

Nuclear Materials

Distribution and Solubility of Radionuclides and Neutron Absorbers in Waste Forms for Disposition of Plutonium Ash and Scraps, Excess Plutonium, and Miscellaneous Spent Nuclear Fuels

Project ID: 60387

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Executive Summary

Successful immobilization of actinides (Am, Cm, Th, Pu, Np, etc.) in crystalline and amorphous host matrices with appropriate neutron absorbers (B, Hf, Gd, etc.) requires sound scientific knowledge of the local chemical environments of both the actinides (An) and the neutron absorbers and their interaction with the host matrices. This understanding leads to a more systematic and efficient approach to predicting solubilities than the strictly empirical approach currently used. The goals of this ongoing research are to determine solubility limits of representative actinides (Pu and U) and neutron absorbers (Hf and Gd) in crystalline and amorphous matrices and to determine solution mechanisms of these species in the two types of systems. Actinides and neutron absorbers in amorphous systems have been studied at PNNL in collaboration with LBNL and University of Michigan and in crystalline systems at ANSTO. We believe that we are in a position to understand the chemical systematics of silicate melts so that the solubility of actinides, neutron absorbers, and, we would suggest, other metal species in glass no longer has to be determined empirically, but can be calculated from a set of equilibrium constants in a similar fashion to aqueous systems.

For the first time, to the best of our knowledge, we have demonstrated in amorphous systems that at least 14.7 mol% Pu(III) plus 4.2 mol% Gd(III) is soluble in an alkali boro-aluminosilicate glass under reducing conditions. Under oxidizing conditions, considerably less Pu(IV) is soluble. X-ray absorption fine structure (XAFS) analyses of these glasses confirms that Pu(III) is a dominant species in the reduced glass and Pu(IV) in the oxidized glass.

The solution behavior of lanthanides [Ln(III): Ln = Gd, La, and Nd] in a variety of Na₂O-Al₂O₃-B₂O₃-SiO₂ glasses was studied with a host of complementary analytical techniques. Results from experiments with the lanthanides, Gd, Nd, and La, suggest that their behavior in the glass melt is similar. The solution behavior of Ln in these glasses was determined by the ratio of excess Na₂O or excess Al₂O₃-to-B₂O₃ in the melt.

In peralkaline melts (Na₂O>Al₂O₃), when the ratio of excess Na₂O (i.e., moles of Na₂O less the moles of Al₂O₃) to B₂O₃ is greater than 0.5, the compound Na_xLn_{9.33-0.33x}Si₆O₂₆ (0<x<1) precipitates from the melt at the Ln₂O₃ solubility limit. The Ln₂O₃ solubility in these glasses is determined by the concentration of each glass former. From the UV-Vis and fluorescence spectroscopy results, lanthanides appear to dissolve uniformly at low concentrations in these glasses. When the B/Ln ratio is ≥3, intermediate-range ordered Ln-borate structural groups appear to form in clusters about 5 nm in diameter. The electron energy loss fine structure (ELFS) results suggest that the structure of these Ln-borate groups resembles lanthanide metaborate crystals. When B/Ln is less than 3, Ln appeared to partition among boron-rich and silicon-rich domains forming different types of intermediate-ordered structural groups. The configuration of these groups has yet to be determined.

When the ratio of excess Na₂O to B₂O₃ is less than 0.5 in these glasses, liquid-liquid phase separation occurs above the Ln₂O₃ solubility limit with one phase being rich in Ln and B. The Ln₂O₃ solubility appears to be determined by the excess Na₂O. In these glasses, the borate and the silicate portions are not well mixed. Phonon side band spectroscopy results suggest that Ln is incorporated into the borate portion of the melt in a double chain structure similar to that in lanthanide metaborate. The Ln behavior in peraluminous melts (moles of Al₂O₃>Na₂O) is similar to the behavior in peralkaline melts. When the excess Al₂O₃/B₂O₃ < 0.4, phase separation occurs at the solubility limit of Ln₂O₃ with one phase rich in Ln and B. When the excess Al₂O₃/B₂O₃ > 0.4, Na_xLn_{9.33-0.33x}Si₆O₂₆ precipitates above the Ln₂O₃ solubility limit.

Based on the assumption that the Pu(III) and Ln(III) solution behavior are similar in these glasses, we anticipate that Pu(III) dissolves in glass in much the same way as Ln(III). Above Ln solubility in some glasses, Na_xLn_{9.33-0.33x}Si₆O₂₆ crystallizes from the melt. If this crystal accommodates significant quantities of Pu(III), the resulting glass ceramic could also be an acceptable waste form.

In contrast to the Gd results, at all concentrations up to the solubility limit, XAFS results indicate that Hf(IV) dissolves in these glass melts as [HfO₆], octahedrally coordinated species in peralkaline glasses and less-than-octahedral in peraluminous glasses without clustering (Hf-O-Hf bonds). In our glasses, HfO₂ solubility is observed to reach a minimum for glasses in which the molar concentrations of Na and Al are equal. Limited increases in Al₂O₃ result in glasses (peraluminous) with slightly increased Hf solubility. Further increases in Al₂O₃ result in glasses that can no longer be melted at 1550°C. When the Na₂O-to-Al₂O₃ ratio is greater than one (peralkaline glasses), there is an increase in the HfO₂ solubility with an apparent increase in the Na₂O content. Results from XAFS suggest that the local structure around Hf is silicate-like for peralkaline glasses and siloxane-like for peraluminous glasses (i.e. the local structure is different for the two glass types). A comparison between the coordination environments of Pu(IV) and Hf(IV) is currently underway. The anticipated results from this study may suggest that An(IV) dissolves in these glass melts as monomeric species.

Compositional effects on HfO₂ solubility are being extensively studied in these glasses. We have been able to model the HfO₂ solubility in these glasses with a rule-of-mixtures approach using the measured HfO₂ solubility in rudimentary compositions such as amorphous analogs of sodium disilicate, sodium diborate, albite, and reedmergnerite. From such a modeling approach, we find that the highest HfO₂ solubility occurs in glasses containing the highest concentration of “NaBO₂” stoichiometric units, perhaps indicating that the chemistry of Na and B in the silicate melt is the determining factor for HfO₂, and perhaps An(IV), solubility.

