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As nuclear waste piles up, scientists seek the best long-term storage solutions

Researchers study and model corrosion in the materials proposed for locking away the hazardous waste

by Mitch Jacoby

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“Regardless of whether you are for or against nuclear power, and no matter what you think of nuclear weapons, the radioactive waste is already here, and we have to deal with it.”

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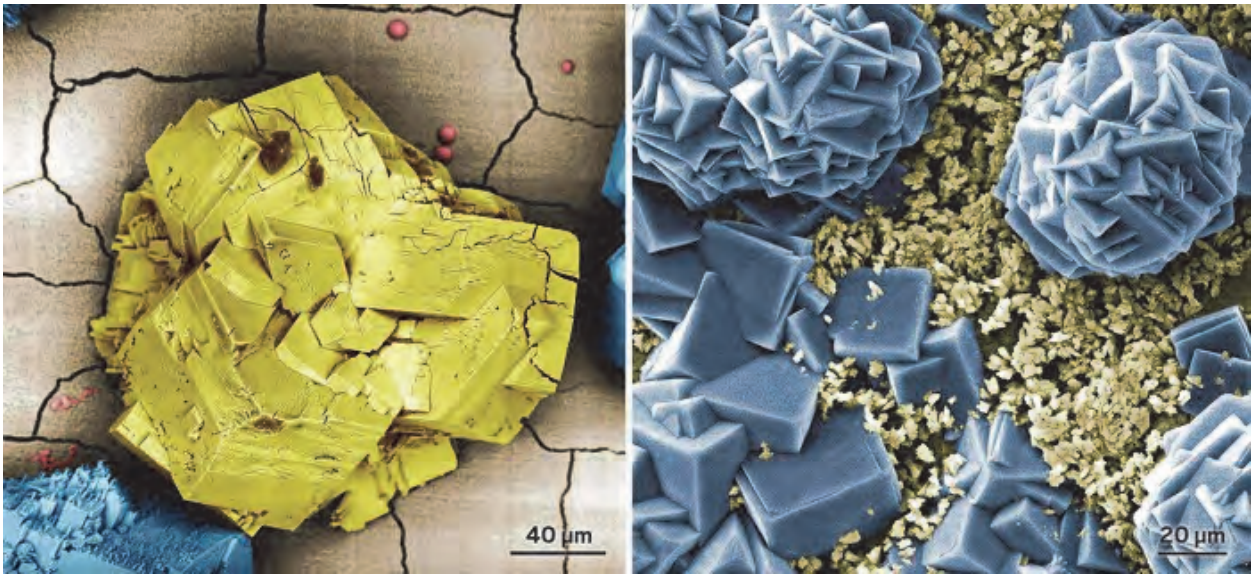
IN BRIEF

More than a quarter million metric tons of highly radioactive waste sits in storage near nuclear power plants and weapons production facilities worldwide, with over 90,000 metric tons in the US alone. Emitting radiation that can pose serious risks to human health and the environment, the waste, much of it decades old, awaits permanent disposal in geological repositories, but none are operational. With nowhere to go for now, the hazardous materials and their containers continue to age. That unsustainable situation is driving corrosion experts to better understand how steel, glass, and other materials proposed for long-term nuclear waste storage containers might degrade. Read on to learn how these researchers' findings might help protect people and the environment from waste leakages.

That's Gerald S. Frankel's matter-of-fact take on the thousands of metric tons of used solid fuel from nuclear power plants worldwide and the millions of liters of radioactive liquid waste from weapons production that sit in temporary storage containers in the US. While these waste materials, which can be harmful to human health and the environment, wait for a more permanent home, their containers age. In some cases, the aging containers have already begun leaking their toxic contents.

"It's a societal problem that has been handed down to us from our parents' generation," says Frankel, who is a materials scientist at the Ohio State University. "And we are—more or less—handing it to our children."

Like other specialists studying the root causes of corrosion and degradation in nuclear waste storage materials, Frankel isn't content to kick the can down the road. Instead of waiting for the leaks to get worse or for governments to finally decide to permanently store the waste, these scientists are investigating how to recognize and predict damage to nuclear waste storage containers and how to control it to safeguard people and the environment.



