

Research Activity: **Heavy Element Chemistry**
Division: Chemical Sciences, Geosciences, and Biosciences
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Portfolio Description:

This activity addresses the scientific principles that form the basis for the understanding of actinide and fission product chemistry.

Areas of interest include, but are not limited to, aqueous and non-aqueous coordination chemistry; gas-phase, solution, and solid-state speciation and reaction kinetics; measurements of chemical, thermodynamic, and magnetic properties; synthesis of actinide-containing materials; chemical properties of the heaviest actinide and transactinide elements; and theoretical methods for the prediction of heavy element electronic and molecular structure and reactivity.

The actinide elements form a unique chemical series in the periodic table due to the filling of the 5f electron shell. Their nuclear properties, and the resulting use of uranium 235 and plutonium 239 in weapons and as energy sources, make the actinide series an essential industrial material. This activity supports efforts to develop a fundamental understanding of chemical bonding of the actinides, and to determine the similarities and differences between the actinides and the 4f lanthanide series or the 3d, 4d, and 5d transition metal series. There is a close and synergistic relationship between the heavy element chemistry activity and the separations activity that deal with radioactive isotopes. This activity also contributes to the maintenance of the scientific infrastructure required to meet future challenges in heavy element chemistry and to provide unique facilities for the training of students.

Unique Aspects:

This activity represents the only source of funding for basic research in the underlying chemical and physical principles of the actinide and fission product materials in the United States. Its major emphasis is on understanding the underlying chemical and physical principles of the actinide and fission product materials. The activity is primarily based at the national laboratories because of the special licenses and facilities needed in order to obtain and to safely handle these radioactive materials.

Relationship to Others:

This activity provides the fundamental understanding of the properties of the actinides and fission product elements that are necessary for the Department of Energy stewardship responsibilities in its defense programs, nuclear energy, and environmental clean-up missions. The heavy element chemistry activity conducts unclassified basic research on all the actinide and trans-actinide elements, while the applied programs generally limit their investigations to the chemical and material properties of specific elements and systems of strategic, economic, or programmatic interest. This activity also has close ties to the DOE BES separations and analysis activities, which have a major focus on the separation of actinides and fission products.

Significant Accomplishments:

The heavy element chemistry activity had its genesis in the Manhattan project, and it continues today as the nation's only basic research program supporting the exploration of the physical and chemical properties of the transuranium elements and their compounds. The early goal was to determine the basic inorganic chemistry and physical properties of the new elements and their compounds and to discover new elements. The chemical properties of the transuranium elements, especially plutonium, originally were determined from microscale experiments. The bismuth phosphate process, used at Hanford for the separation of plutonium from uranium and fission products on an industrial scale, was developed and scaled up from these results. The completion of the High Flux Isotope Reactor (HFIR) at ORNL in the 1960's provided a stable supply of transcurium elements that continues to the present. The basic inorganic chemistry of the elements through einsteinium (Es, atomic number 100) has been determined with macro quantities of the elements. For the elements past Es in the periodic table, tracer techniques

and one-atom-at-a-time chemistry have been developed and carried out through element 108 to determine chemical properties.

Taken together, the results from this activity have confirmed the Seaborg hypothesis that the actinide elements are best represented in the periodic table as a 5f element series placed under the lanthanide or 4f series. Interpretations of spectroscopic results have provided estimates of thermodynamic quantities such as oxidation-reduction potentials and enthalpies of sublimation. Specific electronic transitions determined in this activity have proven useful in developing processes for laser isotope separation of uranium and plutonium. Structural systematics of the actinide metals, oxides, and halides as a function of atomic number have been determined. Magnetic measurements have shown that the light actinide metals have delocalized 5f orbitals (*i.e.*, the 5f electrons form bands), but the f electrons become localized at americium, element 95 in the periodic table. Thus, the magnetic behavior of the first part of the actinide series resembles that of the d-orbital transition metals but the heavier actinides exhibit behavior similar to the rare earth metals.

Mission Relevance:

Knowledge of the chemistry of the actinide and fission product elements is necessary for the successful conduct of many of DOE's missions. In the defense area, understanding the chemistry and material properties of specific actinides was key to the development of our nuclear deterrent, and now plays a major role in the stewardship of the stockpile. This activity conducts the broadly based unclassified research on actinides that provides the scientific basis for framing the narrower issues facing the DOE's defense programs. In the area of nuclear energy, this activity provides the fundamental understanding of actinide and fission product chemistry that underpins the development of advanced nuclear fuels, as well as the predictions of how spent nuclear fuels degrade and radionuclides are transported under repository conditions. Driven by the necessity to identify possible important species in highly basic solutions found in the waste tanks at the Hanford and Savannah River sites, this activity has had a renewed emphasis on the chemistry of the lighter transuranium elements and fission products. Knowledge of the molecular speciation of actinide and fission products materials under tank conditions is necessary to treat these complex mixtures. Molecular speciation information is also needed to predict the fate of actinide and fission product elements accidentally released to the environment. Finally, the analytical methods developed as part of the basic research funded under this activity have broad application across all the applied missions of DOE that deal with nuclear materials.

