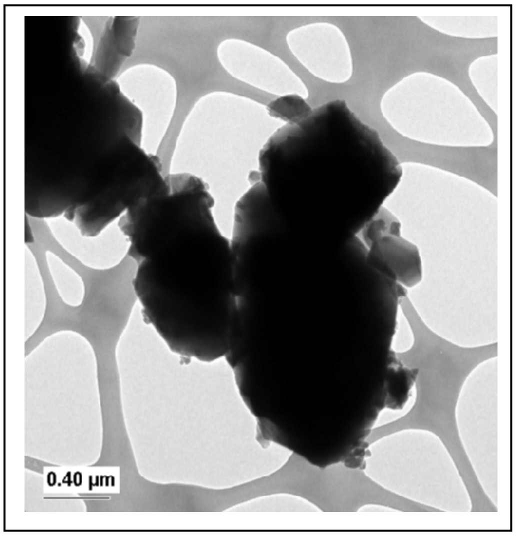
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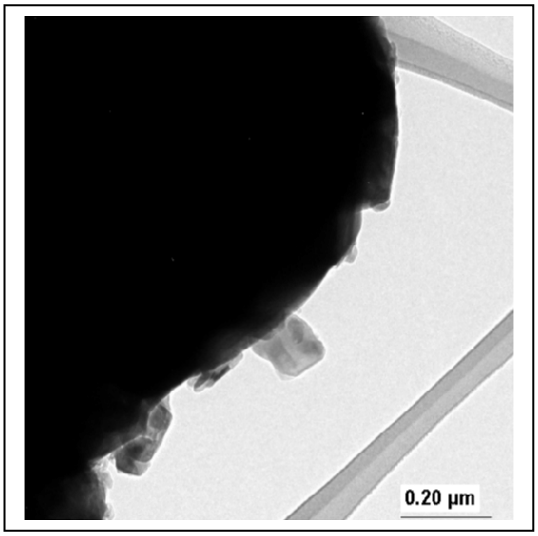
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Figure 1. TEM images of hydroxyapatites investigated in this work: a. synthetic hydroxyapatite, b. 500°C cattle bone hydroxyapatite, c. 700°C cattle bone hydroxyapatite, d. 900°C cattle bone hydroxyapatite, d. 1100°C cattle bone, and e. MgO crystals on the surface of 1100°C cattle bone hydroxyapatite.

Both the HA 900 and HA 1100 samples were well sintered. For the HA 1100 hydroxyapatite, cubic MgO crystals are easily seen on the surface of the hydroxyapatite crystals.

The XRD patterns (Figure 2) are typical for hydroxyapatite and generally show increased crystallization in the order HA 500 > HA SYN > HA 700 >HA 900> HA 1100. This order is consistent with the results from TEM and EDS analysis.

