

## Task 16

# Evaluation of Fluorapatite as a Waste-Form Material

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## BACKGROUND

High Temperature Gas-cooled Reactor (HTGR) systems are being designed and evaluated as part of the Advanced Fuel Cycle Initiative. HTGR designs use a TRISO-coated fuel (a silicon-carbide and pyrocarbon composite coating) to provide much of the passive containment for radionuclides.

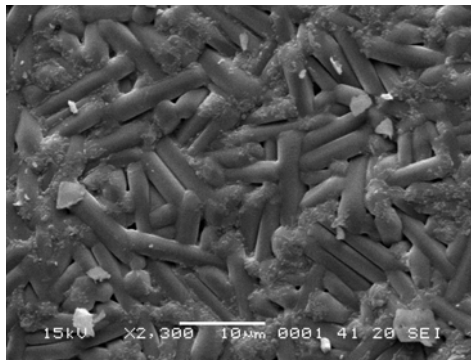
Argonne National Laboratory has proposed a new extraction procedure to handle TRISO-coated fuels, the Fluoride Extraction Process (FLEX). The FLEX process is designed to separate the uranium in the fuel from the actinides and most fission products by taking advantage of the unique properties of uranium hexafluoride ( $UF_6$ ). In the FLEX process, the used TRISO fuel is reacted with zirconium fluoride salt, forming  $UF_6$  and the fluoride salts of the actinides and fission products. At process temperatures, the  $UF_6$  volatilizes into a gas, and is released from the molten salt mixture. This leaves behind the actinides and most fission products in a fluoride salt, which is subsequently processed using pyrochemical techniques to recover the actinides and other long-lived fission products for transmutation. The  $UF_6$  is then cooled, causing it to sublime into solid form, which is then further processed for disposal or reuse.

The primary waste stream from the FLEX process is the fission products from the fuel, which are in a zirconium fluoride salt at the end of the process. Due to the fluorine in this waste stream, the fluoride salts are unsuitable for conversion into the traditional borosilicate waste glass. Therefore, without a suitable disposal form, this process can not be deployed.

## RESEARCH OBJECTIVES AND METHODS

The following were the specific research objectives:

- To develop a waste matrix for the disposal of the fission product waste stream from the FLEX process;
- To develop a process to make synthetic fluorapatite that incorporates the FP-bearing  $ZrF_4$  salt;
- To develop a fundamental understanding of the chemistry of this new waste form in order to better predict its long term behavior in a repository environment; and,



SEM micrograph of  $Ca_4SrFap$  (annealed sample).

- To develop a fundamental understanding of natural, fluoride-bearing mineral phases to use as natural analogs to bound the predicted behavior of the FLEX fission product waste stream.

The research effort was divided along two parallel paths: the *Fabrication Path*, led by collaborators at the Khlopin Radium Institute (KRI) in St. Petersburg, Russia; and the *Characterization Path*, led by researchers from UNLV.

The Fabrication Path focused on examining and evaluating various techniques for fabricating synthetic fluorapatite; synthesizing synthetic fluorapatite; and examining the impacts of waste loading and other fabrication process factors on the performance of the synthetic fluorapatite as a potential waste form.

The Characterization Path focused on adapting and refining the X-ray spectroscopy techniques currently used to characterize borosilicate glass for use in examining the fluorapatite system. This path also encompassed the examination of the ceramic and synthetic mineral waste forms created at KRI, with subsequent examination of these techniques to develop a molecular-level understanding of natural fluorapatite and other fluorine-bearing natural phases as natural analogs for the waste form. These techniques were also used to examine the changes in surface chemistry caused by environmental degradation of these materials.

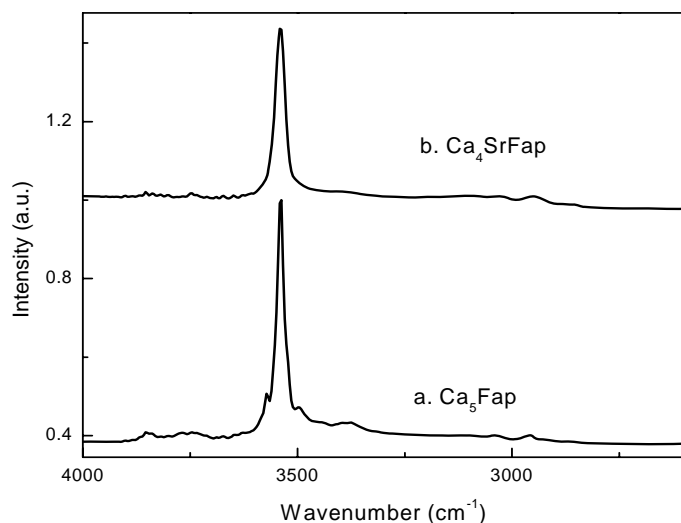
## RESEARCH ACCOMPLISHMENTS

### Microscopy Techniques:

- The microstructure of as-synthesized fluorapatite samples were characterized by transmission electron microscopy (TEM). The phase purity and crystallographic structure of these samples were first verified by X-ray powder diffraction with the help of Rietveld analysis.
- Different methods (solution-drop and microtome cutting) were used to make the samples for TEM analysis. The solution-drop method was suitable to analyze the crystallographic structure of the fluorapatite by high resolution TEM. Furthermore, the solution-drop method was successfully used to study the particle morphology of fluorapatite.
- The microtome cutting method allowed studying both particle shape and cross-sectional morphology of fluorapatite crystals. Microtome cutting, however, introduced periodical fringe artifacts in high resolution TEM imaging due to deformation effects on the material. Therefore, in order to completely characterize the microstructure and morphology of fluorapatite-type particles a combination of both sample preparation techniques was necessary.

