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Evaluation of Fluorapatite as a Waste-Form Material

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Project Title: Evaluation of Fluorapatite as a Waste-Form Material

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- Co-Principal Investigator:** Dale L. Perry (Lawrence Berkeley National Laboratory)
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- International Collaborators:** **V.G. Khlopin Radium Institute**
St. Petersburg, Russia
- Boris E. Burakov (KRI Principle Investigator, Head of Mineralogical Group)
- Evgeniy B. Anderson (KRI Principal Co-Investigator)
- Alexander Rimsky-Korsakov (KRI Director General)
- Collaborators (UNLV):** Gary S. Cerefice (Research Scientist, Harry Reid Center)
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- TRP Research Area:** Separations
- Requested Funds:** \$104,724 (Year Two)

Funding Profile:

Academic Year	2002-2003	2003-2004	2004-2005
UNLV Task 16	\$106,120	\$104,724	~\$100,000
KRI Subcontract	\$74,500	\$62,000	\$0
Total	\$180,620	\$166,724	~\$100,000

Abstract:

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 is for renewal of the UNLV portion of 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. At UNLV, characterization of the material will be accomplished by probing 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 performances 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.

Work Proposed for Academic Year 2003-2004 (8/03 – 7/04), Goals, and Expected Results:

The work in the second year of the project will progress along two parallel paths: Fabrication and Natural-Analog Characterization. The Fabrication path, lead by the KRI team, will examine and evaluate various techniques for the fabrication of synthetic fluorapatite, will synthesize fluorapatite, and will begin the examination of waste loading and fabrication process factors on the synthetic fluorapatite. 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 a prelude to applying the same techniques to more-complex fluorapatite-based waste forms. The ultimate goal is to use these techniques to achieve a molecular-level understanding of natural fluorapatite and other fluorine-bearing phases as natural analogs for the waste-form materials. These techniques will also be used to examine changes in surface chemistry caused by environmental degradation. Preliminary samples of synthetic fluorapatite from the Fabrication path will be examined when available from the international collaborators.

Background and Rationale:

One of the more promising transmutation strategies currently proposed is the dual-strata approach in which plutonium is separated from the minor actinides and burned in reactors while the minor actinides are transmuted using an accelerator-driven system. This method allows energy value to be recovered from the plutonium and reduces the throughput requirements and complexity of the accelerator-driven transmutation system, which would have a smaller volume of material to handle and would not need to provide electricity for the grid.

Among technologies under consideration for the plutonium-burning reactor systems are the new-generation High-Temperature Gas-Cooled (HTGR) reactor designs, such as the Pebble-Bed Modular Reactor (PBMR) and the PRISM HTGR design. Among other attributes, both designs use a TRISO-coated fuel (a silicon-carbide and pyrocarbon composite coating). This fuel form is very stable and is one of the key components in the safety performance of these systems. However, TRISO-coated fuel is more difficult to recycle than other fuels under consideration. Because the plutonium-laden fuel in the second strata will need to be processed to recycle unburned plutonium and to recover for transmutation minor actinides and other fission products produced in the fuel cycle, it is essential the fuel is easily reprocessed. For this purpose, ANL has developed a new, fluoride-salt-based extraction procedure to handle TRISO-coated fuels known as the Fluoride Extraction, or FLEX, Process.

A potential problem with the FLEX process is the primary waste stream is a zirconium-fluoride (ZrF_4) salt containing approximately 15 wt% fluoride salts of fission products (Cs, Sr, rare earths, *etc.*; composition of waste expected to be typical of fission products from commercial spent nuclear fuel; technetium). Fluoride salts are unsuitable for conversion into traditional borosilicate waste glass currently targeted for High-Level-Waste (HLW) disposal in a geological repository. The goal of this project is to develop a waste form for the disposal of this fission-product salt-waste stream, resolving the waste-stream management problem facing the FLEX process, and allowing the national spent-fuel management program to further examine, develop, and potentially deploy a promising new technology.

Research Objectives and Goals:

The research objectives are:

- 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

The goals are:

- To provide a level of understanding of the chemistry involved in the corrosion/dissolution of fluoride-bearing minerals and waste forms
- To develop experience with and a base of knowledge for the fabrication of fluoride-bearing matrices
- To develop a knowledge base to assist others in predicting the impact the FLEX process waste will have on the performance of a HLW repository

Technical Impact:

The proposed work will make a major contribution to the fields of waste management and materials science through the development and characterization of the fabrication, molecular structure, performance, and corrosion mechanisms of fluoride-containing minerals and ceramics. The waste matrices and fabrication processes developed and examined through this work will serve to reduce, or even eliminate, one of the major hurdles facing molten-salt fuel-processing strategies; *i.e.*, how can the salt wastes be stabilized for disposal. The characterization effort will expand our understanding of molecular structure of fluorapatite and other fluoride-bearing mineral and ceramic phases, and will deepen our understanding of bulk and surface processes during environmental degradation of these materials.

