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Getting the Neptunium Out of Nuclear Waste

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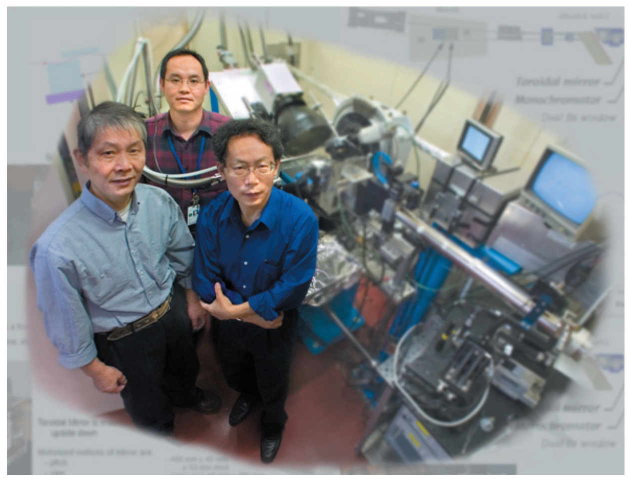
A study done at Berkeley Lab's Advanced Light Source (ALS) has revealed critical new information about neptunium, a radioactive element that poses long-term environmental hazards. The new information holds promise for safely removing neptunium from high-level nuclear wastes, a task that to date has proven extremely difficult.

Linfeng Rao, Guoxin Tian and Jide Xu, researchers at the Glenn T. Seaborg Center of Berkeley Lab's Chemical Sciences Division, used ALS beamline 11.3.1, the small-molecule crystallography beamline, to characterize the molecular structure of a complex of the neptunium cation that contains the most stable form of neptunium. The unique qualities of the beamline enabled them to identify a highly symmetrical chemical complex called a diamide—meaning it contains two amino groups—that could hold the key for improving the extractability of neptunium from other nuclear waste products.



Jide Xu, Guoxin Tian, and Linfeng Rao, researchers at the Glenn T. Seaborg Center of Berkeley Lab's Chemical Sciences Division, used x-ray beams from the Advanced Light Source to gain new information that could help in the effort to safely remove neptunium from nuclear waste. (Photo Roy Kaltschmidt)

"The highly intense and focused beam of monochromatic x-rays at ALS Beamline 11.3.1 made it possible for us to use crystals as small as 20 microns in dimension and collect the data in about one hour," says Rao, a radiochemist who led the project. "The neptunium diamide complex we report is the first neptunium complex that has been characterized by single-crystal x-ray diffraction with a synchrotron radiation source like the ALS."

Rao adds, "The identified structure has provided a convincing interpretation of the absence of optical absorption in the near-infrared region by the complex, which originates from a change in energy levels called an f-f transition."

Neptunium is a silvery metal produced from uranium-238 in breeder reactors as a byproduct of plutonium production; about one part neptunium is produced for every 1,000 parts plutonium. A highly radioactive member of the actinide family of chemical elements, neptunium poses a formidable challenge to underground repositories for high-level radioactive waste, such as the one proposed by the U.S. Department of Energy underneath Yucca Mountain in Nevada. In addition to being difficult to remove from other waste products, neptunium is long-lived—neptunium-237 has a half-life of 2.14 million years—and is highly mobile in geological environments.

"By prediction, neptunium-237 will become a major contributor to the total radiation dose at the Yucca Mountain repository in 10,000 years, reaching 67 percent of the total dose in 75,000 years," says Rao. "If the engineered barrier systems in the repository, such as the waste packages and the drip shields, gradually deteriorate and eventually lose their integrity, neptunium could be mobilized from the degraded waste forms and carried out of the repository and into the environment."

One of the most promising of the proposed strategies for the treatment of nuclear wastes is called the “partitioning and transmutation process.” In this process small amounts of long-lived actinide elements, such as neptunium, are partitioned from other nuclear waste products and converted into short-lived radioisotopes or stable isotopes, either through transmutation in nuclear reactors or in advanced accelerators. However, this technique requires that the actinide to be partitioned must be able to form a strong chemical complex with the ligands (binding agents) of solvents.

The identification of the neptunium diamide complex by Rao and his colleagues suggests new organic ligands could be designed which would be able to effectively bind with the neptunium cation and be used to safely remove the neptunium from the bulk of the nuclear waste.

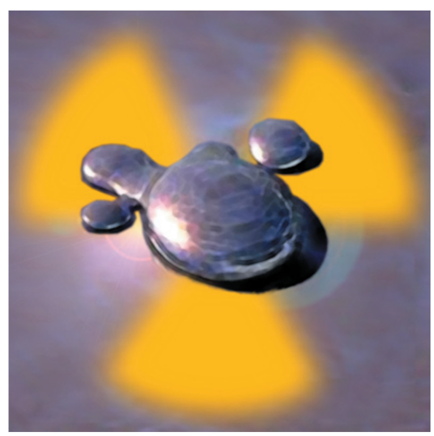
Yucca Mountain, located in Nevada northeast of Las Vegas, is the site of a permanent underground repository for high-level radioactive waste.

“Diamide ligands have received much attention in recent years as extractants for actinide separation because stripping actinides from diamide-containing organic solvents is relatively easy,” says Rao. “In addition, the diamide ligands are completely incinerable, so that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced.”

Rao says that the high degree of symmetry in the neptunium diamide complex indicates that ligands with asymmetric amide groups, one small and one large, would be more effective as extractants for neptunium separation.

“Asymmetric amide groups would guarantee the solubility of neptunium in organic solvents, as well as reduce the significant steric hindrance that arises when symmetric amide groups are used,” says Rao. “Furthermore, we may be able to develop ligands with a rigid backbone, which would also improve their effectiveness as neptunium extractants due to a lower preorganization energy and a larger entropy effect.”

A major factor in the ability of Rao and his colleagues to identify the neptunium diamide complex was the high quality of ALS x-ray beams. The ALS is an electron synchrotron designed to accelerate electrons to energies of nearly 2 billion electron volts (2 GeV), focus them into a tight beam, and send this beam around the curved path of a storage ring for several hours. Beams of x-rays are extracted from the electron beam in the storage ring through use of bending, wiggler, or undulator magnetic devices. The x-ray beams are a hundred million times brighter than those from the best x-ray tubes.



Neptunium is a member of the actinide family of chemical elements known for its long half-life, its mobility, and the difficulty of separating it from high-level nuclear waste.

Rao and his colleagues are now using ALS x-rays to observe the interactions of a variety of ligands with neptunium. They are also extending their studies to other actinide elements of major concern in nuclear wastes.

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