Scientific Challenges:

The role of the 5f electrons in bond formation remains the fundamental unanswered question in actinide chemistry, and hence provides the central focus for this activity. For the light actinide metals and some of their alloys, the 5f orbitals participate in the band structure of these materials. Whether the 5f orbitals participate significantly in molecular compounds is still unclear. Molecular-level information on the geometry and energetics of bonding can now be obtained from experiments carried out at the Nation's synchrotron light sources. These new tools are enabling studies of actinides as small clusters and at interfaces such as between solutions and mineral surfaces or other well-defined solids. However, actinide and fission product samples have to be treated with special consideration because of their radioactivity, which has limited the types of experiments that can be safely conducted. For example, in the soft x-ray regime new sample preparation techniques need to be developed so that micro-quantities of well-characterized actinide samples can be measured using high vacuum techniques, or in "wet" cells to study actinide chemistry at liquid-solid interfaces.

Sophisticated quantum mechanical calculations that treat spin-orbit interactions accurately will need further development before they can be used for predicting the properties of molecules that contain actinides. Development and validation of such codes would provide a means for obtaining fundamental information about actinide species that are difficult to study experimentally. Another goal of such codes is the ability to predict the electronic spectra of important species and to correlate the optical spectra with actinide molecular structure.

Funding Summary:

Dollars in Thousands		
<u>FY 2000</u>	<u>FY 2001</u>	<u>FY 2002</u>
\$6,753	\$8,154	\$7,685
<u>Performer</u>		<u>Funding Percentage</u>
DOE Laboratories		75.0%
Universities		15.0%
Other		10.0%

This activity supports research in heavy element chemistry at universities and encourages collaborations between university and laboratory projects in this area. Graduate and postdoctoral students are trained in this area and provide personnel for the technological challenges associated with the heavy elements. Approximately twenty undergraduate students, chosen from universities and colleges throughout the United States, are given introductory lectures in actinide and radiochemistry each summer in two programs based at BNL and San Jose State University

Projected Evolution:

Kinetic, thermodynamic, and electrostatic effects in separations processes and in synthetic reactions involving the actinides are not well understood. Modern tools brought about by technological innovations can now be brought to bear on these topics. Heavy Element Chemistry research will pursue advances in gas phase actinide ion chemistry that explore new reactivity patterns, high-pressure studies of actinide alloys, and spectroscopic investigations of new actinide materials. Other areas where new advances are expected include: the design, synthesis and effectiveness of preorganized chelating agents for the separations of particular actinide ions; characterization of important actinide and fission product species in separations processes for a more fundamental understanding of why particular separations processes work; effects of temperature on actinide solution structure/property relationships, photophysics and photochemistry of actinide ions in their excited states, actinide organometallic chemistry, and theoretical work on simple actinide molecular compounds.

More sophisticated quantum mechanical calculations of actinide compounds and actinide species in aqueous solution will be undertaken; however, experimental data are needed to develop and test the basis sets used in such calculations. New facilities for safely handling radioactive materials at the synchrotron sources will permit more widespread use of techniques such as XANES, EXAFS, and x-ray scattering on radioactive samples, thus providing more detailed information on actinide speciation in solutions and in crystalline and amorphous solids. These data will complement data from other techniques, and can be used to validate and extend the quantum mechanical calculations.

Improved modeling of actinide transport requires a thorough understanding of the processes describing sorption on surfaces. Many surface complexation models exist, but experimental validation of these models has not been readily available. Technological advances now allow molecular characterization of actinide surface species to be explored. An enhanced program of characterizing and modeling the nature of the interactions of actinides with well-characterized liquid-solid interfaces, including mineral surfaces under environmentally relevant conditions, is needed.

The magnetic and electronic properties of actinide intermetallic systems are not understood. These effects depend on the hybridization of the 5f electrons with conduction electrons. The strength of such hybridization is a direct function of the local metal bond environment around the actinide ion and much work needs to be done, especially on transuranium compounds. Work in this area should provide a much better understanding of the changes in the types of bonding exhibited by the light *versus* the heavy actinides.

Increased emphasis will be placed on encouraging academic investigators to enter this field and to address outstanding questions in heavy element chemistry. Because most academic institutions do not have the facilities necessary to safely handle radioactive materials, it is anticipated that most academic investigators will conduct their experimental work in collaboration with one or more national laboratory. Increased academic involvement is essential for training the next generation of scientists with experience in handling radioactive materials.

Finally, the actinide facilities in the national laboratories are aging. In order to continue to carry out forefront research, infrastructure problems at these laboratories must be addressed.

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