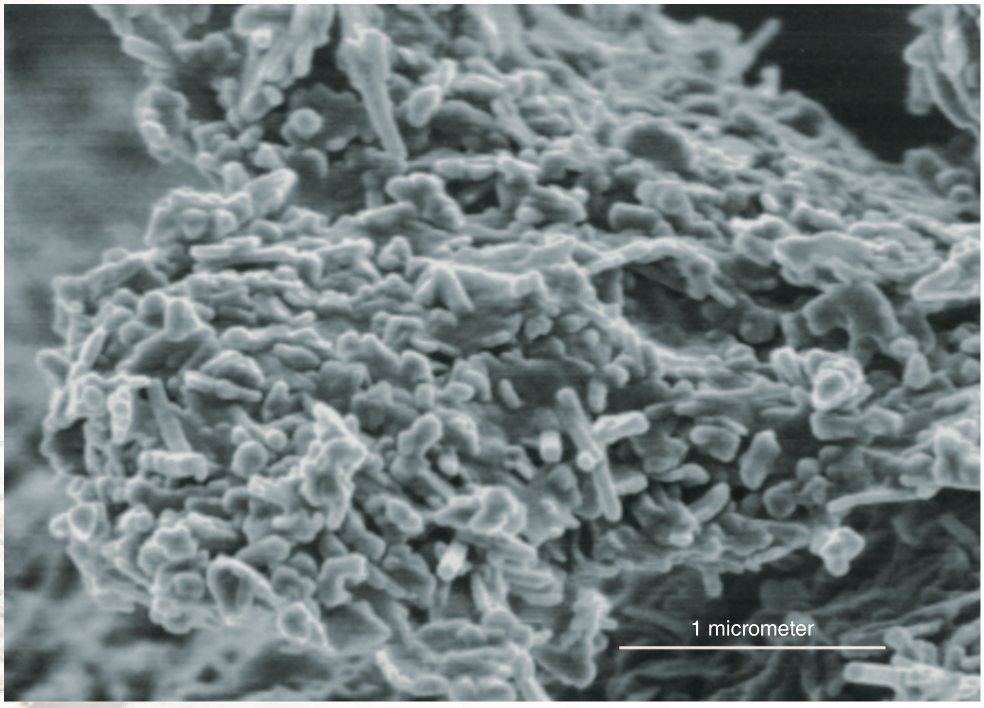
Plutonium Hitches a Ride on Subsurface Particles



Livermore scientists are conducting field studies and microscopic experiments to determine how plutonium is transported in groundwater. Transmission electron microsope images such as the one shown above allowed the researchers to examine colloids taken from groundwater at the Nevada National Security Site (in the background). These studies and others have confirmed that colloids play an important role in transporting plutonium at contaminated sites worldwide.

FOR decades Lawrence Livermore researchers have worked to obtain a detailed understanding of the actinides, a group of 14 radioactive elements that includes plutonium and uranium. The long-standing research is driven by the Laboratory's historic roles in assessing the nation's nuclear stockpile, ensuring the safe storage of nuclear waste, and evaluating the fate and transport of radionuclides in the environment.

Environmental contamination by radionuclides, particularly actinides, is a serious concern at several Department of Energy (DOE) facilities, including the Hanford Site, the Nevada National Security Site (formerly the Nevada Test Site), and the former Rocky Flats Plant, as well as at a number of contaminated sites worldwide. Although concentrations of most of the actinides transported from the original source location are detected at levels below regulatory dose limits, actinides' long half-lives combined with their high toxicity make them of particular concern.

A five-year experimental effort involving about a dozen Laboratory scientists and their collaborators is examining the geochemical processes that control plutonium's sometimes baffling behavior in the ground. The researchers' goal is to gain sufficient understanding of the processes that control plutonium's behavior so they can more accurately predict long-term transport.