For the candidate ceramic host matrices, substitution of Pu, U, Hf and Gd in the host structures is now quantified and broadly understood in terms of the standard rule that the closer the size similarity (~ 15% difference) between the guest and host ions, the higher is the solubility of the guest ions. In the current study, solid solubility limits, in formula units (f.u.) of U, Pu, Hf, and Gd, have been measured for single actinides and neutron absorbers. The matrices were zircon (ZrSiO₄), monazite (CePO₄), titanite (CaTiSiO₅), perovskite (CaTiO₃), and apatite (Ca₁₀(PO₄)₆O). In almost all cases, these limits were not known before this study. Uranium (IV) is highly soluble in apatite achieving

0.5 f.u., while 8 f.u. of Gd is soluble. However, very limited solubility was found for Hf (< 0.1 f.u.). Titanite was observed to accommodate 0.02 f.u. of U(IV) and 0.02 f.u. of Pu(IV), both of which substitute for Ca. At solubility, UO_2 or PuO_2 form. Under reducing conditions, a higher solubility of Pu (0.05 f.u.) as Pu(III) was determined. The use of an argon atmosphere rather than air during sintering of these materials presumably causes Pu(III) to form instead of Pu(IV). Relatively large accommodations of neutron absorbers were observed in titanite, 0.3 f.u. of Gd in the Ca site and 0.5 f.u. of Hf in the Ti site. Plutonium has high solubility in monazite as Pu(IV) at up to 1 f.u. (at firing temperatures of < 800°C) and Pu(III) at 1 f.u., although there is almost no solubility for Hf (< 0.01 f.u.). Perovskite accommodates high concentrations of the neutron absorbers Gd or Hf at 1 f.u. and Pu(III) at 1 f.u., but limited amounts of Pu(IV) (0.13 f.u.) and U(IV) (~ 0.1 f.u.). Previous studies showed that actinides and neutron absorber solubilities are high in zirconolite, 0.7 f.u. for U(IV) and Pu(IV) and 1.4 and 1 f.u. for Gd and Hf, respectively. In pyrochlore, the solubilities were known from previous studies to be 1, 2, 1, 2 and 0.3 f.u. for U(IV), Pu(III), Pu(IV), Gd, and Hf, respectively.

Utilizing the new insight into the Pu, Gd, and Hf behavior in crystalline materials and glass melts, we have identified optimum formulations to incorporate the maximum amount of Pu. Studies are underway to validate these predictions. For crystalline materials, site substitution and charge compensation mechanisms of the actinides and neutron absorbers will be studied further. Interactive effects of actinide and neutron absorbers on their solubilities in both glasses and ceramics will be studied. In particular for glasses, we feel this approach can be extended to other metal species with the ultimate goal to develop a comprehensive model for silicate melts and glasses in which chemical systematics are well defined.

Determination of Transmutation Effects in Crystalline Waste Forms

Project ID: 55382

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Research Objectives

The overall goal of this project was to study key scientific issues related to the long-term stability and performance of crystalline waste forms under consideration for containment and disposal of nuclear waste. Our research efforts were focused on the effects of transmutation of ^{137}Cs to ^{137}Ba in crystalline pollucite ($\text{CsAlSi}_2\text{O}_6$). This transmutation issue is important to all crystalline nuclear waste forms, including spent fuel.

In the research completed, we studied both surrogate samples and actual, ^{137}Cs pollucite radioactive samples (~ 20 years old). Analytical techniques that pushed the envelope of existing capabilities were used, leading to limited, but significant, progress.

This research was done at Argonne National Laboratory in collaboration with Pacific Northwest National Laboratory.

Research Progress and Implications

The effects of transmutation on pollucite were investigated by three complementary methods: solid state nuclear magnetic resonance (NMR), X-ray synchrotron studies (EXAFS/XANES), and transmission electron microscopy (TEM). The NMR and synchrotron approaches are highly developmental analytical approaches that extend current capabilities.

Six sealed capsules of radioactive pollucite, see Figure 1, were utilized at Argonne in this study. These varied in age, total activity, and barium content - so they represented various stages of transmutation. Our initial goal was to analyze these samples *in situ* to avoid the effects of exposure to oxygen and water on the sample. We have since taken three of these radioactive sources apart to extend the range of applicable analytical approaches.

Synchrotron-Based Techniques

Synchrotron methods (XANES/EXAFS) provide the best chance of meaningful *in situ* analysis of radioactive pollucite samples within unopened stainless steel capsules. Analyses of the Cs K-edge, at Stanford Synchrotron Research Laboratory (SSRL) and the Advanced Photon Source (APS), were largely unsuccessful due to limitations in signal intensity and poor signal quality.

The Cs and Ba L-edge absorption (at ~5-6 keV) and K-edge (~35-38 keV) absorption were analyzed at both SSRL and the APS. This was done for the radioactive samples and a series of nonradioactive surrogates to establish structural trends. Significant differences were noted between the K-edge spectra of the radioactive and non-radioactive samples (see Figure 2). These data, although preliminary, show that synchrotron-based methods hold significant potential and promise as a tool to investigate structural/performance issues for complex waste forms.



Figure 1. ^{137}Cs pollucite capsule, shown with a dime for scale.

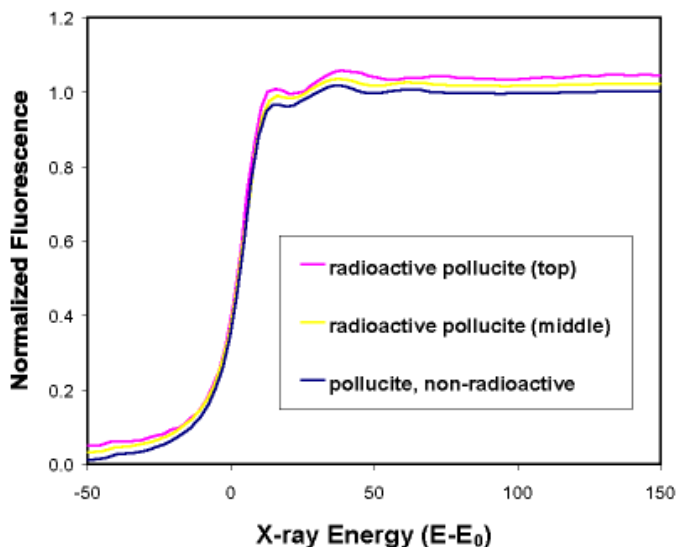


Figure 2. K-edge XANES at the Cs edge for radioactive and non-radioactive pollucite. These data show small but significant differences in the Cs-Al and Cs-O distances that point to differences in the structure due to transmutation.