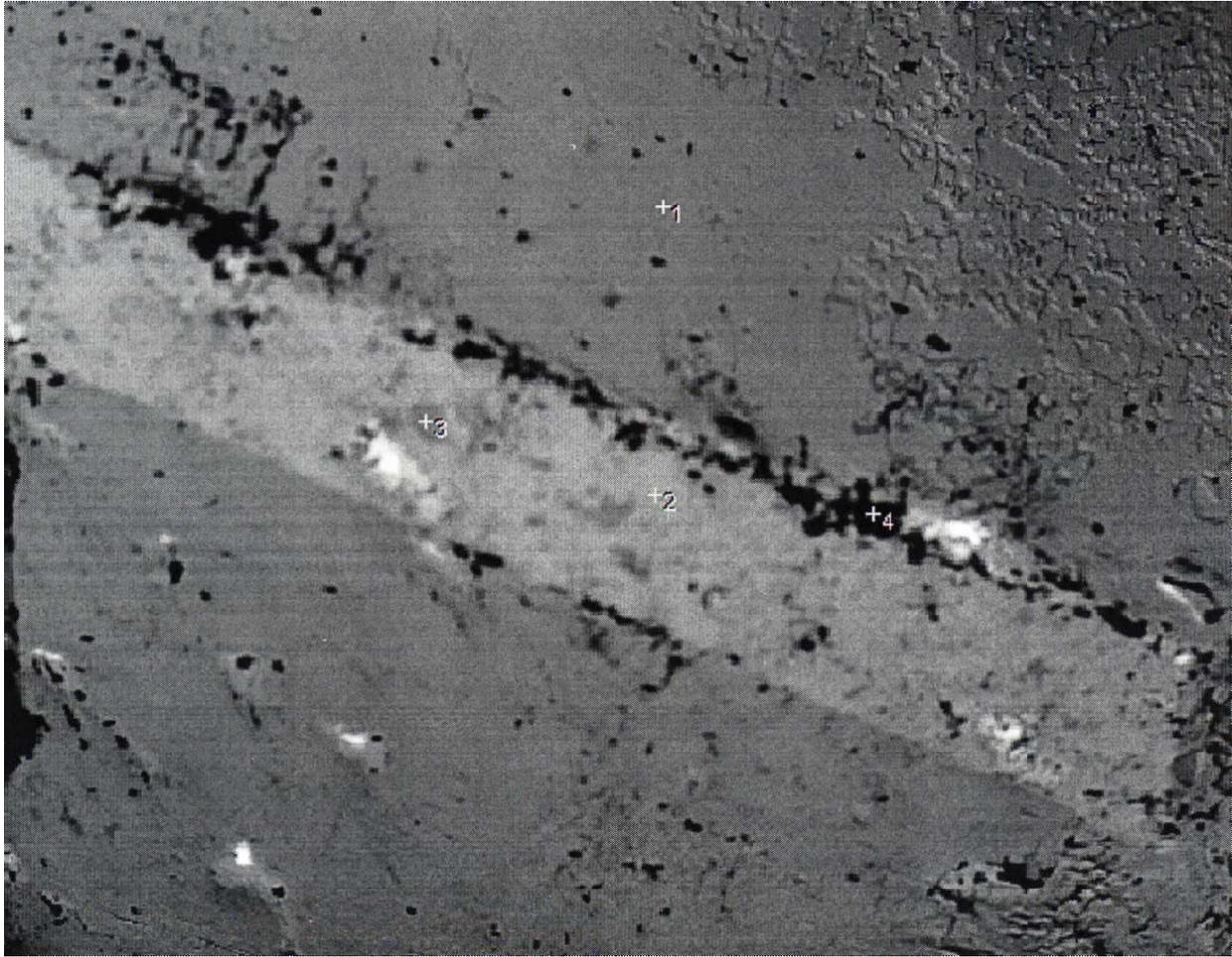
Research Approach:

The research to develop and understand a fluorapatite-based waste matrix for the ZrF_4 -salt fission-product waste stream from the FLEX process will take place along two parallel paths: waste-form development, and waste-form characterization. The waste-form-development work will take place primarily at the Khlopin Radium Institute, and will be led by the KRI Principal Investigator, Dr. Rimsky-Korsakov. It is described in a separate proposal. The waste-form-characterization work will take place primarily at UNLV and using UNLV x-ray facilities at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). The characterization work is led by PI Lindle and co-PI Perry.

