

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 the chemical behavior of actinide and transactinide elements and their compounds, as well as of long-lived radioactive fission products.

Areas of interest are synthesis of actinide-containing materials; coordination chemistry and reaction kinetics of actinides in aqueous and non-aqueous solutions; gas-phase and solid-state chemical bonding; measurements of chemical, thermodynamic, spectroscopic, and magnetic properties; chemical properties of the heaviest actinide and transactinide elements; and theoretical methods for the prediction of heavy element electronic properties, molecular structure, and reactivity.

The actinide elements form a unique chemical series in the periodic table due to the filling of the 5f electron subshell. Their nuclear properties, and the resulting use of uranium and plutonium isotopes as energy sources and in weapons, make some actinide-containing materials essential for national security. The heavy element chemistry activity supports efforts to develop a fundamental understanding of chemical bonding and reactivity of the actinides and transactinides, and to explain the similarities and differences among the actinides, the 4f (lanthanide) elements, the 3d, 4d, and 5d transition metals, and the transactinide elements. There is a close and synergistic relationship between the heavy element chemistry program and the separations science program. The heavy element chemistry program contributes to the maintenance of the scientific infrastructure required to meet future challenges in heavy element chemistry and to provide unique facilities for the education of students.

Unique Aspects:

This activity represents the only source of funding for basic research in the United States into the underlying chemical and physical properties of the actinides, transactinides, and fission products. Its major emphasis is to understand these properties well enough to predict and control the behavior of the heavy elements. The activity is primarily based at the national laboratories because of the special licenses and facilities needed in order to obtain and to handle these radioactive materials safely.

Relationship to Other Programs:

This activity provides the fundamental understanding of the properties of the heavy 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 program sponsors unclassified basic research on all the actinide and transactinide elements as well as on long-lived radioactive fission products, while applied programs generally limit their investigations to the properties of specific materials 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 from other elements.

Significant Accomplishments:

The heavy element chemistry activity had its genesis in the Manhattan Project. 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, were first determined from microscale experiments. The processes for the separation of plutonium from uranium and fission products on an industrial scale were 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 curium and heavier elements that continues to the present. The basic inorganic chemistry of the elements through einsteinium (Es, atomic number 99) has been determined with small but weighable quantities of

the elements. Tracer techniques and atom-at-a-time chemistry have been developed and carried out with international collaborations for the elements heavier than Es through element 108 to determine chemical properties.

Taken together, the results from this activity have repeatedly confirmed the Seaborg hypothesis that the actinides are best represented in the periodic table as a 5f element series placed under the 4f (lanthanide) 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 that the 5f electrons become localized at americium, element 95, and remain localized through Lr, element 103. 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 that of 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 nuclear stockpile. This program 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 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 changing role of the 5f electrons in chemical bond formation across the actinide series remains the fundamental unanswered question in actinide science, and hence provides the central focus for this program. The 5f orbitals participate in the band structure of materials that contain the light actinide metals and some of their alloys. 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 need further development so that they can be used for predicting the properties of molecules that contain actinides. Development and validation of these quantum mechanical calculations will provide a means to obtain fundamental information about actinide species that are difficult to study experimentally, will predict the electronic spectra of important species, and will correlate the optical spectra with actinide molecular structure.

Funding Summary:

Dollars in Thousands		
<u>FY 2002</u>	<u>FY 2003 Request</u>	<u>FY 2004 Request</u>
7,637	8,637	8,625
<u>Performer</u>	<u>Funding Percentage</u>	
DOE Laboratories	75.0%	
Universities	15.0%	
Other	10.0%	

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

This activity supports research in heavy element chemistry at universities and encourages collaborations between university and laboratory scientists. Graduate and postdoctoral students are trained in this area and provide personnel for the unique technological challenges associated with the heavy elements. Twenty-four undergraduate students, competitively chosen from universities and colleges throughout the United States, are given lecture and laboratory instruction in actinide chemistry, radiochemistry, and nuclear medicine each summer in two programs based at Brookhaven National Laboratory 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 behavior of actinide alloys, and spectroscopic transitions in 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. 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 adsorption on surfaces and desorption from surfaces. 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 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. High pressure studies of actinide materials will provide valuable insights to advance the understanding of band formation and polarization behavior of the electrons. 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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