Solid-State NMR

Solid-state NMR studies of milligram levels of Cs, Al, and Si were conducted to establish structural changes in pollucite due to transmutation. The NMR work performed was by far the most developmental of the three techniques used, yet our success in this approach will likely lead to applications beyond the pollucite samples studied. Solid-state NMR can provide nearest-neighbor information relevant to radionuclides within the crystalline waste form.

The most promising NMR results were obtained for ^{27}Al at room temperature (see Figure 3). Spectra recorded with longer pulses showed the narrow central transition peak and a second broader peak at a higher field. This broad resonance may be the central transition for Al nuclei at sites near Ba substitutions, where the electronic environment around Al is distorted from the normal tetrahedral environment in aluminosilicates (T-sites). These results are significant given the importance of Al in many waste forms under consideration.

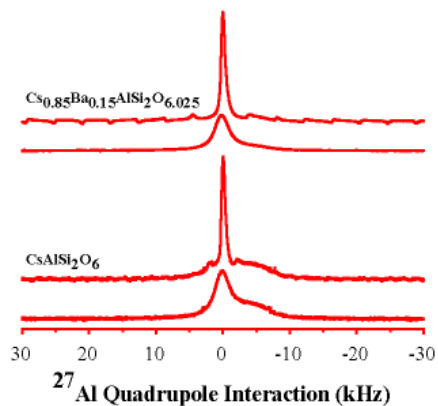


Figure 3. Solid-state NMR spectra of ^{27}Al in pollucite for both magic angle spinning (top of the two curves for each sample) and static toroid cavity NMR (bottom). The similarity in the spectra show that static toroid cavity NMR can be used to obtain nearest-neighbor structural information on milligram level samples.

Planned Activities

This three year research project was completed in September 1999, so no future activities are planned. A renewal proposal to extend the capabilities developed to other waste form issues was submitted.

Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

Project ID: 60118

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Research Objective

The landmark record of decision in January 2000 by the US Department of Energy stated that at least 17 tons of surplus weapons plutonium will be converted to a mineral waste material and disposed of in a geological repository similar to the proposed Yucca Mountain nuclear waste site in Nevada. The need for fundamental thermodynamic properties (e.g., entropy, enthalpy and free energy of formation) of specific actinide-bearing mineral phases, related non-actinide phases, and potential decomposition phases is vital to waste material formulation, fabrication process optimization, environmental modeling, and licensing a proposed mineral waste material. Two and one half years ago we began a study designed to obtain the first measured values for the formation energetics of phases related to the disposal of this surplus weapons plutonium.

Research Progress and Implications

A combination of calorimetric techniques is being used to establish the thermodynamic properties of the mineral waste forms. High-temperature oxide-melt solution calorimetry is being used to establish the enthalpy of formation of the minerals while adiabatic calorimetry is being used to establish the heat capacity and entropy of the minerals. The enthalpy and entropy data are combined to calculate the free energy of formation of the phase. Thermodynamic data are available for (1) CaMTi_2O_7 where $M=\text{Zr, Hf, and Ce}$; (2) AnTi_2O_6 where $\text{An}=\text{Ce, Th, U}$; (3) REPO_4 where $\text{RE}=\text{La, Ce, Nd, Eu, Yb, and Lu}$; (4) $\text{Gd}_2\text{Ti}_2\text{O}_7$; (5) CaTiO_3 ; and (6) MTiO_4 where $M=\text{Zr or Hf}$. The enthalpy of formation of $\text{CaPuTi}_2\text{O}_7$, PuTi_2O_6 , UPO_4 , PuPO_4 , and AmPO_4 was estimated from the systematic trends observed in the measured values of the appropriate aforementioned phases. These trends are only approximations, which result in large error margins on the predicted values. The remaining resources and our efforts are targeting the synthesis, characterization, and measurement of the formation energetics of the Pu-bearing phases.

A high-temperature solution calorimeter has been installed at Los Alamos National Laboratory (LANL) to allow the study of high-activity actinide-bearing materials. Uranium and thorium containing materials were studied at the University of California at Davis (UCD). Optimal experimental conditions, techniques, and solvents have been determined at UCD and this information has been transferred to LANL. Heat capacity data were obtained at Brigham Young University (BYU) on some of the phases of interest. Funding for the BYU studies was through an outside contract from Lawrence Livermore National Laboratory (LLNL).

Planned Activities

We plan to complete the revised 1997 scope of the project. The original scope of work was downsized in 1997 because LANL, UCD, and LLNL received less funding than originally requested. LLNL has synthesized but not fully characterized PuTi_2O_6 . Precursor material for Pu-pyrochlore, $\text{CaPuTi}_2\text{O}_7$, has been prepared but no pyrochlore sample has been synthesized. When synthesis and characterization of these phases is completed, the samples will be transported to LANL where calorimetric studies will be performed.

Additional funding will be sought to fully characterize the thermodynamics of other actinide-bearing mineral waste forms and to establish the energetics of mixing of waste form materials. The energetics of mixing data are needed in modeling the behavior of a multi-component waste material such as the solid solution ($\text{CaHfTi}_2\text{O}_7 + \text{Gd}_2\text{Ti}_2\text{O}_7 + \text{CaUTi}_2\text{O}_7 + \text{CaPuTi}_2\text{O}_7$) proposed as the waste material for surplus weapons plutonium.