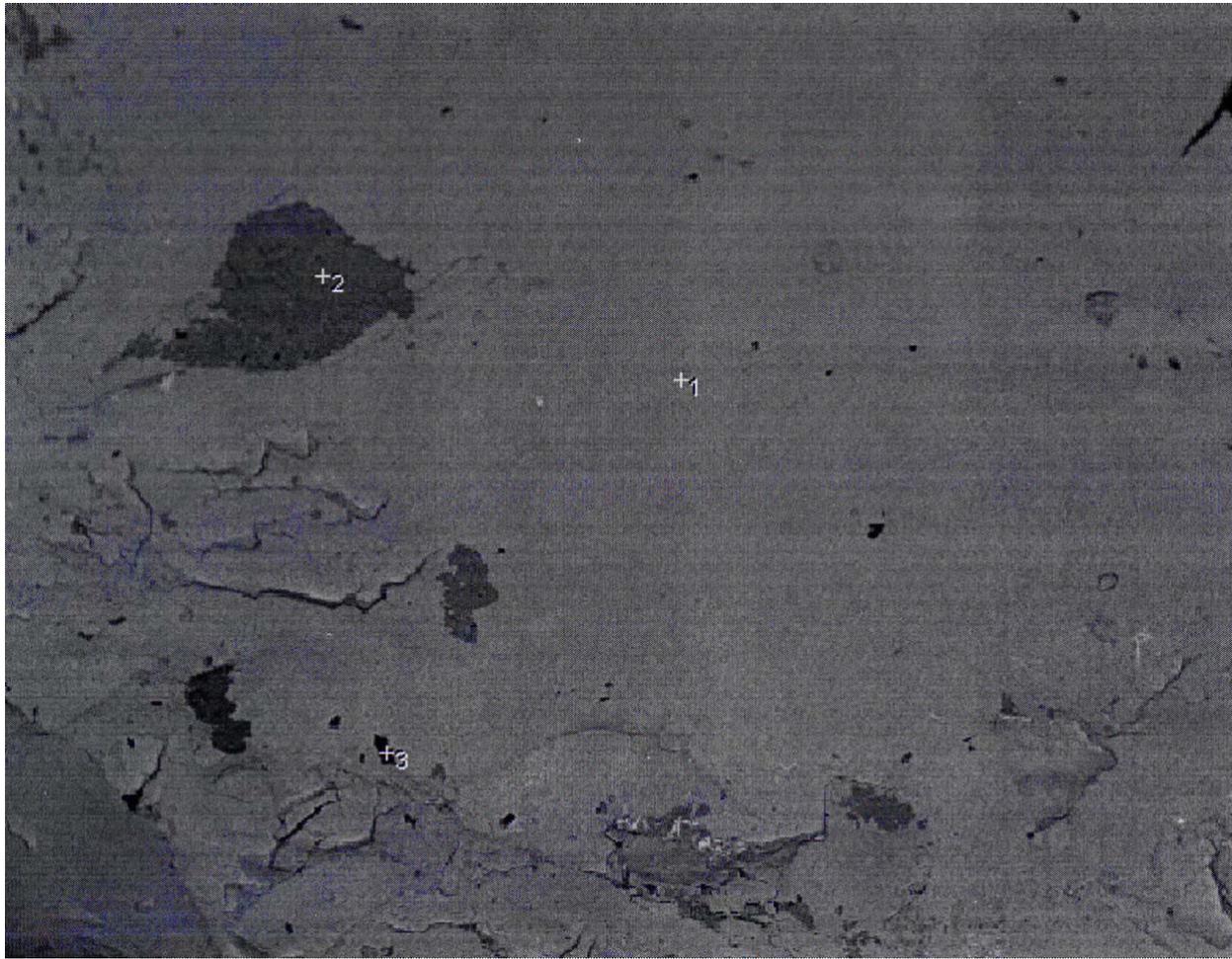
Results from Year 1

Work at UNLV in Year 1 of the project focused initially on training two new UNLV graduate students in the general aspects of x-ray spectroscopy and more-conventional characterization techniques (*e.g.*, FTIR, SEM, XRD, Raman spectroscopy) as well as apatite chemistry and materials properties. Natural crystals of apatite and fluorapatite, as well as commercially available hydroxyapatite powder, were then obtained, and baseline measurements of these “pure” materials using a variety of spectroscopic techniques were begun. The need for baseline measurements stems from the nearly complete lack of published work on these materials using molecular-scale characterization methods; before applying such techniques to waste-form materials, we must first understand the basic backbone material(s) of the waste-form matrix. To date, baseline measurements have been performed using FTIR, Raman, SEM, XRD, and XPS instruments at UNLV on the crystal samples shown in the photographs below, and on hydroxyapatite powder. Examples of SEM and XPS data on these samples also are attached. These results illustrate the potential of natural crystals to act as natural analogs of the waste forms because the crystals contain inclusions of species, such as Ni, which can be treated as surrogates for studying the true waste forms. Understanding chemical and physical properties of naturally included materials in apatite and fluorapatite will provide a bounty of information about waste-form chemistry, structure, and long-term efficacy. During the remainder of Year 1, more-detailed baseline measurements will be made with some of the in-house techniques, and the graduate students will each spend one month at the ALS to study the same samples using synchrotron-radiation-based x-ray techniques. By the end of Year 1, a solid set of baseline measurements should be available. Some chemistry experiments on incorporating contaminants into pristine apatite materials also will be initiated at UNLV this summer.



