

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

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- Boris E. Burakov (KRI Principal Investigator, Head of Mineralogical Group)
- Evgeniy B. Anderson (KRI Co-Principal Investigator)
- Alexander Rimsky-Korsakov (KRI Director General)

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AAA Research Area: Separations

Funding Profile:

Academic Year:	2002-2003	2003-2004	2004-2005
Total (K\$)	\$178,538	\$179K <i>estimated</i>	\$179K <i>estimated</i>

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 will develop a dual-path research project to develop a process to fabricate a synthetic fluorapatite waste form for the ZrF₄, 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.

Work Proposed for Academic Year 2002-2003 (8/02 – 7/03), Goals, and Expected Results:

The work in the first year of the project will progress along two parallel paths: Fabrication and Natural Analog Characterization. The Fabrication path, led by the KRI team, will examine and evaluate various techniques for the fabrication of synthetic fluorapatite, will synthesis 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, will refine the x-ray spectroscopy techniques currently in use to characterize borosilicate glass for HLW disposal and to examine these ceramic and synthetic mineral waste forms, and then apply 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. Preliminary samples of synthetic fluorapatite from the Fabrication path will also be examined as they are available.

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 the 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 [i].

Among technologies under consideration for the plutonium-burning reactor systems are the new-generation High-Temperature Gas-Cooled Reactor (HTGR) 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. Given that the plutonium-laden fuel in the second strata will need to be processed to recycle unburned plutonium as well as to recover for transmutation minor actinides and other fission products produced during the fuel cycle, it is essential that any fuel be 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 Process, or FLEX process.

One potential problem with the FLEX process is that 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; and technetium) [ii]. Fluoride salts are unsuitable for conversion into the 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 currently facing the FLEX process, and allowing the national spent fuel management program to further examine, develop, and potentially (someday) deploy this 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 and a knowledge base with the fabrication of fluoride-bearing matrices;
- To develop a knowledge base to assist others in predicting the impact that 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 material 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, which is how can the salt wastes be stabilized for disposal. The characterization effort will greatly expand our understanding of the molecular structure of fluorapatite and other fluoride-bearing mineral and ceramic phases, and will deepen our understanding of the bulk and surface processes that occur during the environmental degradation of these materials.

Research Approach:

The research to develop and understand a fluorapatite-based waste matrix for the ZrF₄-salt fission product waste stream from the FLEX process will take place through 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. Boris Burakov. The waste form characterization work will take place primarily at UNLV and on the UNLV-beamline/x-ray facility at the Advanced Light Source on the Lawrence Berkeley National Laboratory campus. The characterization work will be led by project PI Dr. Lindle and by Co-PI Dr. Perry.

Waste Form Development (task lead: Dr. Burakov, KRI)

Ceramic samples based on fluorapatite will be formulated, synthesized, and examined to investigate the impact of processing parameters and composition on material properties (i.e. homogeneity, etc.) and performance (via leach testing). Initial work will consist of literature review and scoping experiments to assist in developing fabrication processes for fluorapatite-based ceramics. The most promising fabrication process 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 potentially even alternate waste matrices will be examined and compared against the baseline composition.

Ceramic specimens will be studied at KRI by a variety of methods such as SEM, XRD, EMPA and MCC-1 leach testing to evaluate material properties and potential performance. Promising sample compositions/matrices will be sent to the UNLV team for further characterization.

Waste Form Characterization (task lead: Dr. Lindle, UNLV)

State-of-the-art x-ray spectroscopy and spectromicroscopy techniques will be employed to characterize the molecular structure of both natural fluorapatite and fluoride-bearing minerals and the fluorapatite-based ceramic waste form. The 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 characterization work will begin with method development work to determine the methodologies most appropriate to the fluorapatite system (both natural and synthetic). These techniques are currently being used by the PI, in collaboration with researchers from LBNL, to characterize borosilicate glasses. Using these methodologies, characterization will begin on natural fluorapatites to develop a better understanding of these systems and to establish a knowledge base for the natural analog for the fluorapatite-based waste matrix. Once the baseline formulation becomes available, work on characterizing the waste matrix will begin in parallel.