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Chemical and Ceramic Methods Toward Safe Storage of Actinides Using Monazite

Project ID: 55094

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Executive Summary

The program will address more particularly the section, "Plutonium behavior in mixed matrices - specialized waste forms", with the concept that monazite ceramic will provide the most safe, most secure, geologically tested, very long term, containment for actinides. That monazites are the ideal crystal hosts for containment of actinide or transuranic elements (extremely stable geologically and resistant to radiation damage) is well established. They were proposed a number of years ago as high level nuclear waste forms at Oak Ridge National Laboratory.

Following the deliberations of the Hench Panel in 1984, and the decision to proceed with borosilicate glass as a low level waste, organized research on monazite and other "alternative waste forms" came to an end. As pointed out in a current National Academy of Science Panel report, approximately fifteen years of potential progress in the development of alternative nuclear waste forms were then lost.

We therefore seek to do basic studies of the ceramic nature of monazite utilizing two groups that have a serious previous background in research concerning monazite and radwaste encapsulation. These are complicated fields and, to avoid unnecessary duplication and waste, it should be important to utilize and to extend that already hard won experience.

The group headed by Lynn Boatner at Oak Ridge National Lab has many years of preeminent experience in studying monazite, while that laboratory is, naturally, in a fine position to transfer basic study results to later engineering application.

The group at the Rockwell Science Center, including Alan Harker and Peter Morgan, became well known for its work in the area of ceramic radwaste hosts and contributed considerable basic understanding to the ceramic problems and advantages, particularly pointing out to the community the key role of the grain boundary leaching phenomena (possible glasses, precipitated grain boundary phases, etc.).

The recent discovery by the Rockwell group, including also David Marshall, that monazite provides weak stable interfaces for ceramic matrix composites has stimulated widespread, renewed interest in the properties of monazite as a ceramic.

The main outstanding fundamental research issues facing the use of monazite as a waste form necessitate the development of fundamental understanding of: sintering mechanisms involved in forming high density monazite ceramics; physical and chemical properties of grain boundaries in these ceramics; interactions with impurities and additives used to promote densification; physical properties of polycrystalline monazite ceramics; and the precipitation of monazite phases in an efficient, simple and economical manner. We propose to address these issues to serve as a knowledge base for using monazite as a nuclear waste form.

Development of Nuclear Analysis Capabilities for DOE Waste Management Activities

Project ID: 60077

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Research Objective

The objective of this project is to develop and demonstrate prototypical analysis capabilities that can be used by nuclear safety analysis practitioners to:

1. demonstrate a more thorough understanding of the underlying physics phenomena that can lead to improved reliability and defensibility of safety evaluations; and
2. optimize operations related to the handling, storage, transportation, and disposal of fissile material and DOE spent fuel.

To address these problems, this project has been investigating the implementation of sensitivity and uncertainty methods within existing Monte Carlo codes used for criticality safety analyses. It is also investigating the use of a new deterministic code that allows for specification of arbitrary grids to accurately model geometric details required in a criticality safety analysis. This capability can facilitate improved estimations of the required subcritical margin and potentially enable the use of a broader range of experiments in the validation process. The new arbitrary-grid radiation transport code will also enable detailed geometric modeling valuable for improved accuracy in application to a myriad of other problems related to waste characterization. Application to these problems will also be explored.

Research Progress and Implications

This report summarizes work after 2-1/2 years of a 3-year project. Since the work on the project began, significant advances in the state-of-the-art in nuclear criticality safety analyses have been achieved. One substantial accomplishment is the completion of a working version of the three-dimensional (3-D) Sensitivity Analysis Module for SCALE (SAMS)¹ and enhancements to the KENO V.a Monte Carlo code to calculate the angular neutron fluxes and flux moments necessary for sensitivity analyses. With these codes, which are now in limited internal use as beta versions, it is possible to calculate sensitivity parameters for several reaction types for any system that can be modeled using the Criticality Safety Analysis Sequence (CSAS) of SCALE which applies the KENO V.a Monte Carlo code.

Through this project, new techniques have been developed for the calculation of angular neutron fluxes and flux moments in Monte Carlo calculations. With these first-of-their-kind capabilities, it is now possible to calculate sensitivity parameters for numerous important reactions in criticality safety calculations. These reaction types include the total reaction rate, multiple types of scattering, numerous absorption reactions, and fission as well as $\bar{\nu}$, the average number of neutrons produced per fission, and χ , the energy spectrum for neutrons emerging from fission. Many of the limitations that were placed on this methodology early in the research process have been resolved, and the solution

techniques have been demonstrated to produce accurate solutions for many different types of systems. The systems investigated included those with thermal, intermediate and fast neutron spectra, mixed-oxide and uranium-fueled systems, and various geometrical configurations ranging from simple spheres to large arrays of fuel rods. These systems have also included various moderating materials. Although the calculation time and computed uncertainties in the results varied widely for the various systems, the validity of the methodology has been demonstrated.

This new technology is currently being used in conjunction with sensitivity and uncertainty (S/U) techniques recently developed at ORNL to assess the applicability and completeness of certain sets of critical experiment benchmarks for code validation for desired DOE Office of Environmental Management (EM) applications.^{2,3} The use of sensitivity coefficients generated from the SAMS module has enabled researchers to greatly expand the number of experiments that can be considered using these new S/U techniques. Prior to this work, only 1-D and 2-D models of systems could be considered.

The generalized geometry deterministic neutron transport code NEWT has also evolved significantly since the inception of this project. The method for obtaining adjoint solutions was improved and debugged. Binary interface files were created to allow forward and adjoint flux data to be read by sensitivity/uncertainty analysis modules. The use of a hybrid differencing scheme and improved grid generation method have significantly improved the speed and accuracy of the calculations.

Much work has been directed toward improvements in the code's user interface. An automated grid-generation scheme has been implemented, to provide the user with an easy-to-use input process that will rapidly and flexibly generate complex geometric models. Grid schemes are generated based on the specification of elementary bodies in a problem domain, with user-defined grid refinement parameters. More recent work has focused on an input scheme that includes array capabilities, which allow one to build a sequence of repeating structures. Efforts are being made to create an input format similar to the KENO V.a Monte Carlo code commonly used in criticality analysis, so that input will be familiar to KENO users.

