2007

Evaluation of Fluorapatite as a Waste-Form Material

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Repository Citation

Lindle, D. W., Hemmers, O., Perry, D. L. (2007). Evaluation of Fluorapatite as a Waste-Form Material. 36-37.
Available at: https://digitalscholarship.unlv.edu/hrc_trp_separations/62

Task 16

Evaluation of Fluorapatite as a Waste-Form Material

D.W. Lindle, O. Hemmers and D.L. Perry

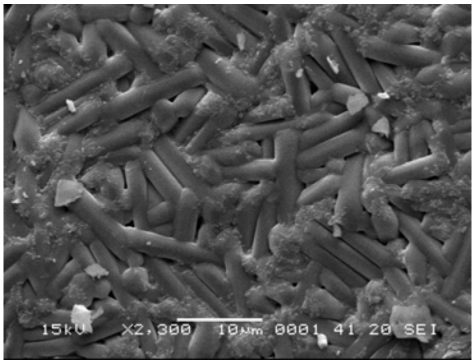
BACKGROUND

High Temperature Gas-Cooled Reactor (HTGR) systems are currently being designed and evaluated as part of the Advanced Fuel Cycle Initiative, both as a future nuclear reactor type (in the Generation IV reactor program) and as a potential system for burning plutonium in a dual-tier transmutation strategy. HTGR designs use a TRISO-coated fuel (a silicon-carbide and pyrocarbon composite coating) to provide much of the passive containment for radionuclides.

Although this fuel form is quite stable and comprises one of the key components in the safety performance of these reactor systems, TRISO-coated fuel is comparatively difficult to recycle. If HTGR systems are to be used as part of either the first tier of a transmutation strategy or as primary power reactors, the plutonium and other actinides in the used TRISO fuel must be processed to recycle plutonium and permit recovery of minor actinides and other fission products produced.

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 volatizes 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.



SEM micrograph of Ca_4SrFap (annealed sample).

This research attempts to develop a waste form for disposing of the zirconium fluoride fission product waste stream. Fluorapatite, a naturally-occurring fluorinated calcium phosphate, has been identified as a potential matrix for the entombment of this waste stream. 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.

RESEARCH OBJECTIVES AND METHODS

The following are the specific research objectives:

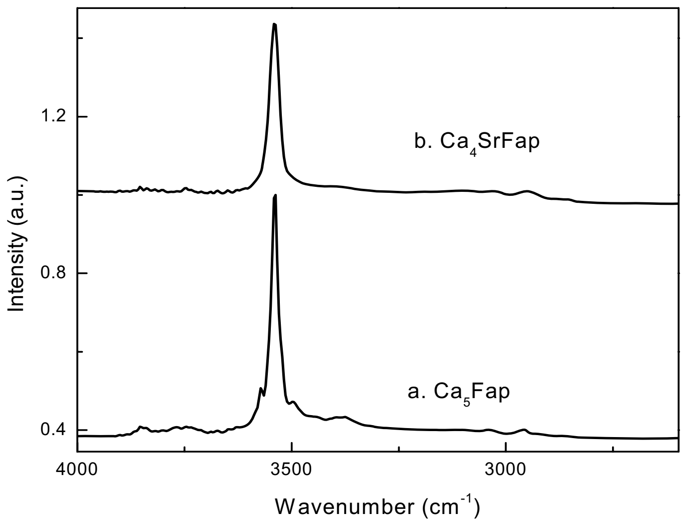
- To develop a waste matrix for the disposal of the fission product waste stream from the FLEX process;
- To develop a process to make synthetic fluorapatite that incorporates the FP-bearing ZrF_4 salt;
- To develop a fundamental understanding of the chemistry of this new waste form in order to better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

Originally, the research effort had been 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 is 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 is 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 will also be used to examine the changes in surface chemistry caused by environmental degradation of these materials.

Waste form development at KRI involves the formulation, synthesis, and examination of ceramic samples to investigate the impact of processing parameters and composition on material properties (e.g. homogeneity) and performance (via leach testing). The



IR spectra of Ca$_5$Fap and Ca$_4$SrFap after annealing.

most promising fabrication process developed will be used to synthesize the ceramic in varying compositions to examine the impact of process parameters, ceramic formulation, and waste loading on the final ceramic phase. Based on these experiments, a baseline composition and fabrication process will be established. Finally, alternate fabrication processes, compositions, and potential alternate waste matrices will be examined and compared against the baseline composition.

Waste form characterization carried out at UNLV employs state of the art techniques that characterize the molecular structure of both natural fluorapatite and fluoride-bearing minerals and the fluorapatite-based ceramic waste form. Changes in the surface/interfacial chemistry of these materials as they undergo reactions with species in the environment will also be examined to help develop a basis for understanding the corrosion chemistry that the waste form and its natural analogs may experience under repository conditions. The UNLV researchers also synthesized several surrogate samples with help of the KRI collaborators in order to study their properties.

RESEARCH ACCOMPLISHMENTS

Research highlights for the third year of the project can be summarized as follows:

- Applying x-ray spectroscopy and more-conventional characterization techniques (e.g., Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy (SEM), X-ray Diffraction, and Raman Spectroscopy) to synthesized samples of apatite and fluorapatite doped with surrogates and compared those with baseline measurements of "pure" materials.
- Chemically prepared several samples in which some of the calcium in apatite materials is substituted by non radioactive actinide surrogates (Zn, Sr, Yt, Cs, Cu, Ni, Zr) or elements produced by decay of actinides.
- Chemically prepared apatite samples containing different Ca:Surrogate weight ratios and studying the physical properties of these apatites with different calcium to phosphorous molar ratios.
- Studied metal-containing apatites and fluorapatites with the same cadre of characterization techniques noted above to assess the degree of incorporation and any changes in the physical and chemical structure of the materials.

ACADEMIC YEAR HIGHLIGHTS

- ♦ G. Silva presented a paper "Characterization of the Thermal Stability of Zinc Containing Fluorapatite" at the American Nuclear Society Student Conference, Columbus, OH, April 14-16, 2005.
- ♦ C. Rodrigo presented a paper "Characterization of Fluorapatite as a Waste Form Material" at the American Nuclear Society Student Conference, Columbus, OH, April 14-16, 2005.

FUTURE WORK

The work is completing its third and final year of the project with the two graduate students finishing their Masters degree. The Characterization Path, led by the UNLV team, has been performing baseline spectroscopic studies of natural and pristine (no artificially added impurities) apatite materials as well as of surrogate loaded samples. The studies found that it is possible to load surrogates successfully into apatites and that it is important to control the by-products such as metal phosphates and metal fluorites that weaken and/or destroying the crystal structure. The amounts of surrogates that can be loaded strongly depend on the type of surrogate and these amounts still need to be determined. The ultimate goal is to use these techniques to achieve a molecular-level understanding of fluorapatite and other fluorine-bearing phases as natural analogs for waste-form materials. These techniques will also be used to examine changes in surface chemistry caused by environmental degradation.

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