The 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. Several previous studies of fluorapatite using different types of spectroscopy and microscopy have clearly demonstrated this approach that yields data vital for predicting performance and integrity of a target compound. For example, Raynaud et al. [iii] used high-temperature x-ray diffractometry, FTIR spectroscopy, and other techniques to study the thermal stability of apatites with different calcium/phosphorus ratios. The same group also studied characteristics and significant differences of apatites as a function of small changes in composition [iv]. Other studies have made infrared vibrational assignments of apatites [v] and studied synthesis of apatites as a function of molecular stoichiometry [vi]. 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 [vii]. 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.

Expected Technical Results:

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

Capabilities at UNLV, LBNL, and KRI:

UNLV and LBNL

All of the equipment required for the proposed research is available to the PIs now or is under development in their laboratories and will be operational in the first year of the project; no equipment request is being made to AAA 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. Dr. Lindle also has preferred access to two high-resolution x-ray beamlines at the LBNL Advanced Light Source (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 all of the x-ray techniques described in the Appendix 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 and managed by Dr. Lambis Papelis and Prof. Allen Johnson.

The LBNL PI has a wide variety of equipment available for materials research. Facilities at LBNL for the synthesis and characterization of fluorapatite and fluorapatite-substituted materials and substrate applications are very extensive. Synthetic chemical laboratories include standard chemical hoods for the preparation of solid-state materials, both pure and doped. These laboratories are equipped for syntheses of materials involving gel processing, heavy metal-organic intermediate-route synthesis, and high-temperature solid-state reactions. The major laboratory facilities include machine shops, glass shops, welding shops, electronics shops, and shops for specialty-equipment fabrication, instrument repair, and calibration. Instrumentation for the 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 dedicated a few years ago. 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 wish to 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 light in physics experiments. The need of any UNLV program to perform part of its experimental work at the

ALS in order to access its unique facilities does not imply a lessening of UNLV credit or responsibility for the program.

Finally, the experimental techniques to be used (see Appendix) have proven productive in the hands of both PIs and their collaborators. The proposed research uses the techniques of XES spectromicroscopy, XPS, and Auger electron spectroscopy (AES) to study metal ions and their reaction chemistry within fluorapatite materials. Perry and co-workers [viii, ix, x] have used XPS to study several metal-ion systems, and combined XPS/AES [xi] to study lead oxides and associated compounds [xii]. Vibrational spectroscopy, including infrared and Raman spectroscopy, has been used by the Perry group to study the chemistry and bonding of a variety of metals, including uranium [xiii, xiv]. Dr. Lindle and co-workers have used NEXAFS, XPS, and XES extensively (over 100 published papers) to study gas-phase species. The Lindle group has recently expanded these capabilities to use them on a variety of condensed-phase materials; most of the equipment developed for molecular studies is directly usable for solids, and the physical interpretations are often quite similar. In fact, Dr. Lindle has an existing DOE EPSCoR State-National Laboratory Partnership Grant [DOE co-PI: David Shuh (LBNL)] to perform very similar research on borosilicate glasses as waste-form materials. The techniques developed to study borosilicate glasses will be directly applicable to fluorapatite materials, and comparison between the two categories of waste-form materials will enhance both projects.

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-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, $(Y, Ca, An, \dots)_3(Al, \dots)_5O_{12}$, (where An = U, Pu, Np, Am, Cm). 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 evaluate their impact on the waste matrix without needing to bring in additional collaborators. The Laboratory of Applied Mineralogy and Radiogeochemistry also has the experience 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 of highly radioactive materials.
- The chain of glove-boxes equipped with ball-mill, cold press, special furnaces for precursor calcination and ceramic synthesis by sintering (or melting) in air at temperature up to 1500-1600°C. Design of glove boxes allows us to handle up to 1.5-2.0 grams of ^{239}Pu and 0.1-0.2 grams of ^{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 us to determine valence state of actinides and other elements incorporated by crystalline materials.
- Special TeflonTM vessels and thermostatic ovens to carry out MCC-1 leach test 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 structural features (porosity, grain sizes, etc.) of actinide-doped ceramics.
- Licensed premises to work with actinides on the level higher than 10.0 mCi.