"We want to provide decision makers with the scientific basis to support plans for the remediation and long-term stewardship of legacy sites where plutonium contamination occurred," says Livermore geochemist Annie Kersting, leader of the plutonium transport effort and director of the Livermore branch of the Glenn T. Seaborg Institute, one of the world's leading centers for actinide research. Other Livermore researchers include lead scientist Mavrik Zavarin, Susan Carroll, Zurong Dai, Ross Williams, Scott Tumey, Pihong Zhao, Ruth Tinnacher, Patrick Huang, Harris Mason, James Begg, and Ruth Kips. Collaborators include Brian Powell (a former Livermore postdoctoral researcher) from Clemson University in South Carolina and Duane Moser from Desert Research Institute in Nevada. The group's research is funded by the DOE Office of Science's Biological and Environmental Research Program.

Plutonium Is a Perplexing Element

Scientists regard plutonium as one of the most complex and perplexing elements in the entire periodic table. For example, its transport in groundwater strongly depends on its oxidation state, and plutonium is one of the few elements that can exist in four unique oxidation states simultaneously. Plutonium has been shown to migrate while associated with small (less than 1 micrometer in diameter) particles, or colloids. It may also migrate while associated with mobile organic matter.

For many years, scientists had assumed that plutonium, because of its low solubility in water and its strong tendency to sorb (adhere) to soil and rocks, does not migrate. However, in 1999, Kersting and colleagues from Lawrence Livermore and Los Alamos national laboratories detected plutonium in groundwater at the Nevada Site. Isotopic signatures showed that it originated from a specific nuclear test conducted years earlier more than 1.4 kilometers away. The team found that the plutonium was associated with colloids in the groundwater. Since 1999, additional studies by this team and fieldwork by other scientists have confirmed that colloids play an important role in transporting plutonium at a number of other contaminated sites around the world.

Past laboratory experiments aimed at understanding how plutonium moves in the subsurface were performed at concentrations higher than those observed in the field. However, the dominant geochemical processes operating at higher concentrations may not be the same as those that occur in nature at much lower concentrations. New analytical tools developed at Livermore are providing an opportunity to conduct experiments at the much lower concentrations measured in nature. The extremely sensitive instruments allow researchers for the first time to mimic environmental conditions. Much of the Livermore team's focus is on determining how plutonium hitches a ride on colloids. These microscopic colloidal particles are found in all waters and can be composed of organic material, inorganic minerals (for example, clays), or microbes.

Kersting says it is important to capture processes such as colloidal transport of contaminants so that models can accurately estimate how much, how far, and how fast plutonium can travel. "Colloidal transport was originally not considered in most transport models. Now, researchers are trying to understand when colloids are important in transport and when they are not," she says. Currently, a basic understanding of how plutonium adheres to mineral colloids (and desorbs from them) is lacking. In particular, transport models suggest that the rates of sorption and desorption control colloid-facilitated actinide transport, but the factors affecting reaction rates have not been determined experimentally.

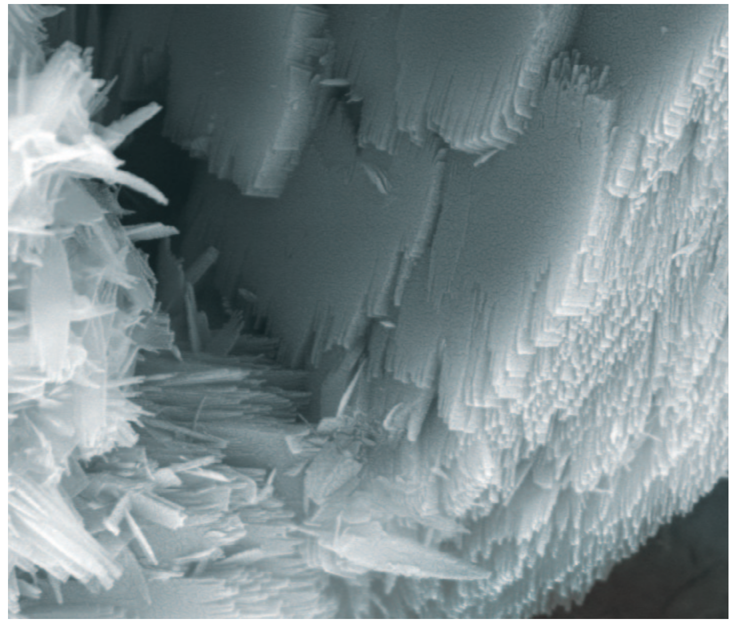
Sensitive Instruments Provide Unique Opportunity