An input interface consistent with the specifications typically used by control modules of the SCALE code system has been developed for the application of NEWT. In addition, NEWT is being implemented within a 2-D depletion sequence that is under development as part of SCALE. Using the arbitrary-grid capabilities of NEWT, it is possible to obtain accurate 2-D flux distributions which, when used within the depletion sequence, will allow improved characterization of the complicated, heterogeneous fuel assemblies typical of the DOE-owned and EM-managed spent fuel inventory. An operational prototype of this sequence has been completed and is undergoing testing and debugging.

Planned Activities

During the remaining 6 months of this project, work will be performed to further refine the capabilities of these new computational tools. An automated SCALE sequence SEN3 will be developed to simplify the input for the 3-D sensitivity calculations. Further refinements will be made to NEWT to improve the code performance and user interface. Collaborative funding has been provided by the Idaho National Engineering and Environmental Laboratory (INEEL) to apply these prototypic sensitivity analysis tools to DOE/EM fuel storage applications. These applications will help demonstrate benefits and to understand limitations of the tools and techniques developed under this project. Where possible, enhancements will be made as identified via applications.

Information Access (References)

1. B. T. Rearden, "Development of SAMS: A Sensitivity Analysis Module for the SCALE Code System Using KENO V.a in the CSAS25 Sequence," Ph.D. Dissertation, Texas A&M University (December 1999).
2. B. L. Broadhead, C. M. Hopper, R. L. Childs, and C. V. Parks, *Sensitivity and Uncertainty Analyses Applied to Criticality Safety Validation: Methods Development*, NUREG/CR-6655, Vol. 1 (ORNL/TM-13692/V1), U.S. Nuclear Regulatory Commission, Oak Ridge National Laboratory, November 1999.
3. B. L. Broadhead, C. M. Hopper, and C. V. Parks, *Sensitivity and Uncertainty Analyses Applied to Criticality Safety Validation: Illustrative Applications and Initial Guidance*, NUREG/CR-6655, Vol. 2 (ORNL/TM-13692/V2), U.S. Nuclear Regulatory Commission, Oak Ridge National Laboratory, November 1999.

Miniature Nuclear Magnetic Resonance Spectrometer for In-Situ and In-Process Analysis and Monitoring

Project ID: 60247

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Alan Feinerman, University of Illinois at Chicago

Research Objectives

The main purpose of this research is to develop a nuclear magnetic resonance (NMR) spectrometer that is small enough to be held in the palm of a hand. Such an instrument could be used in many applications of importance to DOE as well as to industry. These applications would include in-field characterization of contaminants, monitoring and analysis of chemical processes in chemical plants and other environmental monitoring applications. In addition to having drastically reduced size and cost, a miniature NMR instrument would be ideally suited for chemical analysis of volume limited samples which frequently occur in biological, medical and drug development applications.

Research Progress and Implications

As of June 15th, 1998 several important results have been obtained. First of all, the miniature NMR probe which was built in the first year of the project was analyzed and tested for various properties. Secondly, design of the miniature permanent magnet for NMR started in the first year of the project was finalized and its fabrication was initiated. Lastly, preliminary designs of the shimming coils were evaluated.

To appreciate the significance of the various NMR components mentioned above to the entire NMR spectrometer it is worth briefly reviewing the basic principles of a NMR spectrometer. In NMR, nuclei of a sample that possess magnetic moments are excited into precessional motion around the direction of a static magnetic field. The frequency of this precession is proportional to the strength of the static field and is usually in the range of radio frequencies (40-500MHz). This precession is detected using a NMR probe, which is usually a radio frequency coil. The signal thus obtained by the NMR probe from the precession of magnetic nuclei contains frequencies not only related to the static magnetic field, but also to local molecular scale fields. This allows characterization of the collection of nuclei chemically and makes NMR spectrometer an important tool in analytical chemistry.

There are two main difficulties in most NMR spectrometers. One is related to the weakness of the NMR signal. This is usually dealt with by increasing the strength of the static magnetic field and by designing more sensitive NMR probes. The other difficulty is related to the uniformity of the static magnetic field over the extent of the sample. Non-uniform static field limits the spectral resolution and of the spectrometer and its usefulness as an analytical tool by obscuring the presence of the local molecular interactions. Field correction constant current coils called shimming coils are most frequently used to improve field uniformity.

In the miniature NMR spectrometer being developed in this project, the static magnetic field of strength 1 and 2 Tesla will be produced by a permanent magnet over the extent of about 100 cubic millimeters. The radio frequency coil acting as the NMR probe will consist of flat ribbon of copper conductor wound in a scroll around a small (0.5 mm) diameter capillary used to hold the liquid sample. The NMR probe and the capillary will be placed between two silicon wafers on which shimming coils will be patterned.

Having developed and constructed 0.5 and 0.8 mm scroll-style NMR probes in the first year of the project, the sensitivity and spectral resolution of these probes were studied theoretically and tested experimentally this year. A semi-analytical technique was developed to analyze spectral resolution

of the miniature scroll probes. This technique is based on calculation of equivalent magnetic charges induced on the surfaces of the scroll probe by the external static uniform magnetic field used to produce nuclear magnetic precession. Physically the equivalent magnetic charges are related susceptibility differences between the sample and the NMR probe. The presence of such susceptibility difference turns out to be a critical factor limiting spectral resolution in miniature NMR because the surface of the NMR probe is in much closer proximity to every point within the volume of the sample than in large scale instruments. The method of calculating non-uniformity in the static magnetic field caused by the susceptibility mismatch and of the resulting spectral distortions caused by the NMR probe appeared in [1].

In addition to developing theoretical methods that could be used to analyze spectral distortions caused by miniature NMR probes, these theoretical methods were tested experimentally this year. The experimental testing of the spectral distortions was carried out using NMR facility at the Research Resources Center at the University of Illinois at Chicago. The results of these experimental tests as well as theory and design of scroll-style NMR probes were submitted as a paper to the Journal of Magnetic Resonance. They were also part of a Master's Thesis of my student Eric Growney.