Project Timeline:

Timeline Narrative

This proposal describes a three-year collaborative research program. The timeline below describes expected technical results, milestones, and deliverables for the first year only; second- and third-year milestones will depend on results in Year 1. More importantly, this project will lead to the training of a graduate student and a post-doctoral researcher during the course of research. Not only will they become familiar with AAA-related science and technical issues, but they also will have the 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 1:

- Review of synthesis methods for fluorapatite-based matrices;
- Development of laboratory-scale fabrication process and bench-scale fabrication line;
- Fabrication of initial fluorapatite-based ceramics for evaluation;
- Preliminary composition analyses of solid-state phases of fluorapatite and derivatives;
- Preliminary IR studies of fluorapatite and its derivatives: vibrational band assignments;
- Initial studies of environmentally simulated reactions;
- Initial studies of waste-loading in fluorapatite materials: fabrication and integrity issues.

Milestones for Year 1:

- Selection of synthesis process for fluorapatite-based matrices;
- Development of synthesis capability for fluorapatite-based matrices at KRI;
- Synthesis of initial fluorapatite composition;
- Familiarization by the students and post-doc with techniques available at the ALS;
- Familiarization by the students and post-doc with the fluorapatite literature;
- First compositional analyses measurements and first infrared measurements;
- First x-ray experiments on a model fluorapatite system.

Deliverables for Year 1:

- **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 AAA quarterly meetings.
- **Annual Report:** Written reports detailing experiments performed, data collected and results to date.

Data to be incorporated into student thesis and/or peer-reviewed publications.

Appendix: Experimental Techniques

Samples of fluorapatites and their environmentally simulated reaction-induced products will be characterized using a number of experimental techniques, including the following:

1. Near-Edge X-ray Absorption Fine Structure (NEXAFS). This technique, a synchrotron-radiation-based x-ray spectroscopy, can provide chemical and electronic-state information about the different elements contained in fluorapatite and its substituted phases. One of the great strengths of NEXAFS is the ability to probe unoriented amorphous phases such as might be found in degradation products of fluorapatite after undergoing environmental alteration.
2. Infrared spectroscopy/microscopy. Infrared data can be taken from both a broad area on a sample using stand-alone instrumentation and, using synchrotron-radiation-based infrared spectromicroscopy, from a small domain with lateral resolution of about 10 μm . Infrared spectra are indicative of both the chemical species, and, in most cases, the structural polymorphs, i.e., different structural phases of the same compound. Because spectromicroscopy has a spatial resolution of a few microns along the surface of a sample, it will permit the study of subtle changes in the chemistry of the fluorapatites as a function of environmental effects.
3. X-Ray Diffraction (XRD). In this technique, an x-ray source illuminates the sample, and an imaging plate collects the diffraction pattern. XRD is useful in identifying solid-phase materials from both the chemical-composition and crystallographic-polymorph standpoints, allowing differentiation among various crystal structures of phases with identical chemical composition, i.e., it provides a structural “fingerprint” of the solid phase under study. These measurements will be performed at x-ray-diffraction facilities available at UNLV and LBNL.
4. X-ray Photoelectron Spectroscopy (XPS). In this technique, x-rays illuminate a sample, and the resulting photoelectrons are energy analyzed to convert their kinetic energies into binding energies. The binding energies are representative of elements and their specific chemical and electronic states. Ejection of a photoelectron is usually followed by ejection of an Auger electron(s) from the sample, and the Auger transitions likewise are correlated to chemical-state information for individual elements in the sample. Stand-alone XPS instruments are available at UNLV and LBNL for this work. In addition, micro-XPS work, which combines the capability of elemental mapping with the traditional strengths of XPS, will be conducted at the ALS.
5. X-ray Emission Spectroscopy (XES) and X-Ray Fluorescence (XRF). Synchrotron-radiation-based x-ray-fluorescence (XRF) spectroscopy and x-ray-emission spectroscopy (XES) are sensitive analytical techniques for direct quantitative information on chemical composition. The XRF technique can provide a detailed mapping (with 1 μm spatial resolution) of the heavy-metal ions of interest to this program. The sensitivity of the XRF microprobe at the ALS approaches the femtogram (10^{-15}g) level for many metals, one of the most sensitive of spectroscopic techniques also providing microscopic imaging. Synchrotron-based XRF microprobe techniques have been used by Perry and co-workers [xv] to map metals such as calcium, nickel, and potassium in films of complex quaternary metal oxides, complex phases which are similar to those of fluorapatite materials. The synchrotron-based XRF measurements will be performed at the ALS, while more-traditional XRF measurements will be made at LBNL using standard XRF equipment for larger samples. The Lindle group has two XES instruments available to probe x-rays emitted from solid samples. This high-resolution spectroscopic technique is very sensitive to the electronic structure of the sample and can also provide structural information from amorphous materials by measuring either the polarization or the angular distribution of the characteristic x-rays emitted from the sample.