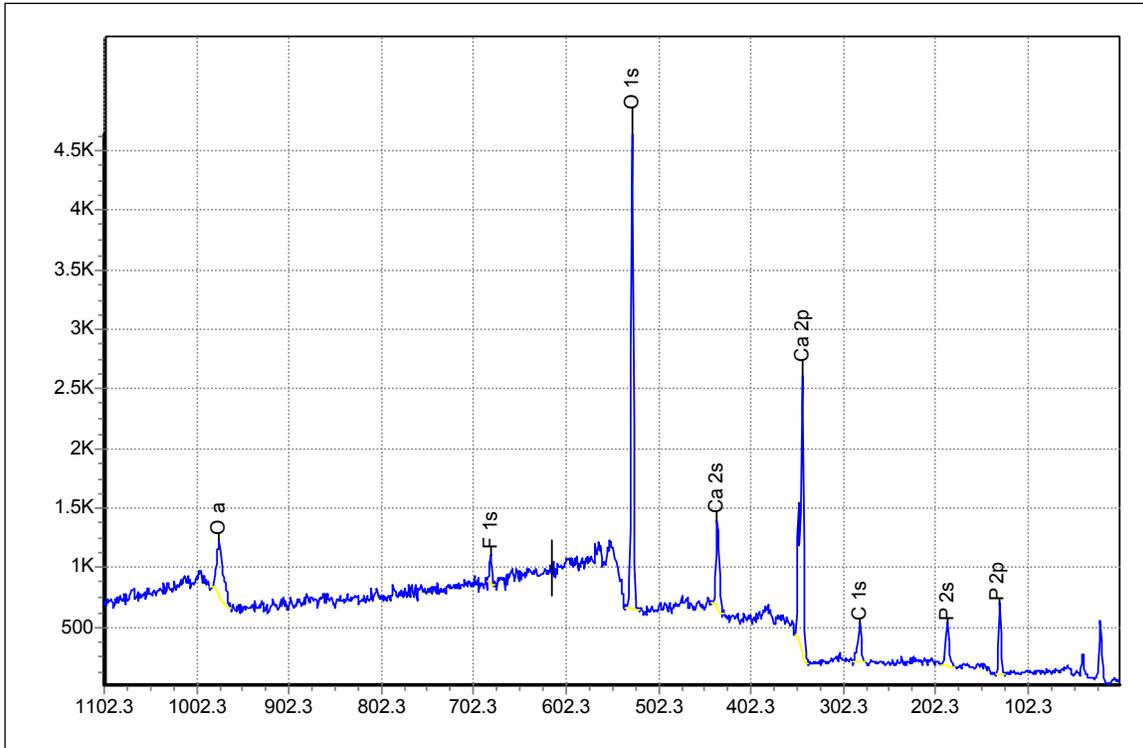


Green Colored Crystal (Fluorapatite)			
Location (1)		Location (3)	
Element	Percentage	Element	Percentage
O	54.20	O	36.87
F	7.67	F	4.02
P	12.97	Mg	0.01
Ca	25.11	Si	0.01
Ni	0.05	P	18.05
and Trace amounts of other elements		Cl	0.16
		Ca	40.83
Location (2)		Fe	0.02
Element	Percentage	Ni	0.02
O	54.00	and Trace amounts of other elements	
F	7.90		
P	12.93		
Ca	25.03		
Fe/Ni	0.14		
and Trace amounts of other elements			



White Colored Crystal (Fluorapatite)				
Location (1)			Location (3)	
Element	Percentage		Element	Percentage
O	44.23		F	72.43
F	9.13		Na	2.96
Na	0.20		Mg	1.03
P	15.08		Si	0.93
Ca	31.49		P	5.95
K	0.13		S	2.09
and Trace amounts of other elements			Cl	1.73
Location (2)			K	0.79
Element	Percentage		Ca	11.62
O	57.45		Ti	0.27
F	6.93		Mn	0.10
Ca	34.49		Ni	0.12
and Trace amounts of other elements			and Trace amounts of other elements	

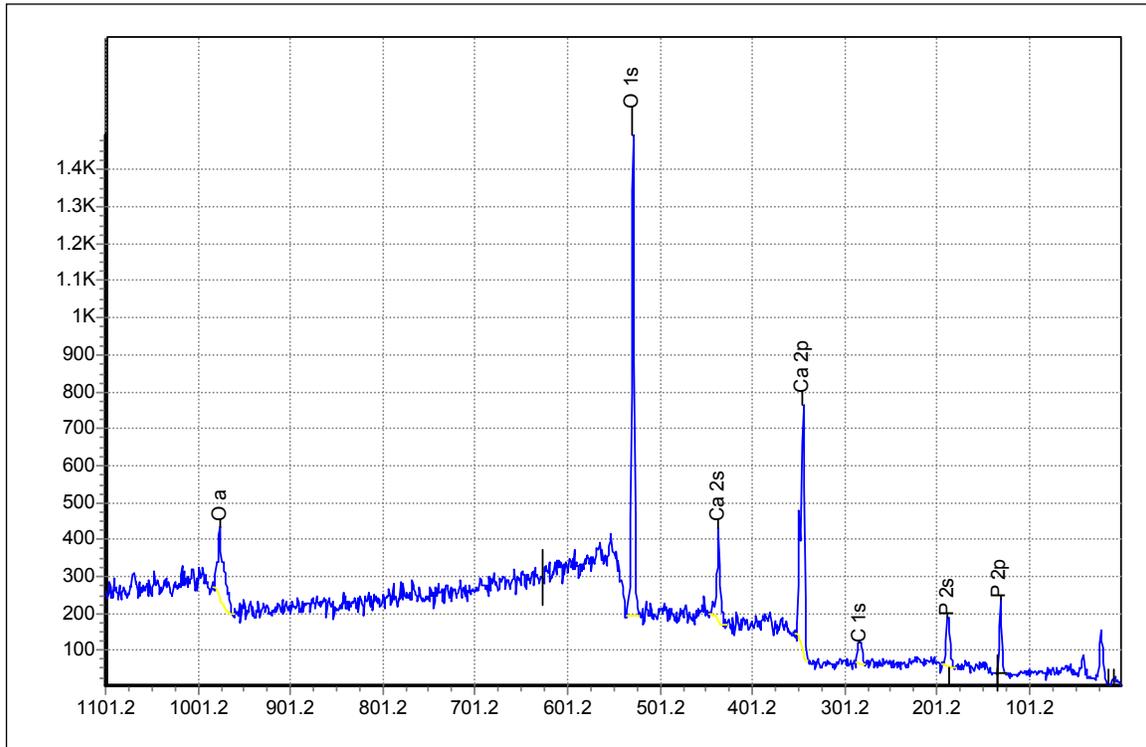
XPS data for Crystal (clear) of apatite:



Composition table

XPS Line	Chem Shift	Adj'ed Be	Norm Area	Atom %
C 1s	.000	284.600	84.682	1.139
O 1s	-1.056	530.944	319.989	4.302
Ca 2p	-.074	346.926	127.994	1.721
F 1s	-1.818	684.182	14.138	.190
P 2p	-2.504	132.496	88.310	1.187

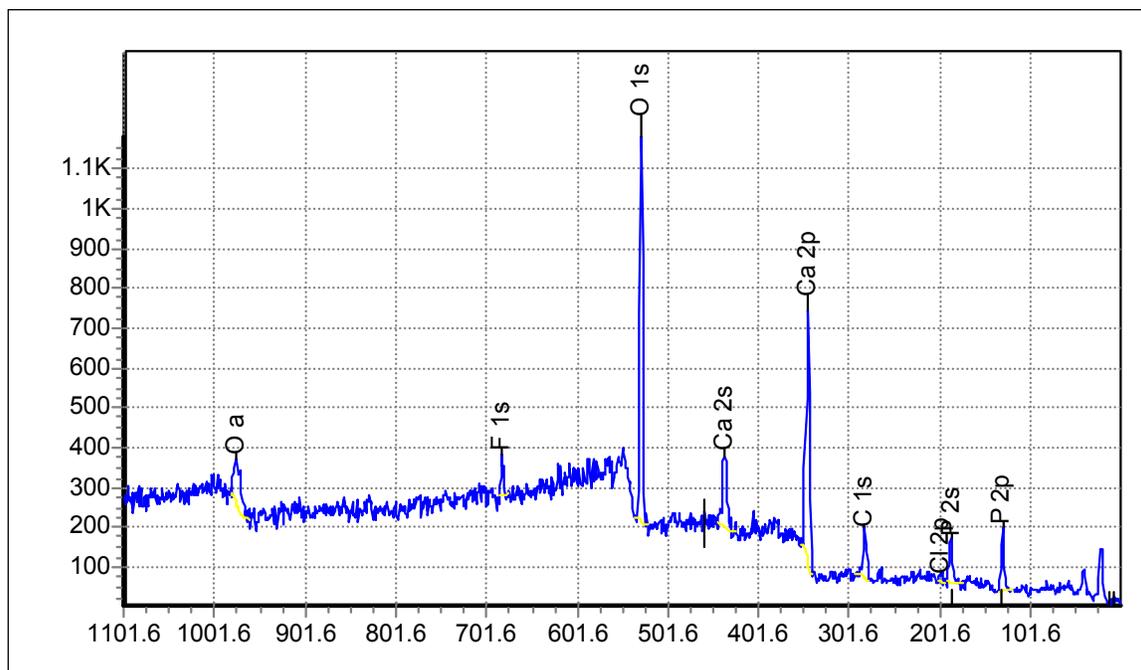
XPS data for Hydroxyapatite:



Composition Table

XPS Line	Chem Shift	Adj'ed Be	Norm Area	Atom %
C 1s	-.001	284.599	18.412	9.142
O 1s	-1.527	530.473	114.995	57.098
Ca 2p	-.640	346.360	38.265	18.999
P 2p	-2.844	132.156	29.728	14.761

XPS data for Fluorapatite:



Composition Table

XPS Line	Chem Shift	Adj'ed Be	Norm Area	Atom %
C 1s	.003	284.603	33.995	16.494
F 1s	-1.607	684.393	6.006	2.914
O 1s	-1.050	530.950	95.982	46.569
Ca 2p	-.210	346.790	39.869	19.344
Cl 2p	.068	200.068	2.062	1.000
P 2p	-2.415	132.585	28.192	13.679

Due to complications in setting up the subcontract between UNLV and the Khlopin Radium Institute, the contract for the work described in the Fabrication path was not initiated until May 2003. The first year's work scope for this subcontract will continue in FY03, through May 2004.

Plans for Year 2

State-of-the-art x-ray spectroscopy and spectromicroscopy techniques will be employed to characterize molecular structure of both natural fluorapatite and fluoride-bearing minerals and the fluorapatite-based ceramic waste forms. Changes in the surface/interfacial chemistry of these materials as they undergo reactions with species in the environment also will be examined to help develop a basis for understanding corrosion chemistry the waste form and its natural analogs may experience under repository conditions. Inclusion of molecular-scale characterization of fluorapatite materials in the research approach is necessary to fully understand and predict macroscopic properties and functionality of the materials. Previous studies of fluorapatite using different types of spectroscopy and microscopy have demonstrated this approach yields data vital for predicting performance and integrity of a target compound. Molecular-based reaction mechanisms, crucial to the design of useful fluorapatite materials, have been devised for reactions and thermal stability of apatite and apatite-related materials as well as decomposition into mixtures of other products. It is now known very slight alterations in molecular composition of these materials affects stability, mechanical integrity, and other performance characteristics. As a result, a rigorous molecular-based understanding of apatites and their fluorinated derivatives is needed in order to properly model the materials and their applications.