In addition to studying spectral distortions caused by miniature NMR probes, the study of sensitivity of miniature scroll and wire-style NMR probes was carried out. Analytical calculations of the signal-to-noise ratio in these probes were performed. Subsequently, Finite Element method was used to refine the calculations of the signal-to-noise ratio. These calculations required computation of radio frequency field and losses within the NMR probes. The above theoretical developments demonstrated how the NMR probes behave with varying number of layers. We are the first group to study the use of multi-layer radio frequency coils for use as NMR probes. The Finite Element calculations were compared with electrical tests of losses in scroll-style miniature NMR probes that were conducted in the first year and good agreement between theoretical predictions and the tests was found. Moreover, tests of relative signal-to-noise ratio of the NMR probes with different number of layers were performed this year using NMR data directly this year. These tests also showed very good agreement with the theoretical calculations. The results of theoretical signal-to-noise ratio calculations and comparison with NMR and electrical measurements were submitted in a paper to the IEEE Transactions on Magnetics. This work also appears partly in the Master's Thesis of my student Lisa Murphy and is also a part of PhD work by Samuel Grant.

In studying the problem of noise and losses in NMR probes, a general method for calculation of excess losses (losses due to high frequency currents) in conductors of arbitrary shape was developed. The main difference of this method over other methods previously employed to solve this type of problem is that it allows an easily computable estimate of losses and, therefore, of noise. This method of calculation of losses was discussed in a paper submitted to the Journal of Applied Physics and will be presented at the MMM-99 conference.

In addition to finalizing the design, analysis and experimental testing of miniature NMR probes this year work was performed on modeling of permanent magnet materials that could be used in producing static magnetic fields for NMR. One of the main difficulties in designing high uniformity NMR permanent magnets is understanding and control of permanent magnetization. That, in turn, relies on understanding of hysteresis. Work was started in the first year on the development of hysteresis model that could be used for this purpose. This work was completed this year and a paper about this work appeared [2]. The most important result of this work was that conditions were established that allows one to determine with certainty if the suggested hysteresis model is applicable to a given magnetic material. Work was also performed this year on the measurement methods that could be used to identify parameters of the vector-type hysteresis model developed. This work used Vibrating Sample Magnetometer available in the laboratory of Prof. James Kouvel at the Physics Department at the University of Illinois at Chicago. The paper containing the proposed hysteresis model and measurement of its parameters was submitted to the Journal of Applied Physics. The results of this paper will also be presented at the MMM-99 conference. This work was performed with the help of my student Yikun Huang.

Analysis of the permanent magnet structure was also finalized this year. This permanent magnet design differs from the one originally proposed (described in the original proposal). Its main advantage is that it is azimuthally symmetric and allows complete access to the NMR sample and probe from all

sides as well as axially. It also allows axial spinning of the magnet to improve the apparent uniformity of the static magnetic field produced. A paper summarizing the detail of the permanent magnet design was submitted to the IEEE Transactions on Magnetics. This magnet is currently being manufactured with the assistance of the Dexter Magnetics Corporation.

Lastly, this year we began designing shimming coils that could be used for correction of static magnetic field non-uniformity. So far, it looks like planar coil array called Anderson coils will be the best for our purposes. The design and modeling of shimming coils is being carried out with the help of my student Muqu Sun.

Planned Activities

We plan to finish the fabrication of the permanent magnet by February 2000. Testing of the magnet and of the magnetic field uniformity produced by this magnet will be conducted until about June 2000. At the same time we plan to finish design and fabrication of the shimming coils by June 2000. Starting around June 2000 and until January 2001 the entire miniature NMR spectrometer will be tested.

Publications and Presentations

Refereed Publications

- [1] E. Growney, G. Friedman, R. Gerald, "Computation of distortions in magnetic field and spectrum for NMR instruments", J. Appl. Phys., Vol. 85, No. 8, April, 1999, p. 5205
- [2] G. Friedman, "Conditions for the representation of vector hysteresis by the vector Preisach model", J. Appl. Phys., Vol. 85, No. 8, April, 1999, p. 4379
- [3] G. Friedman, "A method for characterization of hysteresis in two dimensions", to appear in IEEE Transactions on Magnetics
- [4] G. Friedman, "Second order Preisach model of scalar hysteresis", to appear in Physica B
- [6] E. Growney, S. Grant, G. Friedman, "Calculations and experimental verification of spectral distortions due to miniature NMR probes", submitted to Journal of Magnetic Resonance
- [7] S. Grant, L. Murphy, R. Magin, G. Friedman, "On the computation and experimental verification of signal to noise ratio for miniature radio frequency coils used as NMR probes", submitted to IEEE Transactions on Magnetics
- [8] G. Friedman, I.D. Mayergoyz, "On the estimate of excess eddy current losses in current carrying conductors", submitted to Journal of Applied Physics
- [9] Y. Huang, G. Friedman, I. Obaidat, J. Kouvel, "Identification of the switching field function of bistable elements in vector hysteresis models", submitted to Journal of Applied Physics

Conference Presentations

- a) Growney, E.; Friedman, G.; Gerald II, R.; Klingler, R.; Rathke, J.; "BOUNDARY ELEMENT TECHNIQUE FOR CALCULATIONS OF FIELD AND SPECTRAL DISTORTIONS", ISMRM Workshop on Computational Electromagnetics in Magnetic Resonance, College Station, TX. May 30 - June 1, 1998.
- b) Growney, E.; Friedman, G.; Gerald II, R.E.; Klingler, R.J.; Rathke, J.W.; Nunez, L.H.; Aumeier, S.E.; "NMR FOR NONDESTRUCTIVE EVALUATION OF NUCLEAR MATERIALS", NMR Symposium of the 40th Rocky Mountain Conference on Analytic Chemistry, Denver, CO. July 25-30, 1998.
- c) Growney, Eric; Friedman, Gennady; Gerald II, Rex; Klingler, Robert; Rathke, Jerome; Nunez, Luis; "EVALUATION AND DESIGN OF TOROID CAVITY PROBES BASED ON CALCULATED DISTORTIONS", The 40th Experimental Nuclear Magnetic Resonance Conference, Orlando, FL. February 28 - March 5, 1999.
- d) Growney, Eric; Friedman, Gary; "COMPUTATIONS OF DISTORTIONS IN MAGNETIC FIELD SPECTRUM FOR NUCLEAR MAGNETIC RESONANCE INSTRUMENTS", The 43rd Annual Conference on Magnetism and Magnetic Materials, Miami, FL. November 9-12, 1998.
- e) Grant, Samuel; Growney, Eric; Magin, Richard; Friedman, G.; "SIGNAL-TO-NOISE IMPROVEMENT WITH MULTILAYERED RF MICROCOILS", The 40th Experimental Nuclear Magnetic Resonance Conference, Orlando, FL. February, 28 - March 5, 1999.

