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Evaluation of Fluorapatite as a Waste-Form Material: First Quarter Report, January 1 - March 31, 2005

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First Quarter Report 2004-5

Evaluation of Fluorapatite as a Waste-Form Material

01/01/05 – 03/31/05

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Project Description

Fluorapatite, fluorinated calcium phosphate, has been identified as a potential matrix for the entombment of the zirconium fluoride fission product waste stream from the proposed FLEX process. If the efficacy of fluorapatite-based waste-storage can be demonstrated, then new and potentially more-efficient options for handling and separating high-level wastes, based on fluoride-salt extraction, will become feasible. This proposal will develop a dual-path research project to develop a process to fabricate a synthetic fluorapatite waste form for the ZrF_4 , FP waste stream, characterize the waste form, examine its performance under environmental conditions, and correlate the behavior of the waste form with natural analogs. Characterization of the material will be accomplished through probing the molecular-scale electronic and geometric structure of the materials in order to relate them to macroscopic properties, with the goal of developing techniques to evaluate and predict the performance of different waste-form materials. Time and funding permitting, other waste forms for the zirconium fluoride, fission product salt waste stream will be examined and benchmarked against the fluorapatite matrix baseline.

Highlights of Accomplishments

- 1) Obtained SEM/EDS, FTIR and XRD for Zn-containing samples prepared using 75, 50 and 25% Ca/Zn molar ratios and the sintered sample of Ca/Zn molar ratio 75%. Additionally, XPS data were obtained for these samples together with a fluorapatite and a 100% Zn sample.
- 2) Prepared 4 different amounts of Zr-containing apatites using precipitation method and sintered these 4 samples at 1200 degrees of centigrade for one hour. SEM, XRD, FTIR and high temperature TGA/DSC data were obtained for these samples. A detailed analysis is in progress.
- 3) Determined the dependability of the Ca/P and (Ca +Sr)/P ratios in FAP based on the amount of Sr surrogate used in synthesis.
- 4) Preparation of Cu and Ni containing fluorapatite samples and powder diffraction spectra were obtained for the Cu-FAP sample.

Technical progress

During last quarter we investigated procedures to re-synthesize fluorapatite with some success. As mentioned before fluorapatite is a naturally occurring mineral with a strong crystal structure and it is an abundant mineral around the world. It is desirable to find a way to use natural apatite to synthesize nuclear waste bearing apatite rather than using the more expensive pure chemical reactants to begin with. This time we tried to re-synthesize fluorapatite at lower temperature after the first attempt at boiling temperature was partially successful. The re-synthesized sample was annealed and analyzed using the X-ray powder diffraction method and photoacoustic infra-red spectroscopy. We found that low temperature re-synthesis of apatite results in large quantities of undesired products such as calcium phosphate, unlike the high temperature synthesis (99% apatite). The annealed product is also brittle and less dense than synthetic (or natural) fluorapatite, which makes it less suitable as storage matrix.

Experiments have been carried out to determine the change of the Ca/P ratio in fluorapatite (FAP) based on the amounts of Sr surrogates included in FAP samples. Energy Dispersive X-ray Spectra (EDS) have been obtained for various Ca:Sr ratios in synthesized FAP samples. Fluorapatite has the chemical formula $Ca_5(PO_4)_3F$ and Ca and P maintains the atomic ratio of 1.667 ($=5/3$) in any pure apatite sample. The accuracy of this ratio has been used as an index of composition and thermal behavior.¹ The following samples have been synthesized and analyzed:

1. Fluorapatite (FAP)
2. Ca: Sr = 4:1 FAP
3. Ca: Sr = 3:2 FAP
4. Ca: Sr = 2:3 FAP
5. Ca: Sr = 1:4 FAP

The following table shows the observed atomic percentages and Ca/P ratios.