To continue to move toward this overarching goal, work in Year 2 will finalize creation of the baseline spectroscopic information for the "pure" apatite materials, and detailed measurements with synchrotron-radiation-based x-ray techniques will be done in earnest. With the powerful capabilities available at the ALS, we expect to be able to see components of natural apatite crystals and waste-form materials hitherto unmeasurable with conventional techniques. Such information from natural crystals will provide excellent comparisons to the species to be incorporated into waste forms. All of this work will be a prelude to studying apatite materials incorporating wastes and waste surrogates fabricated by our KRI colleagues, providing a direct connection between molecular-scale understanding and waste-form processing. Finally, the chemistry of waste-form incorporation will be studied at UNLV by performing a few 'simple' benchmark experiments under well-defined conditions; mixtures of well-characterized materials, both apatite and waste (or surrogate), will be chemically or physically prepared, then subjected to the same battery of spectroscopic techniques used for the baseline measurements from Year 1. The goal is to understand the structure of the resulting materials, as well as the specific chemical or physical processes by which they form. This information can then feed into spectroscopic studies of true waste-form materials, such as those to be fabricated at KRI.

The work in the Fabrication path will also be continued in FY03. The subcontract with KRI will run through May 2003, and should encompass the preliminary work for the fabrication of synthetic fluorapatite. The details of the second work scope, for FY03 (expected to begin May 2004), will be determined based on the results from the first work scope, but are expected to include the detailed analysis of the impact of fabrication parameters, such as waste loading, sintering temperatures, etc., on the performance and molecular structure of the synthetic waste forms.

Expected Technical Results:

- Development of a fluorapatite-based waste form for the FLEX process fission product waste stream
- Characterization of the molecular structure and corrosion behavior of natural fluorapatites
- Characterization of the molecular structure and corrosion behavior of fluorapatite-based waste forms
- Development of experimental techniques to predict the general efficacy of waste-form materials

Capabilities

UNLV and LBNL:

All of the equipment required for the proposed research is available to the PIs; no equipment request is being made to TRP as part of this proposal.

The UNLV PI has access to a variety of state-of-the-art instrumentation for materials research, including: (1) a stand-alone X-ray Photoelectron Spectroscopy (XPS) apparatus; (2) a Near-Edge X-ray Absorption Fine Structure (NEXAFS) chamber for mapping chemical structure of a sample with micron spatial resolution; and (3) two high-resolution X-ray Emission Spectroscopy (XES) instruments covering the ranges 100-800 eV and 2000-6000 eV, exactly the energy regions needed to probe the elemental species in fluorapatite samples. In the near future, the XPS analyzer in (1) will be adapted to apparatus (2) to allow micro-XPS experiments. Lindle also has preferred access to two high-resolution x-ray beamlines at the ALS, spanning the photon-energy range 100-6000 eV. This range includes core-level thresholds for all elements in the fluorapatite materials of interest (Ca, P, O, F, C) as well as in the waste materials (Cs, Sr, rare earths), allowing the full complement of x-ray techniques to be applied. Other equipment is available at UNLV, such as an x-ray-diffraction system in the lab of Prof. Malcolm Nicol and a second, higher-spatial-resolution XPS apparatus housed at DRI.

At LBNL, instrumentation for determination of sample compositions includes two scanning-electron microscopes (SEM), one for analytical work and one for high-resolution work. An ISI WB-6 microscope is coupled to a KeveX energy-dispersive x-ray analyzer capable of detecting characteristic x-rays for elements heavier than $Z = 9$ in regions as small as one micron. A second SEM, ISI Model DS-130, is available for still higher resolution. Atomic-resolution microscopy is available through the National Center for Electron Microscopy (NCEM) at LBNL, including the One Angstrom Microscope and the Spin-Polarized Low-Energy Electron Microscope. Ultra-high-sensitivity spectroscopy and spectromicroscopy techniques are available at the ALS, including beamlines for x-ray fluorescence, FTIR, and XPS. Appropriate laboratories and facilities are available at LBNL for handling and manipulation of solid-state compounds including those comprised of heavy-metal ions.

We emphasize the necessity of using x-ray facilities at the ALS; it is a unique national asset with unparalleled x-ray flux, brightness, and beam collimation in the photon-energy range needed for this program. Quite simply, the proposed research cannot be fully accomplished without performing experimental work at the ALS. Despite partial reliance on the ALS national-user facility, it is important to realize existing UNLV efforts and instrumentation at the ALS are fully recognized by the relevant communities as components of UNLV research programs, rather than as DOE or LBNL programs; the ALS serves solely as a key tool, just as a research-quality laser might in physics experiments.