Thermodynamics of the Volatilization of Actinide Metals in the High-Temperature Treatment of Radioactive Wastes

Project ID: 60319

Dr. Ken Jackson, Lawrence Livermore National Laboratory

Donald R. Olander, University of California at Berkeley

Research Objective

We are performing a detailed study of the volatilization behavior of U, Pu and possibly Am and Np under conditions relevant to the thermal treatment (destruction) of actinide-containing organic-based mixed and radioactive wastes. The primary scientific goal of the work is to develop a basic thermochemical understanding of actinide volatilization and partitioning/speciation behavior in the thermal processes that are central to DOE/EM's mixed waste treatment program. This subject addresses at least two key technical needs/problem areas recently identified by DOE/EM's Office of Science & Technology: emission-free destruction of organic wastes, and interactions between actinides and organic residues in materials stabilization.

A sound basis for designing safe and effective treatment systems, and the ability to allay public concerns about radioactive fugitive emissions, will be the principal benefits of the project. The proposed work is a combination of experimental studies and thermodynamic modeling. Vapor pressure measurements will be made to determine U, Pu and possibly Am volatile species and the extent of their volatilization when UO_2/U_3O_8 , PuO_2 and AmO_2 solids are heated to temperatures of 500 to 1200 C under pyrolyzing (reducing) conditions or under oxidizing conditions in the presence of chlorine. Work on uranium volatilization under reducing conditions is being performed in a laboratory at UC Berkeley in a collaboration with Professor D.R. Olander. In parallel with the experimental effort, a complete thermodynamic database for expected actinide gaseous species will be developed from literature data, from the proposed measurements, and from data predictions using bond energy correlation and statistical thermodynamics estimation methods.

Research Progress and Implications

This report summarizes work performed since June 1 1998 in the second year of a 3-year project.

At UC Berkeley, Professor D.R.Olander and a graduate student (J.C.Cole) continued work on uranium oxide volatilization under reducing/gasification conditions. They have used the thermal transport furnace built during the first year to conduct two series of vaporization experiments on UO_2 -containing organic specimens in flowing Ar- H_2 - H_2O -CO-CO $_2$ atmospheres. The simulated waste specimens comprised (i) epoxy pellets filled with U_3O_8 powder and (ii) a dry Amberlite cation-exchange resin previously loaded with uranyl ions. Using a very sensitive neutron activation analysis technique and the TRIGA reactor at Oregon State University, they have been able to detect nanogram quantities of uranium on downstream deposition tabs, and hence show that some uranium transport has occurred at specimen temperatures as low as 600C. Currently, using high temperature filters, efforts are being made to understand the mechanism of uranium transport, and to characterize the suspected aerosol particles collected on the deposition tabs using electron microscopy. After unsuccessfully trying to obtain small quantities of bis(phthalocyaninato) uranium(IV) or superphthalocyaninine uranium(VI) commercially, we ended up synthesizing 50 mg of the latter compound at LLNL. Anhydrous uranium chloride starting compounds were kindly provided by

Dr. Carol Burns at LANL. It is intended to use this material as a model organouranium transportable specie in imminent transport experiments.

Preparations for the planned transuranium (Pu, Np, Am) volatility measurements using the transpiration technique have proceeded slowly, mainly due to unexpected B151 facility requirements to upgrade the ventilation system for the chosen room and glovebox from the category of Workplace Type 2 to Workplace Type 3. This necessitates the installation of additional ducting, blowers and HEPA filters, and has required numerous ES&H reviews and approvals. A postdoctoral fellow, Dr Nadia Hakem, was hired to work on this project in September 1998. Assembly of the glovebox in which the experiments will be performed, and associated equipment such as the furnace and controller, gas distribution and control circuits and the toxic gas cabinet, etc, is about 90% complete. The furnace has been tested to its maximum operating temperature (1200C), and the temperature profile of the transpiration tube has been determined.

In support of our thermodynamic database compilation effort, we have acquired, and are in the process of installing, the latest stand-alone version of the FACT/EQUILIBRIUM computer code (V3.0). Like other FACT users, we have encountered difficulty running this software under Windows NT 4.0. Dr Hakem is trying to resolve this problem, and, in the process, is becoming familiar with the FACT/EQUILIBRIUM program and its ability to make speciation predictions.

Planned Activities

During the remainder of the current fiscal year (June – September 1999), we expect to complete both the B-151 room modification and installation of the glovebox and related transpiration system equipment. A new series of uranium volatility experiments will be conducted at UC Berkeley. Having recently obtained evidence of uranium migration, these experiments will be designed to characterize the mechanism of transport of uranium under gasification conditions, and possibly to identify the responsible specie(s). Provided continued good progress is made, it is expected that these experiments will be continued through FY2000. We expect to conduct the planned transpiration experiments on Pu, Am, and possibly Np oxides in chlorine-containing atmospheres in the newly installed glovebox during FY2000. Before this, the glovebox will be activated using uranium oxide as a surrogate for plutonia. Also during FY2000, as time and funding allow, we will continue to estimate key thermodynamic parameters for actinide vapor species of interest and to develop the database that will be used in thermochemical prediction models.

Information Access (Publications)

Two manuscripts dealing with thermodynamic data estimations for uranium and plutonium vapor species are in preparation.