Biographical Information:

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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).
- D.L. Hansen, O. Hemmers, H. Wang, D.W. Lindle, P. Focke, I.A. Sellin, C. Heske, H.S. Chakraborty, P.C. Deshmukh, and S.T. Manson, "Validity of the Independent-Particle Approximation in X-Ray Photoemission: The Exception, Not the Rule," *Phys. Rev. A, Rapid Communications* **60**, R2641 (1999).
- D.W. Lindle and O. Hemmers, "Breakdown of the Dipole Approximation in Soft-X-Ray Photoemission," *J. Electron Spectrosc.* **100**, 297 (1999) - (invited paper).
- A. Derevianko, O. Hemmers, S. Oblad, P. Glans, H. Wang, S.B. Whitfield, R. Wehlitz, I.A. Sellin, W.R. Johnson, and D.W. Lindle, "Electric-Octupole and Pure-Electric-Quadrupole Effects in Soft-X-Ray Photoemission," *Phys. Rev. Lett.* **84**, 2116 (2000).
- H.S. Chakraborty, D.L. Hansen, O. Hemmers, P.C. Deshmukh, P. Focke, I.A. Sellin, C. Heske, D.W. Lindle, and S.T. Manson, "Interchannel Coupling in the Photoionization of the M Shell of Kr Well-Above Threshold: Experiment and Theory," *Phys. Rev. A* **63**, 042708 (2001).

- P.W. Langhoff, J.C. Arce, J.A. Sheehy, O. Hemmers, H. Wang, P. Focke, I.A. Sellin, and D.W. Lindle, “*On the Angular Distributions of Electrons Photoejected from Fixed-in-Space and Randomly Oriented Molecules,*” J. Electron Spectrosc. **114-116**, 23 (2001).
- D.W. Lindle and O. Hemmers, “*Time-of-Flight Photoelectron Spectroscopy of Atoms and Molecules,*” J. Alloys and Compounds **328**, 27 (2001).
- W.C. Stolte, D.L. Hansen, M.N. Piancastelli, I. Dominguez Lopez, A. Rizvi, O. Hemmers, H. Wang, A.S. Schlachter, M.S. Lubell, and D.W. Lindle, “*Anionic Photofragmentation of CO: A Selective Probe of Core-Level Resonances,*” Phys. Rev. Lett. **86**, 4504 (2001).
- H. Wang, G. Snell, O. Hemmers, M.M. Sant’Anna, I.A. Sellin, N. Berrah, D.W. Lindle, P.C. Deshmukh, and S.T. Manson, “*Dynamic Relativistic Effects in the Angular Distributions of Xenon 4d Photoelectrons in the Vicinity of the Cooper Minimum,*” Phys. Rev. Lett. **87**, 123004 (2001).
- J.C. Arce, J.A. Sheehy, P.W. Langhoff, O. Hemmers, H. Wang, P. Focke, I.A. Sellin, and D.W. Lindle, “*On the Angular Distributions of Molecular Photoelectrons: Dipole Cross Sections for Fixed-in-Space and Randomly Oriented Molecules,*” Chem. Phys. Lett. **346**, 341 (2001); Erratum **349**, 349 (2001).
- O. Hemmers, H. Wang, P. Focke, I.A. Sellin, D.W. Lindle, J.C. Arce, J.A. Sheehy, and P.W. Langhoff, “*Large Nondipole Effects in the K-Shell Photoionization of Molecular Nitrogen,*” Phys. Rev. Lett. **87**, 273003 (2001).