### Calcium Substitution by Zinc:

- Substitution of calcium in fluorapatite by zinc is possible and was demonstrated to be concentration dependent. The phase purity of fluorapatite in the samples decreases with the increase in zinc substitution.
- A 25 mol % of zinc substitution leads to a single-phased fluorapatite, but the formation of a secondary phase was



*Infrared spectra of  $Ca_5Fap$  and  $Ca_4SrFap$  after annealing.*

identified when the zinc level increased to 50 mol %. A fluorapatite phase could not be identified in samples with 75 mol % and 100 mol % zinc substitution.

- The two samples synthesized using 25 mol % and 50 mol % of zinc showed some similar morphological and microstructural properties to that of phase-pure fluorapatite. However, the closest similarities to pure fluorapatite were identified in the 25 mol % sample.
- The 50 mol % sample shows a lower thermal stability that decreases with increasing zinc level. The low thermal stability of the 50 mol % sample is most likely due to the identified secondary chemical phase.
- The sintering properties of the 25 mol % sample are similar to pure fluorapatite. However, complete decomposition of the zinc-incorporated fluorapatite chemical phase in the calcined 25 mol % sample results in lower thermal stability than for phase-pure fluorapatite.

#### Calcium Substitution by Strontium:

- The synthesis of foreign cation-incorporated fluorapatite, in this case strontium ions, was achieved successfully. XRD powder patterns of fluorapatite and Sr-fluorapatite showed identical peaks except for slight peak shifts and peak merging.
- Increasing strontium content showed a linear relationship with unit cell dimensions, the relationship of which can allow one to measure unknown percentages of strontium in fluorapatite.
- It has been shown that Sr occupies only Ca sites and not P or O sites.
- Scanning electron microscope images of strontium-incorporated fluorapatite showed the formation of hexagonal crystals on the surfaces of most samples. Formation of

fluorapatite crystals has not been observed in the same samples before annealing at 1200 °C.

- Re-synthesis of apatite using natural fluorapatite as a starting material was achieved. The final product contained fluorapatite, chloroapatite and hydroxyapatite phases and it is inconclusive as to which was the major component.

#### **TASK 16 PROFILE**

Start Date: August 2002

Completion Date: August 2005

#### Theses Generated:

G.W. Chinthaka Silva, M.S., Chemistry, "Evaluation of Apatites as a Matrix for the Waste Stream of the Flex Process," June 2005.

Chirantha P. Rodrigo, M.S., Chemistry, "Synthesis and Characterization of Strontium Fluorapatite," August 2005.

#### Journal Articles:

G.W.C. Silva, L. Ma, O.A. Hemmers, and D.W. Lindle, "Micro-Structural characterization of precipitation-synthesized fluorapatite nano-material by transmission electron microscopy using different sample preparation techniques," *Micron*, 39/3, 269-274, 2007.

G. W. Chinthaka Silva, Oliver Hemmers, Ken R. Czerwinski, and Dennis W. Lindle, "Investigation of microstructure and thermal behavior of zinc-substituted fluorapatite" submitted to *Journal of Inorganic Chemistry*, 2008.

#### Conference Proceedings:

C.P. Rodrigo, G.W.C. Silva, O. Hemmers, D.L. Perry, and D.W. Lindle, "Evaluation of Fluorapatite as a Waste Form," ANS Student Conference, UW at Madison, WI, April 1-3, 2004.

G.W.C. Silva, D.L. Perry, A.L. Johnson, O. Hemmers, and D.W. Lindle, "Characterization of the thermal stability of apatites containing different cations," ANS Student Conference, University of Wisconsin at Madison, WI, April 1-3, 2004.

G.W.C. Silva, D.L. Perry, A.L. Johnson, O. Hemmers, and D.W. Lindle, "Characterization of the thermal stability of apatites containing different cations," Graduate and Professional Student Research Forum, UNLV, Las Vegas, NV, April 17, 2004.

G.W.C. Silva, O.A. Hemmers, and D.W. Lindle, "Characterization of the Thermal Stability of Zinc-containing Fluorapatite," ANS Student Conference, Columbus, OH, April 2005.

C.P. Rodrigo, O.A. Hemmers, and D.W. Lindle, "Characterization of Fluorapatite as a Waste Form," ANS Student Conference, Columbus, OH, April 2005.

#### **Research Staff**

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