CLEANING UP NUCLEAR WASTES

Environmental management is a key DOE mission, in large part because five decades of nuclear weapons production and nuclear energy research have left behind huge quantities of radioactive waste. To make matters worse, large quantities have leaked from underground storage tanks into surrounding soils. DOE has already spent many billions of dollars in cleanup efforts and is expected to spend much more. Thanks to two decades of research supported by DOE's Basic Energy Sciences (BES) office, however, there is now an elegant new cleanup technology that will speed up the process and save over a billion dollars. Furthermore, science supported by BES has greatly improved the ability to assess the remaining risks and predict subsoil migration of leaked waste.

Double-shell tanks being built in 1978 at Savannah River, South Carolina, to store radioactive nuclear waste. *(U.S. DOE)*

Modular unit nearing completion at the Savannah River Site for removal of radioactive cesium using the chemistry developed at Oak Ridge National Laboratory. *(U.S. DOE Savannah River Site)*

Efforts to produce plutonium for nuclear weapons have generated a substantial amount of nuclear waste. The production process involved converting a form of uranium into plutonium in nuclear reactors, then separating the plutonium from other materials, including many highly radioactive substances. One of the most common of those substances is the element *cesium*, whose isotopes can remain dangerously radioactive for over 100 years and which, in the chemical form found in the wastes, dissolves in water and so can readily move into soils and disperse. Over 35 million gallons of radioactive waste are stored in tanks at the Savannah River production site in South Carolina, and even larger quantities are stored at the Hanford production site in Washington. Some of the tanks have leaked wastes into the ground, which at Hanford have started to migrate towards the Columbia River.

Decades before the waste cleanup was initiated, work towards a solution began unintentionally with the 1967 discovery by a DuPont chemist of organic molecules that have the ability to selectively bind a variety of metal ions, including cesium. That finding stimulated expanded research by university scientists in California and France, some of it funded by BES, to refine these properties and improve the selectivity of the binding molecules. The importance of these compounds for many areas of chemistry was recognized in 1987 with a Nobel Prize. It also attracted the attention of a research chemist at Oak Ridge National Laboratory, Bruce Moyer, who was interested in the nuclear waste problem confronting DOE. He recognized that although cesium accounted for over 90 percent of the radioactivity in the waste that can dissolve in water, it amounted to a tiny fraction of the total waste—less than 1/10,000th by weight—so that it might be possible

Solvent extraction equipment used at the Savannah River Site to separate radioactive cesium from legacy nuclear waste. *(U.S. DOE Savannah River Site)*

to greatly decontaminate the waste by removing the small amount of cesium. With BES support beginning in the mid-1980s, he put together a team of scientists to adapt molecules "tuned" for removing metals like cesium from complex solutions like the nuclear wastes.

The scientists studied methods for synthesizing the molecules, analyzed their structure, and explored relevant extraction processes. Armed with an understanding of the chemistry developed under BES sponsorship, the scientists approached DOE's Environmental Management office with a specific plan to remove cesium from the wastes. The subsequent applied research eventually perfected a series of chemical steps: first pull cesium into a solvent containing the specialized binding molecules; then separate the solvent from the waste; then free the cesium atoms and capture them in glass for secure burial; and finally, recycle the binding molecules to capture more cesium. It took nearly two

Once separated from the wastes, cesium is safely captured in an inert glass for permanent disposal. *(U.S. DOE Savannah River Site)*

Box

THE WIDE IMPACT OF BES RESEARCH

The key scientific idea underlying the nuclear waste clean-up process is what is known as molecular recognition: how to design a "host" molecule to recognize and bind to a specific target molecule. The BES-funded research on cleaning up nuclear waste led to a broader effort on molecular recognition, using high performance computers as well as laboratory experiments to help design host molecules. The research, now funded by a number of federal agencies, turns out to have application for a broad range of important problems:

- **Critical materials.** These are rare elements such as *neodymium* and *ytterbium* that are essential components of technologies needed for national defense and a number of key industries. At present, the U.S. is largely dependent on China for these materials, but they are also present in very low concentrations in deposits of phosphate rock, of which the U.S. has a huge supply. So inexpensive host molecules that could recognize and help extract these elements would remove a potential threat to national security.
- **Sensors for radioactive materials.** A terrorist group or a rogue nation developing nuclear weapons is likely to inadvertently release trace amounts of radioactive materials. Appropriately-designed host molecules in sensors carried by drones or otherwise deployed could give early warning of such activities.
- **Cleaning up the "back end" of the nuclear fuel cycle.** Intensely radioactive elements such as *americium* need to be removed when spent nuclear fuel is reprocessed and prepared for reuse. Specially-designed host molecules that recognize and capture these elements would simplify the process and make it safer.

None of these problems are yet fully solved—the science is not yet complete. But there is already significant progress. Some of it has been aided by a new DOE funding model, a Critical Materials Hub supported by the Energy Efficiency and Renewable Energy office that brings together a concentrated applied research effort involving dozens of scientists from different universities and national laboratories. It illustrates the patient, step-by-step approach—basic science, then applied research—that leads to practical solutions.

decades to work out all the chemistry, demonstrate that the plan would work, and optimize the process. DOE's Environmental Management office built on the science to design and implement an automated industrial process, which is already at work on the Savannah River waste tanks. The result will be a far more rapid and less expensive cleanup of the wastes, including disposal of the remaining (largely non-radioactive) materials left after removal of the cesium.

The challenges at Hanford are more difficult, both because the chemistry of the tank wastes is more complicated—a "witches brew" some experts call it—and because some of the wastes that have already leaked into the ground are being transported through the soil and into groundwater. To assess and manage that problem, scientists needed to understand the physical and chemical processes that determine whether chemical wastes are retained by minerals in the soil or migrate to other locations. This in turn depends greatly on the chemical reactions that occur at the surfaces where minerals come in contact with water and the wastes. BES funded research with X-ray and neutron probes to understand the atomic structure of mineral surfaces, learn how these react with water and chemical waste materials, and then model these processes with high-performance computing.

One of the discoveries from the research is that the size and distribution of tiny pores in soils and rocks play a critical role in determining how chemical wastes dissolved in water migrate through soils and groundwater. Soils and rocks vary markedly in their pore structure—some have tiny pores that permit only gradual diffusion of chemicals, and others have large, interconnected pores that allow chemicals to migrate readily. Mapping the distribution of different soil and rock types, and combining results with models of chemical processes, has led to predictive models of where and how waste chemicals would be retained or transported in the soil. These models have allowed DOE's Environmental Management office to develop new science-based strategies for dealing with the contamination from nuclear waste at Hanford, Savannah River, and elsewhere.

There is still much more work to be done to finally clean up the nuclear legacy of the wastes. But with the benefit of the detailed, molecular-level understanding of the processes involved—either in the ground or in removing radioactive cesium from the tanks—there is a now a systematic way to proceed.