Compound	Ca [%]	Sr [%]	P [%]	(Ca+Sr)/P
Ca5-FAP	18.57	0.00	11.28	1.65
Ca4Sr-FAP	11.49	2.55	9.04	1.55
Ca3Sr2-FAP	13.21	8.30	11.63	1.85
Ca2Sr3-FAP	8.81	13.38	11.17	1.98
CaSr4-FAP	3.73	11.50	7.90	1.92

Even though the expected value for Ca/P is 1.667, only pure FAP has a value closest to the theoretical value. The ratios of Ca/P increase with increasing Sr content but starts at a lower value (1.55) when only one of the five Ca atoms is replaced by one Sr atom. This dependency is partially based on the considerable amounts of impurities ($\text{Sr}_3(\text{PO}_4)_2$ and $\text{Sr}_2\text{P}_2\text{O}_7$) formed during the synthesis process. Another possible reason might be the replacement of fluoride ions by CO_3^{2-} ions. This is a commonly found ion in fluorapatite and excessive inclusions of carbonate ions form carbonate-fluorapatite. The presence of the carbonate group was confirmed by FTIR spectra that were obtained for all the samples (2350 cm^{-1}). It might be necessary to use an inert atmosphere inside the synthesis flask to avoid contamination with CO_2 in order to get more accurate values.



Figure 1: SEM micrograph of sintered fluorapatite at 1200°C

The third experiment performed during the last quarter was the synthesis of Cu and Ni containing fluorapatite using the same procedure as for fluorapatite and Sr-apatite (strontium containing fluorapatite). One change was made to the original procedure by not adding NH_4OH to keep the pH value at 9. Instead, the pH was kept at 7 in order to prevent the formation of the $\text{Cu}(\text{NH}_3)_2^{2+}$ complex. The following table summarizes the initial compositions used for synthesis and weight load percentages.

Ion type	Initial concentration (mol/L)	Expected formula	Weight load (%)
Cu^{2+}	0.0392 (in 0.353M Ca^{2+})	$\text{Ca}_9\text{Cu}(\text{PO}_4)_6\text{F}_2$	6.16
Ni^{2+}	0.0196 (in 0.373M Ca^{2+})	$\text{Ca}_{9.5}\text{Ni}_{0.5}(\text{PO}_4)_6\text{F}_2$	3.14

The un-annealed Cu-apatite sample shown in figure 1 has a light blue color and the color faded off as the temperature was increased during the annealing process. The first annealed sample became “char” when reaching the annealing temperature of 1200°C . Then the sample was heated at several lower temperatures (600°C , 700°C , 800°C and 1100°C) with similar results. A power X-ray diffraction (XRD) pattern was obtained for the Cu-apatite sample that was annealed at 600°C and is shown in figure 2. The XRD pattern confirms the formation of an apatite structure and also shows the higher percentage of fluorite (CaF_2) in the product. The corresponding peaks for fluorite have been marked by arrows in the spectrum. A more refined procedure to synthesize Cu-apatite has to be found in order to reduce the fluorite by-product formation.

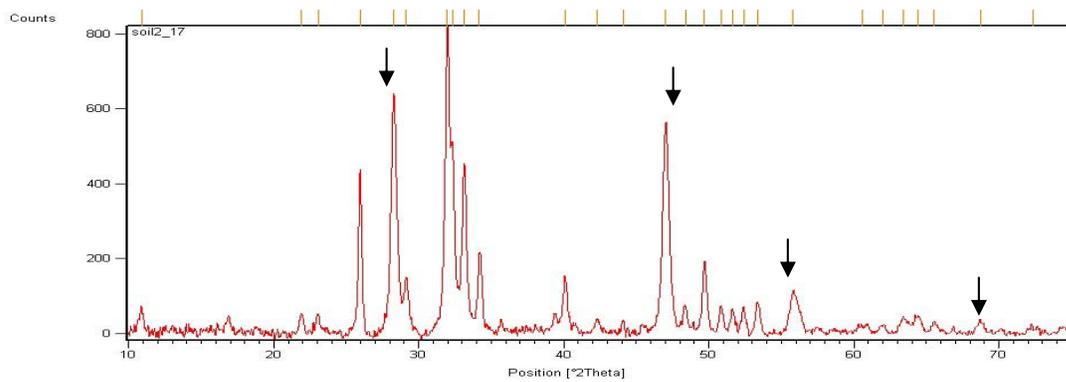


Figure 2. XRD patterns of fluorapatite before and after sintered at 1200⁰C

1. Champion, E. *et al*, Calcium phosphate apatites with variable Ca/P atomic ratio I. Synthesis, characterization and thermal stability of powders, *Biomaterials*, 23, 1065, (2002)