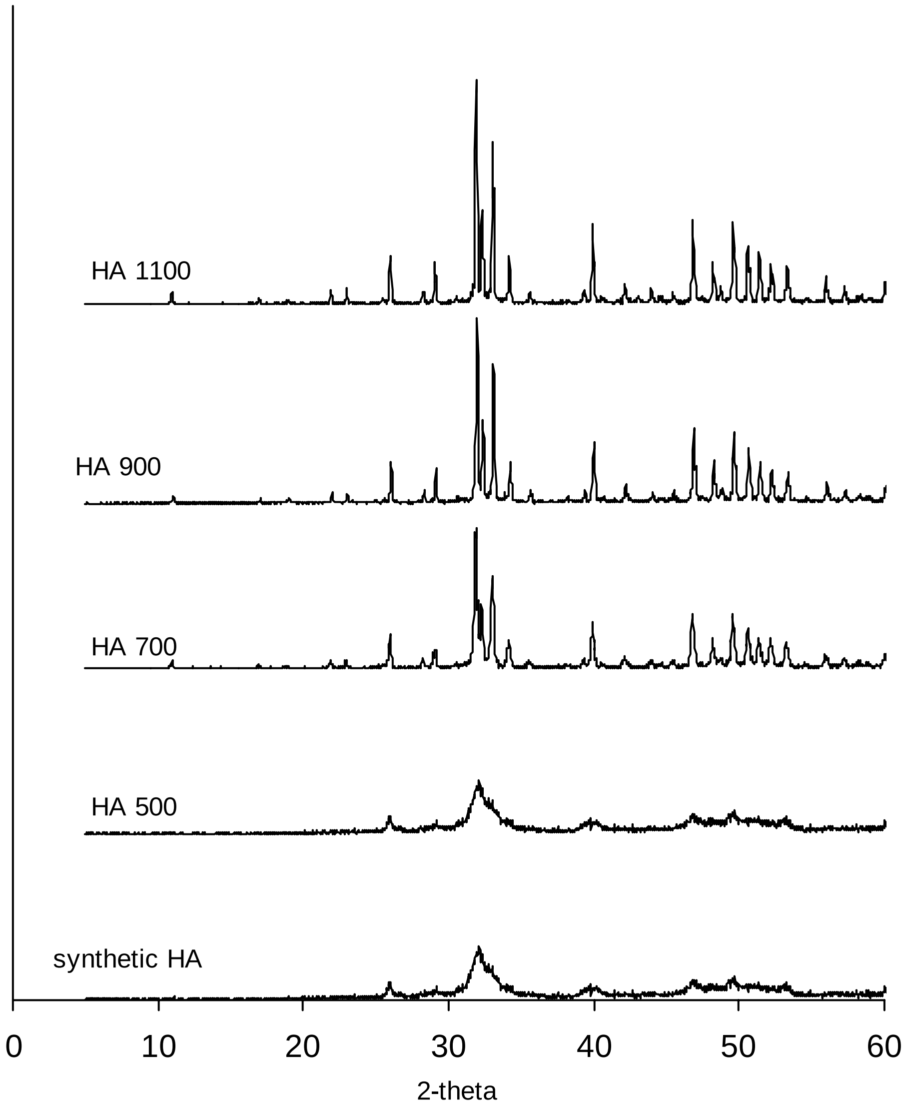

Figure 2. X-ray diffraction patterns for hydroxyapatites studied in this work. Patterns for cattle born hydroxyapatites illustrate the increase in crystallinity with increasing calcination temperature.

The FT-IR spectra are typical of apatite (Figure 3). For the cattle bone hydroxyapatites, an increase in resolution with increasing calcinations temperature is seen for the P-O absorption band at 620, 600, and 564 cm^{-1}. This can be attributed to the increase in crystallinity or the presence of impurities such as Mg or CO_3 in the hydroxyapatite structure. Also seen with increasing calcination temperature is a decrease in the intensity of the absorption bands at 873 and1114 cm^{-1} indicating a decrease in carbonate concentration. There was little water adsorbed to any of the hydroxyapatites indicated by the lack of absorption from 3000 to 4000 cm^{-1}. No absorption is seen at 865 cm^{-1} indicating the absence of significant amounts of HPO_4^{3-} in any of the hydroxyapatites.

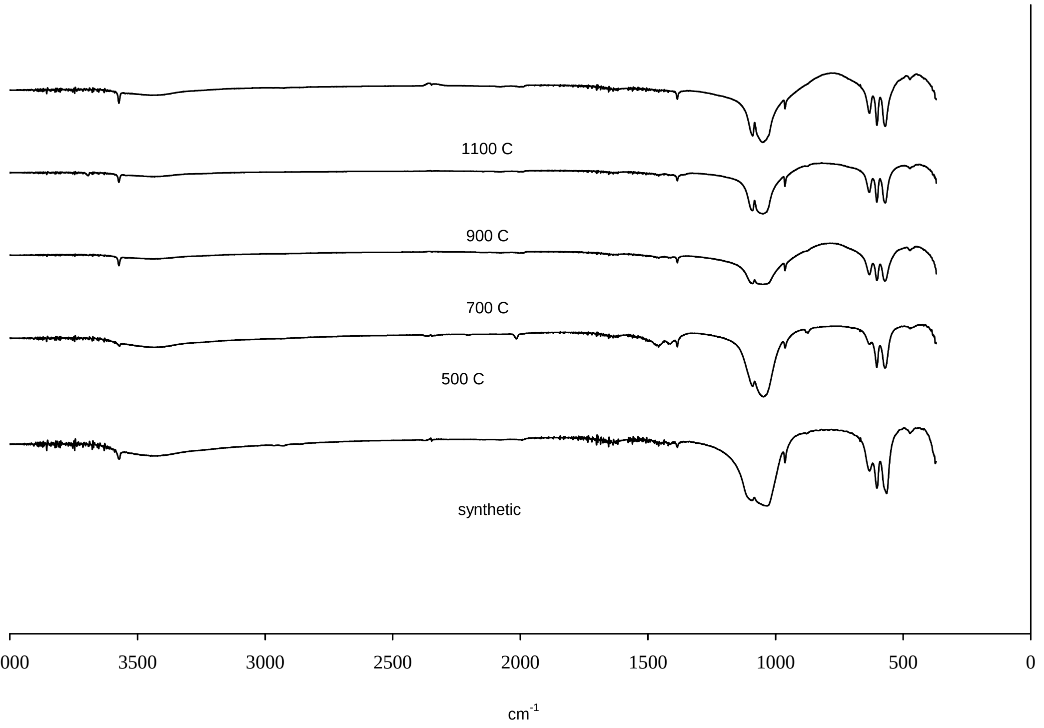

Figure 3. FT-IR for the hydroxyapatites studied in this work. For the cattle bone hydroxyapatites, an increase in resolution with increasing calcinations temperature is seen for the P-O absorption band at 620, 600, and 564 cm^{-1}. With increasing calcination temperature a decrease in the intensity of the absorption bands at 873 and1114 cm^{-1} indicating a decrease in carbonate concentration. No absorption is seen at 865 cm^{-1} indicating the absence of significant amounts of HPO_4^{3-} in any of the hydroxyapatites.