KRI

Since 1990 the Laboratory of Applied Mineralogy and Radiogeochemistry of V.G. Khlopin Radium Institute (KRI) has studied different types of crystalline host-phases for use as potential waste matrices, and for the immobilization of actinides for geological disposal. The lab has significant experience in waste form development, including the development of actinide (An)-doped ceramics based on the following host-phases: zircon $[(Zr, An, \dots)SiO_4]$, zirconia $[(Zr, Hf, An, \dots)O_2]$, monazite $[(Ce, La, An, \dots)PO_4]$, and garnet $[(Y, Ca, An, \dots)_3(Al, \dots)_5O_{12}]$. This unique expertise will allow the Applied Mineralogy group not only to develop a waste matrix for the ZrF_4 -fission product salt waste stream, but will also prove vital in evaluating the process for use with highly radioactive solutions. If necessary, this experience will also allow for the inclusion of technetium and minor actinides to directly evaluate their impact on the waste matrix without needing to bring in additional collaborators. The Laboratory of Applied Mineralogy and Radiogeochemistry also has the experinec and facilities to examine the material properties of these waste forms and to examine the leach resistance/environmental performance of the various compositions to be developed.

The following are the methods and equipment to be used in the research effort:

- Quantitative XRD analysis (using "Geiger-Flex" Rigaku XRD Spectrometer) to identify crystalline phases and their amounts in matrices of actinide-doped and non-radioactive ceramics. KRI developed the original method of precise XRD analysis for highly radioactive materials.
- The chain of glove boxes equipped with the following: ball mill, cold press, calcinations furnaces, and ceramic synthesis furnaces. These boxes are designed to handle up to 2 grams of ^{239}Pu and 0.2 g ^{238}Pu .
- Scanning electron microscopy (SEM) combined with microprobe analysis (EPMA) and cathodoluminescence (CL) spectrometry (using MS-46 Camebax with installed original CL-spectrometer) will be used to determine chemical composition of actinide host phases and separated actinide species. In some cases the CL method allows the determination of the valence state of the actinides and other elements incorporated by the crystalline materials.

- Special Teflon™ vessels and thermostatic ovens to perform MCC-1 leach tests of actinide-doped and non-radioactive ceramic samples.
- Optical microscopy (in reflected light) – using high-quality Russian microscope МИМ-10 equipped with digital photo camera – to observe visually the structural features (porosity, grain size, etc.) of actinide-doped ceramics.
- Fully licensed facility for working with the actinides at levels greater than 10 mCi.

Project Timeline:

Timeline Narrative

The timeline below describes expected technical results, milestones, and deliverables for Year 2. This project will contribute to the training of two graduate students. Not only will they become familiar with TRP-related science and technical issues, but they also will have an excellent opportunity to work at a DOE National Laboratory and a DOE-operated national user facility on an international collaborative effort.

Expected technical results for Year 2:

- Composition analyses of solid-state phases of fluorapatite and derivatives
- Spectroscopic studies of fluorapatite and derivatives, including some waste-loaded materials
- Initial studies of environmentally simulated reactions
- Initial studies of waste-loading in fluorapatite materials

Milestones for Year 2:

- Completion of baseline spectroscopic measurements for waste-free apatite and fluorapatite materials
- First detailed synchrotron-radiation-based x-ray measurement and analysis of apatite materials
- Initial studies of waste-loaded materials fabricated at KRI
- Preliminary studies of simple chemical and physical processes involved in waste incorporation

Deliverables for Year 2:

- **Collaboration with DOE:** Regular communication with DOE collaborator to assess progress, discuss problems, and allow for refocusing if necessary to address shifts in direction by the National Project.
- **Quarterly Progress Reports:** Brief reports indicating progress will be provided every quarter in support of the DOE AFCI quarterly reports and semi-annual review meetings.
- **Annual Report:** Written reports detailing experiments performed, data collected and results to date.

Data will be incorporated into student theses and peer-reviewed publications.

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Education

1983 Ph.D. in Chemistry, University of California, Berkeley.
1978 B.S. with Honors in Chemistry, Indiana University.

Professional Positions

2001- Professor, Department of Chemistry, University of Nevada, Las Vegas.
1996-2001 Assoc. Professor, Department of Chemistry, University of Nevada, Las Vegas.
1991-96 Asst. Professor, Department of Chemistry, University of Nevada, Las Vegas.
1986-91 Physicist, Quantum Metrology Division, National Institute of Standards and Technology, Gaithersburg, MD.
1983-86 Post-Doctoral Research Associate, Advanced Light Source, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley.
1978-83 Teaching and Research Assistant, Department of Chemistry, University of California, Berkeley (Research Advisor: David A. Shirley).

Professional Honors and Awards

1998-99 UNLV Barrick Scholar Award.
1998-99 Nevada Board of Regents Outstanding Faculty Member.
1997 UNLV College of Sciences Distinguished Researcher Award.

Current Research Interests

Core-level spectroscopy of atoms, molecules, and materials; X-ray-emission spectroscopy; Molecular photofragmentation; Synchrotron-radiation research.

Time Allocation for Project Year 1

Teaching: 4 months. Research: 4 months. Mentoring students, including those involved in this project: 3 months. Professional service: 1 month.

Recent Publications

D.L. Hansen, J. Cotter, G.R. Fisher, K.T. Leung, R. Martin, P. Neill, R.C.C. Perera, M. Simon, Y. Uehara, B. Vanderford, S.B. Whitfield, and D.W. Lindle, "Multi-Ion Coincidence Measurements of Methyl Chloride Following Photofragmentation Near the Chlorine K Edge," *J. Phys. B* **32**, 2629 (1999).

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Author or co-author of over 100 refereed journal publications.

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M.S., 1972, Chemistry (Synthesis and Spectroscopy, Inorganic Chemistry), Lamar University. Major field: Chemistry and spectroscopy of uranium.