Aqueous Electrochemical Mechanisms in Actinide Residue Processing

Project ID: 59967

Dr. David E. Morris, Los Alamos National Laboratory

Dr. Carol J. Burns, Los Alamos National Laboratory

Dr. Wayne H. Smith, Los Alamos National Laboratory

Dr. David L. Blanchard, Pacific Northwest National Laboratory

Research Objectives

New and/or improved solutions to stabilization and volume reduction of nuclear materials processing residues are urgently needed. Mediated electrochemical oxidation / reduction (ME/OR) processes are one approach for incinerator ash, combustibles, and other solid residues. However, questions remain concerning the mechanisms of these processes, and how they might be optimized. In addition, further research is merited to extend their range of applicability. We will develop a deeper understanding of the thermodynamic and mechanistic aspects of heterogeneous electron transfer that lie at the heart of these MEO/R processes. We will also develop and test new approaches based on the results of these fundamental studies using actual residue materials. Key aspects of this proposal include:

- Determination of the potential windows for oxidation / reduction of colloidal actinide oxides and actinide-bearing oxide and organic substrates and the e⁻-transfer kinetic parameters that govern the current - overpotential characteristics.
- Development of adaptations of mediation schemes and application of co-mediation reagents for oxidative and reductive dissolution based on complexation of the surface-bound or solid-phase actinides and/or the dissolved redox mediator.
- Execution of bench-scale tests of new MEO/R schemes on actual residue materials.

Research Progress and Implications

This report summarizes work after ~ 2.3 years of a 3 year project. The emphasis is on significant progress made in the past 12 months as described in detail in the Information Access items listed below. These new results have led to a presentation at a national meeting of the American Chemical Society and a manuscript accepted for publication.

Our research focus continues to be on the redox kinetics and energetics of UO_2^{2+} and Eu^{3+} (as a Pu surrogate) sorbed onto metal oxide phases that are constituents in incinerator ash residue. Detailed sorption studies versus pH and ionic strength have clearly shown that the sorption mechanism for both metals entails inner-sphere complexation. The strength of this interaction is greater for uranyl than europium on both substrates and greater for both metals on titania than on silica. Surface complexation has also been characterized by luminescence spectroscopic studies of the supernate and solid phases resulting from the sorption reactions. These data show significant differences in the spectral characteristics of the surface-bound metals relative to the metal species in solution in the equilibrium reactions. In particular, for the Eu^{3+} surface complexes the hypersensitive transition in the emission spectrum shifts in a manner consistent with lowering of the symmetry of the metal ion as a result of the perturbing influence of the inner-sphere surface interactions. In addition, the emission lifetime for these Eu^{3+} surface complexes decreases in a manner consistent with the replacement of inner-sphere coordinated H_2O with surface hydroxyl groups. Similar results were obtained for the UO_2^{2+} surface complexes. Finally, the sorption samples were also subjected to heating at ~ 200 °C to mimic calcination. The impact on the surface speciation was significant. In effect, the variation in

surface speciation seen with pH for the hydrated samples was removed, and all samples exhibited ~ constant surface complexation characteristic of intimate interaction between the metal species and the surface.

Voltammetric data have also been obtained for aqueous suspensions of the Eu^{3+} - and UO_2^{2+} -laden silica and titania samples. All data were collected at a static mercury drop electrode using a linear potential sweep method. The redox characteristics of these surface-supported analytes show a number of perturbations relative to the dissolved metal species in similar solutions. Both strong and weak sorption interactions of the colloidal material with the Hg electrode surface have been identified. The electrode sorption is stronger for the titania substrates than the silica. Surprisingly, however, the potential for substrate-bound metal reduction is not dramatically changed from what is observed in homogeneous solution. One of the more interesting observations from this work relates to the electron-transfer dynamics for the dehydrated samples. The dehydrated $\text{Eu}^{3+}/\text{SiO}_2$ sample actually shows faster electron-transfer than does Eu^{3+} in bulk homogeneous solution. In contrast, dehydrated $\text{UO}_2^{2+}/\text{SiO}_2$ shows slightly slower electron-transfer dynamics than UO_2^{2+} in bulk homogeneous solution. This behavior is almost certainly related to the nature of the interaction of the metal ions with the metal-oxide surfaces. However, since Pu^{4+} is expected to have a chemically similar surface complexation environment to that of Eu^{3+} , this result suggests that plutonium should also have more favorable electron-transfer kinetic properties on the residue surface than in bulk solution. Initial experiments have also been conducted in the presence of several simple complexing agents including acetate and carbonate. These results are still under analysis.

Planned Activities

The remainder of this aspect of the project will be devoted to a comparable suite of experiments using the aluminous phase gibbsite and to further investigations of the role of homogeneous complexants on the dissolution/redox properties of the substrate-bound metals. The studies with gibbsite are intended to broaden the impact of this work to include solids isolated from HLW tanks at Hanford and Savannah River which include substantial solid aluminum phases. Other ongoing efforts supported at Los Alamos and by our PNNL collaborator include studies of MEO dissolution of organic substrates, voltammetric detection of plutonium at dilute concentrations, and spectroscopic (principally x-ray absorption) characterization of actinide chelate complexes.

Information Access

Refereed Publications: “ Eu^{3+} and UO_2^{2+} Surface Complexes on SiO_2 and TiO_2 ,” T.A. Diaz, D.S. Ehler, C.J. Burns, and D.E. Morris, First Accomplishments of the DOE Environmental Management Science Program, American Chemical Society, **in press**.

Presentations: “Aqueous Electrochemical Mechanisms In Mediated Dissolution Of Actinide Residues,” D.E. Morris, C.J. Burns, W.H. Smith, D.L. Blanchard, and T. Diaz, Abstracts Of Papers Of The American Chemical Society, v. 218(pt.1) pp. 91-NUCL AUG 22, 1999

Optional Information

Ms. Tammy Diaz, a senior environmental geology major at New Mexico Highlands University who did a summer research internship in FY99 working on this EMSP project, was awarded a U. S. Department of Energy 1999-2000 DOE Environmental Management Scholarship Program Hispanic Scholarship Fund grant.