The degree of crystallization and solubility of the cattle bone hydroxyapatites was found to be inversely related to BET surface area where HA SYN , HA 500, HA 700, HA 900 and HA 1100 had surface areas of 76 m^2/g, 109m^2/g, 8.2 m^2/g, and 2.7 m^2/g, and 2.2 m^2/g, respectively. This is in agreement with the results of Nilce et al.[7]. Ca/P ratios for HA SYN, 500 HA, HA 700, HA 900, HA 1000 were 1.65, 1.55, 1.61, 1.62, and 1.64, respectively. The value for a theoretically perfect hydroxyapatite is 1.67. Hydroxyapatite solubility at pH 8.0 decreased significantly with calcination temperature (Table 1).

Table 1. Solubility of Hydroxyapatite at pH 8.0.
Ca and PO4 concentrations determined by ICP-MS or IC

hydroxyapatite	Ca^{2+} mmole/L	PO_4^{3-} mmole/L
synthetic	0.04	0.11
HA 500	0.12	0.28
HA 700	0.03	0.1
HA 900	0.02	0.07
HA 1100	0.01	0.05

3.2 Sorption Experiments

Sorption of U is expressed as distribution constants, K_d, in units of L/g given as:

$$K_d = (\text{moles U sorbed/g hydroxyapatite})/(\text{U concentration in solution, M})$$

Sorption of U was strong regardless of apatite type (Figure 4). K_d values exceeded 10^5 in the pH range of 6 though 8 but decreased as pH increased above 9. The decrease in U sorption above pH 9 is likely the result uranyl carbonate formation that has been documented to strongly affect sorption of uranium (Boult et al., 1998;). Interestingly, the sorption of U by the synthetic hydroxyapatite was less sensitive to pH than the bovine apatites. Nevertheless, K_d values remained above 10^4 even for the bovine apatites equilibrated at pH 11. Negligible amounts of U were released in desorption studies. Desorption, expressed as percent of sorbed U released back into solution, ranged from <0.001% to 0.1%. Although the hydroxyapatites examined in this work had different physical and chemical properties, variation in their sorption potential for U was minimal. These data clearly indicate that bovine apatites may be a viable economic alternative to the more costly synthetic apatites.

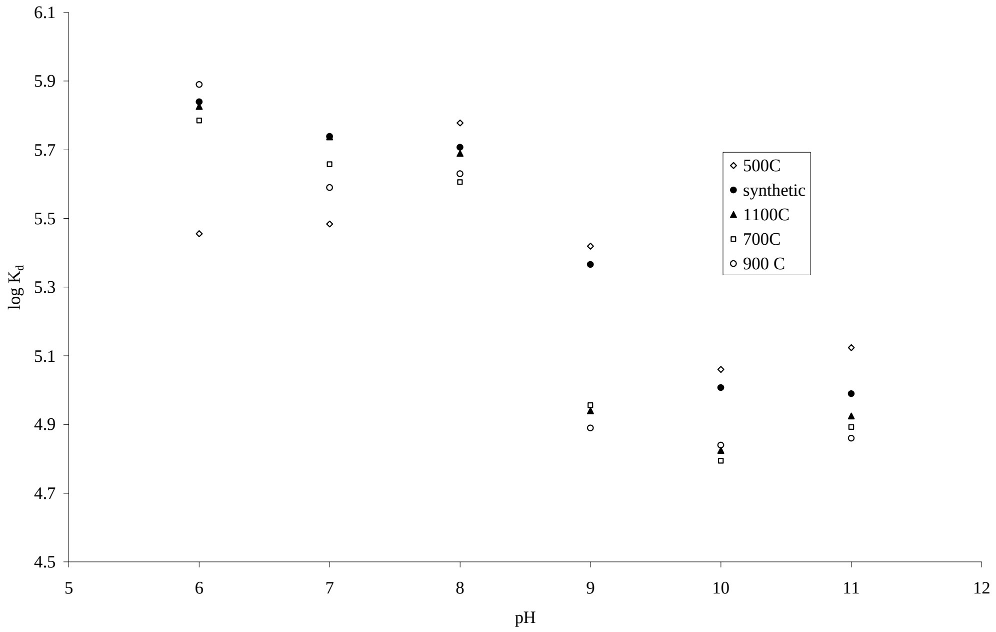

Figure 4. Sorption of uranium as a function of pH for synthetic and cattle bone derived hydroxyapatite. Initial U concentration was 5.1 x 10^{-6}M. Sorption is expressed as distribution constants K^d = (moles U sorbed/moles hydroxyapatite)/ U in solution.

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