B.S., 1969, Chemistry, Midwestern State University.

Professional Positions

SENIOR SCIENTIST, Solid State Chemistry and Spectroscopy, Lawrence Berkeley National Laboratory, University of California, Berkeley, California. 1/87—Present.

Principal investigator (9/81—Present), staff scientist (9/79—9/81), Group leader, Chemistry and Geochemistry, 1985—1989. SYNTHESIS, REACTION CHEMISTRY, SPECTROSCOPY OF INORGANIC SOLID-STATE CHEMISTRY.

MILLER FELLOW, Dept. of Chemistry, University of California, Berkeley, 9/77—8/79.

NSF FELLOW, Department of Chemistry, Rice University. 1/75—8/77.

RESEARCH ASSISTANT, Department of Chemistry, University of Houston, 6/72—12/74.

Professional Honors and Awards

Miller Fellowship, Department of Chemistry, University of California, Berkeley, 1977—79; National Science Foundation (NSF) Postdoctoral Fellowship, Department of Chemistry, Rice University, 1975—76; Sigma Xi National Research Award and Traineeship, Department of Chemistry, University of Houston, 1974; Annual Graduate Research Award, Department of Chemistry, University of Houston, 1973; Fellow, Royal Society of Chemistry (London), elected 1988; American Men and Women of Science, elected 1989.

Current Research Interests

Applications of surface techniques such as x-ray photoelectron and Auger spectroscopy to surface chemistry of solid-state materials; synthesis, reaction chemistry, and spectroscopy of inorganic complexes; chemistry, spectroscopy, and bonding of actinides; applications of spectroscopy to bonding studies of solid-state materials; spectroscopy of inorganic compounds as surface model species; synthesis and study of high-temperature inorganic oxides and sulfides; chemical corrosion mechanisms of metals and alloys; surface-reaction syntheses of composite materials; high-purity inorganic-crystal growth; inorganic thin-film synthesis by chemical vapor deposition (CVD) and aqueous techniques; inorganic polymers; superconducting metal oxides.

Time Allocation for Project Year 2

Research on this project, including mentoring students and post-doc: 2 months. Research on other projects: 9 months. Professional service: 1 month.

Recent Publications

²⁰⁷Pb NMR Study of Novel Pb-Pb Chemical Bonding in Lead Monoxides, a-PbO and b-PbO, S. P. Gabuda, S. G. Kozlova, V. V. Tersikh, Cecil Dybowski, Guenther Neue, and Dale L. Perry, Chem. Phys. Lett., **305**, 353 (1999).

Real-Time Characterization of Biogeochemical Reduction of Cr(VI) on Basalt Surfaces by SR-FTIR Imaging, Hoi-Ying N. Holman, Dale L. Perry, Michael C. Martin, Geraldine M. Lamble, Wayne R. McKinney, and Jennie C. Hunter-Cevera, *Geomicrobiology*, **16**, 307 (1999).

^{207}Pb NMR in Minium, Pb_3O_4 : Evidence for the $[\text{Pb}_2]^{4+}$ Ion and Possible Relativistic Effects in the Pb-Pb Bond, S. P. Gabuda, S. G. Kozlova, V. V. Terskikh, Cecil Dybowski, Guenther Neue, and Dale L. Perry, *Solid State Nucl. Mag. Resonance*, **15**, 103 (1999).

Near-Infrared Turbidity of b-FeOOH Particle Suspensions, Paul Berdahl, Luis Espinoza-Nava, David Littlejohn, Donald. Lucas, and Dale L. Perry, *Appl. Spectrosc.*, **54**, 262 (2000).

Correlation and Relativistic Effects in b-PbO and Other Lead(II) Oxides: A Quantum Ab Initio Explanation of the ^{207}Pb NMR and XANES Spectra, Cecil Dybowski, S. P. Gabuda, S. G. Kozlova, Guenther Neue, Dale L. Perry, and V. V. Terskikh, *J. Sol. State Chem.*, **157**, 220 (2001).

Spectroscopy of a Eu(III)-Imidazole Complex, F. Ragot, V. Ivanov, J. Wery, A. Garcia, Dale L. Perry, G. Ouvrard, and Eric Faulques, *Synthetic Metals*, **120**, 773 (2001).

Neutron-Induced Prompt-Gamma Activation Analysis (PGAA) of Metals and Non-Metals in Ocean-Floor Geothermal Vent-Generated Samples, Dale L. Perry, Richard B. Firestone, Gabor L. Molnar, Zs. Kasztovszky, Raymond C. Gatti, and Pat Wilde, *J. Analyt. Atom. Spectrom.*, **17**, 32 (2002).

Investigation of Corrosion of Steel by Lead-Bismuth Eutectic, by Daniel Koury, Allen L. Johnson, Dale L. Perry, and John W. Farley, *J. Nucl. Mater.* (in press).

Use of Synchrotron Reflectance Infrared Spectromicroscopy as a Rapid, Direct Non-Destructive Method for the Study of Inks on Paper, T. J. Wilkinson, D. L. Perry, M. C. Martin, W. R. McKinney, and A. A. Cantu, *Appl. Spectrosc.* (in press).

Author and co-author of approximately three hundred contributed scientific presentations, refereed journal publications, book chapters, and numerous invited seminars at universities, national laboratories, and industry.