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

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Education

Ph.D., 1974, Chemistry (Synthesis and Spectroscopy, Inorganic Chemistry), University of Houston.
Major field: Chemistry and spectroscopy of tin.

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 1

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. Terskikh, 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 α - 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 α - 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.

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PROFESSIONAL PROFILE:

- Experienced in material study of natural and artificial radioactive minerals, crystalline ceramic, glass etc.;
- Experienced in handling of highly radioactive materials including spent fuel and weapons Pu;
- Experienced in work under conditions of severe nuclear accident in Chernobyl.

EDUCATION:

MS Degree, *Geology-Geochemistry-Mineralogy*, Leningrad State University, former Soviet Union, graduation: June 1986; Ph.D, *Mineralogy*, Institute of Chemical Technology, Moscow, graduation: December 1991.

EXPERIENCE:

1985-86	Laboratory worker in V.G.Khlopin Radium Institute;
1986-91	Engineer-researcher in V.G.Khlopin Radium Institute, mineralogical and geochronological study of uranium ores;
1991-present time	Head of Mineralogical Group, V.G.Khlopin Radium Institute;
1990-92	Participation in the investigation of Chernobyl accident, material study of destroyed spent fuel, Chernobyl «lava» and hot particals;
1996	An expert of International Atomic Energy Agency (IAEA), personal No T636373, Nature of Services «Environmental Impact for the Chernobyl NPP Unit 4, Study of Interaction of Water and FCM»;
1990-present time	Experimental research on the synthesis and examination of crystalline ceramic for immobilization of HLW including TRU and weapons Pu.

SELECTED PUBLICATIONS:

- (1) Burakov,B.E, Anderson,E.B. (1998) Development of Crystalline Ceramic for Immobilization of TRU Wastes in V.G.Khlopin Radium Institute. *Proceedings of the 2nd NUCEF International Symposium NUCEF'98, 16-17/11/98, Hitachinaka, Ibaraki, Japan, JAERI-Conf.99-004 (Part I)*, 295-306.
- (2) Burakov,B.E, etc. (1999) Ceramic Forms for Immobilizing Pu Using Zr, Y, Al Metal Additives. *Environmental Issues and Waste Management Technologies IV*, 349-356.
- (3) Burakov,B.E, Anderson,E.B, Zamoryanskaya,M.V, Petrova,M.A. (2000) Synthesis and Study of ²³⁹Pu-Doped Gadolinium-Aluminum Garnet. *Material Research Society Symposium Proceedings Scientific Basis for Nuclear Waste Management XXIII, Vol.608*, 419-422.
- (4) Burakov,B.E, Hanchar,J.M, Zamoryanskaya,M.V, Garbuzov,V.M, Zirlin,V.A. (2002) Synthesis and Investigation of Pu-Doped Single Crystal Zircon, (Zr,Pu)SiO₄, *Radiochimica Acta*, 90, 95-97.