Research Activity: **Heavy Element Chemistry**

Division: Chemical Sciences, Geosciences, and Biosciences
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Portfolio Description:

This activity supports research in the chemistry of actinide elements (a family of radioactive elements that includes uranium and plutonium), transactinides, and long-lived radioactive nuclear reactor fission products such as technetium. Areas of interest are the chemical bonding and reactivity of actinide ions in solids, solutions, and gases; synthesis, structure, and properties of actinide materials; theoretical methods to predict heavy element electronic and molecular structure and reactivity; and chemical properties of the transactinide elements. The central themes are the properties that results from the electron orbitals available to these elements, especially the 5f orbitals.

The program emphasis is the chemistry of technetium, uranium, and transuranic elements, driven by the necessity to characterize and control long-lived radioisotopes produced in power reactors and found at Department of Energy (DOE) legacy waste sites. Knowledge of the chemical bonding of legacy actinide and fission products is necessary to predict the properties of these complex mixtures and to treat them. This activity is coupled to the BES Separations and Analysis activity, to actinide and fission product chemistry research in DOE's Environmental Remediation Sciences Program, and to nuclear fuel cycle research within DOE's Office of Nuclear Energy. The education of undergraduates, graduate students, and postdoctoral researchers in radiochemistry at national laboratories and universities is an important responsibility of this activity.

Unique Aspects:

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

Relationship to Other Programs:

This activity provides the fundamental understanding of the properties of the actinides and fission product elements that support DOE missions in advanced nuclear energy, stewardship responsibilities for defense programs, and environmental clean-up. The heavy element chemistry program conducts unclassified basic research on all the actinide and transactinide elements, while applied programs (nuclear energy, environmental, stockpile stewardship) generally limit their investigations to the chemical and material properties of specific elements and systems of strategic programmatic interest. This activity also has close ties to the BES separations activity, which has 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. The early goals were to discover new elements and to determine their chemical and physical properties from microscale and tracer experiments. Processes for the separation of plutonium from uranium and fission products on an industrial scale were then developed. The chemistry of the elements through einsteinium (Es, atomic number 99) has been determined with small but weighable quantities. For the elements heavier than 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. Organometallic chemistry has been enriched by discovery of many unique organoactinide compounds.

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 thermodynamic quantities such as oxidation-reduction potentials and enthalpies of reactions. Specific electronic transitions determined in this activity have proven useful to develop processes for laser isotope separation of uranium and plutonium. Magnetic measurements have shown that the light actinide metals have delocalized 5f orbitals and resemble d-orbital transition metals, whereas the f electrons become localized at americium, element 95; thus the heavier actinide metals 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 success of many DOE missions. 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. 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. Driven by the necessity to identify and treat radioactive species in caustic solutions found in or near many waste tanks at DOE sites, this activity has had a renewed emphasis on the molecular speciation of the transuranium elements and fission products. Finally, the analytical chemistry methods developed under this activity have broad application across the applied missions of DOE that deal with nuclear materials.

Scientific Challenges:

The role of the 5f electrons in bond formation remains the fundamental topic in actinide chemistry and is the central focus for this program. The 5f orbitals participate in the band structure of materials that contain the light actinide metals and their alloys. Evidence is accumulating that the 5f orbitals participate significantly in molecular compounds, for example, compounds required for advanced nuclear energy systems. Molecular-level information on the geometry and energetics of bonding can now be obtained at the Nation's synchrotron light sources and from multi-photon laser excitation studies. These new tools enable studies of actinides in the gas phase, as clusters, and at interfaces between solutions and surfaces of minerals and colloids in solution. Actinide and fission product samples must be handled in special facilities because of their radioactivity, which limits the types of experiments that can be safely conducted.

Sophisticated quantum mechanical calculations that treat spin-orbit interactions accurately need further development so that they can be used to predict the properties of molecules that contain actinides. Development and validation of computer codes will provide a means for obtaining 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. Improved modeling of actinide transport requires understanding of the processes describing sorption on surfaces such as colloidal particles. Surface complexation models can predict the migration of radioactive species; experimental validation of the theoretical properties of models will be the key to understanding the role of the 5f electrons.

Funding Summary:

Dollars in Thousands

FY 2007	FY 2008	FY 2009 Request
9,427	9,427	18,789

Performer	Funding Percentage
DOE Laboratories	81%
Universities	18%
Other	1%

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, encouraging collaborations between university and laboratory projects in this area. Twenty-four undergraduate students, chosen competitively from universities and colleges throughout the United States, are taught actinide chemistry and radiochemistry each summer in two programs at Brookhaven National Laboratory (BNL) and San Jose State University. Graduate and postdoctoral students are educated to provide personnel for the technological challenges associated with the heavy elements.

Projected Evolution:

At the frontier of the periodic table, theoretical chemists predict the properties of actinides and transactinides in gaseous molecules, clusters in liquids, and solid species, using modern calculation tools such as density functional theory. Because most actinide species have partly filled 5f electron subshells and all have highly charged nuclei, both spin-orbit and relativistic effects must be included in the calculations. More sophisticated quantum mechanical calculations of actinide compounds and actinide species in environmental media are being developed. Heavy Element Chemistry research pursues advances in gas-phase chemistry that explore new reactivity patterns, photophysics and photochemistry of actinide ions in their excited states, and organoactinide chemistry.

Support of research to understand the chemical bonding of elements that have 5f electrons will lead to fundamental understanding of separations processes and to the design and synthesis of preorganized chelating agents for the separations of particular actinide ions. Research in bonding, reactivity, and spectroscopic properties of molecules that contain heavy elements and of actinides in environmentally relevant species aids the development of ligands to sequester actinides in the environment and to remove toxic metals from the human body. Better characterization and modeling of the interactions of actinides with well-characterized liquid-solid interfaces, including mineral surfaces under environmentally relevant conditions, is needed.

Research on synthesis, crystal structure, and bonding in actinide solids leads to materials that are designed to be especially stable in environments such as nuclear fuels and nuclear waste forms. Spectroscopic investigations of new actinide materials and high-pressure studies of actinide metals elucidate the unique bonding properties and electronic characteristics attributable to 5f electrons. New facilities for safely handling radioactive materials at the synchrotron sources will permit more widespread use of techniques such as x-ray absorption spectroscopy and scattering on radioactive samples, providing detailed information on actinide speciation in crystalline and amorphous solids such as spent fuel and radioactive waste forms.