Livermore instruments allow researchers to conduct experiments involving extraordinarily low (but environmentally realistic) levels of plutonium in the picomolar to attomolar range (10^{-15} to 10^{-18} moles per liter, with a 10^{-18} concentration of plutonium being roughly equivalent to dissolving one grain of salt in 100 Olympic-size swimming pools). Instruments include the accelerator mass spectrometer at the Laboratory's Center for Accelerator Mass Spectrometry and the newest generation of inductively coupled plasma–mass spectrometers. With these extremely sensitive instruments, researchers can identify where the plutonium is sited on a microscopic colloid, determine how it was deposited on the colloid, and elucidate the geochemical processes controlling its mobility.

Plutonium-containing colloids are being characterized in terms of their inorganic, organic, and microbial associations by using a transmission electron microscope and a nanometer-scale secondary-ion mass spectrometer. The Livermore experiments entail reacting extremely low concentrations of plutonium with different materials such as mineral colloids, organic matter, and microbes, and determining to what extent changing parameters, such as pH and concentration, affect the interaction of plutonium with these substrates.

"The experiments show that each mineral colloid interacts with plutonium in a unique manner," says Zavarin. For example, one form of plutonium, nanocrystalline plutonium-4–oxygen-7 (Pu_4O_7),

Collaborator Duane Moser from the Desert Research Institute collects groundwater containing plutonium from the Nevada Site.



A scanning electron microscope image shows colloidal particles produced during the reaction of nuclear melt glass in groundwater at the Nevada Site.

readily precipitates on goethite, an iron oxide and a common constituent of soil. The team is examining the surface deposition of Pu_4O_7 to determine why plutonium molecules bind so tightly to goethite. The research indicates that plutonium surface precipitates become distorted as they are deposited, which apparently strengthens the bond between goethite and plutonium. In contrast, this process does not occur when plutonium interacts with quartz (silica dioxide), one of the many silicates found in soil.

The experimental results are being compared to samples taken from contaminated sites at Nevada, Rocky Flats, Hanford, and Russia's Mayak nuclear complex. Kersting notes that colloids may not play a major transport role at all sites and that the depositional geology and hydrology affect transport. "We're slowly filling in the scientific gaps," she says.

One undetermined factor is how microbes affect plutonium transport. Desert Research Institute scientists have collected microbes at the Nevada Site colocated with plutonium contamination, identified and cultured the microbes, and shipped them to Livermore for studying the interaction between plutonium and microbial communities.

Leveraging Research Results

Zavarin notes that other actinides are present at contamination sites, and the team's research results may also shed light on how these elements are transported. "We want to apply our resources to other actinides such as neptunium, americium, and uranium," he says. The research is also applicable for European scientists and decision makers who are planning the construction of facilities to store high-level waste from nuclear power plants. Kersting's team is collaborating with several international scientists in this effort.

An added benefit of the Livermore research is the opportunity for a new generation of actinide scientists to work with plutonium. Several postdoctoral researchers and summer graduate students are contributing to the research, with some participating in the Seaborg Institute's Nuclear Forensics Summer Internship Program, funded by the Department of Homeland Security. Thanks to the research, the most perplexing element on the periodic table is slowly losing some of its mystery about how it travels underground faster and farther than anyone at first expected.

—Arnie Heller

Key Words: actinide, Glenn T. Seaborg Institute, Hanford Site, Mayak nuclear complex, Nevada National Security Site, Nevada Test Site, nuclear forensics, plutonium, Rocky Flats Plant.

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