Credit: John Vienna/Pacific Northwest National Laboratory

Scientists are studying glass samples to understand long-term corrosion of vitrified nuclear waste. These micrographs show the results of accelerated aging tests on two types of aluminosilicate glasses. Ions have leached from the glasses and crystallized on their surfaces: the largest of these false-color crystals (yellow on left, pale blue on right) are sodium aluminum silicate hydrates of various composition and structure.

Highly radioactive waste, often called high-level waste, comes mainly in two forms. One is leftover fuels that were used in nuclear power plants to generate electricity. The other is the waste made by facilities involved in nuclear weapons production or by facilities that reprocess and recycle used power plant fuel.

All these wastes can remain dangerously radioactive for many thousands of years. For that reason, they must be disposed of permanently, experts say. About a dozen countries, including Finland, Switzerland, and other European nations, are planning deep geological repositories for their nuclear waste. In the US, government officials have proposed storing the country's waste in a repository beneath Yucca Mountain in Nevada. The site lies about 300 m below ground level and 300 m above the water table. But the Yucca Mountain site has gone in and out of favor with changes in the US's leadership. For now, waste accumulates mainly where it's generated—at the power plants and processing facilities. Some of it has been sitting in interim storage since the 1940s.

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Gerald S. Frankel, *materials scientist, Ohio State University*

During World War II and throughout the Cold War era, the US generated millions of liters of radioactive waste—a mix of liquid, sediment, and sludge—in the name of national defense. The toxic waste, a by-product of creating plutonium for nuclear bombs, was collected for 45 years in underground storage tanks mainly in Hanford, Washington, and the Savannah River Site in South Carolina.

In Hanford alone, more than 200 million L of this waste still sits after many decades in underground tanks waiting to be processed, according to Thomas M. Brouns, who leads the environmental management sector at nearby Pacific Northwest National Laboratory (PNNL). About one-third of the nearly 180 storage tanks, many of which long ago outlived their design lives, are known to be leaking, contaminating the subsurface and threatening the nearby Columbia River. Another 136 million L of the stuff awaits processing at the Savannah River Site.

Related: Proposed nuclear waste storage materials may have a corrosion problem

Today, no nation in the world would consider storing high-level liquid waste indefinitely like this, says PNNL materials scientist John D. Vienna. “That’s a thing of the past,” he adds.

Credit: US Department of Energy

These underground tanks in Hanford, Washington, were built in the 1940s to store liquid radioactive waste from plutonium production. Today, the contents have been transferred to newer tanks in preparation for vitrification.

NUCLEAR WASTE BY THE NUMBERS

~442

Number of nuclear power reactors operating worldwide

96

Number of commercial nuclear power reactors currently operating in the US

>90,000 metric tons

Total mass of highly radioactive nuclear waste in the US, including spent fuel and other material

212 million L

Volume of radioactive waste in underground storage tanks in Hanford, Washington

Sources: US Energy Information Administration, US Government Accountability Office, World Nuclear Association, International Energy Agency, Hanford Vit Plant.

One way that scientists have come up with to store liquid nuclear waste more permanently is to vitrify it. In this process, the hazardous material is converted to a more easily managed immobile solid—glass. Not only does glass prevent toxic species from leaking into the environment, but it also provides some shielding against radioactivity leakage and is highly durable.

For years, India, France, the UK, and other countries have carried out vitrification of liquid waste from weapons production and fuel recycling—and still do. In the US, operators at Savannah River have been vitrifying weapons-related waste for about 20 years. And although the US does not currently recycle fuel, it did so in the 1960s and '70s near Buffalo, New York, in a program known as the West Valley Demonstration Project. The operation generated 275 canisters of glass from vitrifying high-level waste; the canisters are stored there and await permanent disposal in a repository.

At Hanford, the site is gearing up to vitrify its waste. The work will be done on-site at the Hanford Tank Waste Treatment and Immobilization Plant. Also known as the Hanford Vit Plant, the multibillion-dollar Department of Energy (DOE) facility has been under construction since 2002. According to the DOE, some of the waste treatment operations are scheduled to begin by 2023, but the massive project has already seen several delays and may see more.

Stabilizing nuclear waste via vitrification isn't a new idea. The process involves blending waste materials with glass precursors, heating the mixture to above 1,000 °C to melt the components, pouring the molten glass into a storage container, and letting it cool and solidify, locking the harmful constituents in the glass matrix.

"Vitrification of nuclear waste seems to be well established by now, but actually it still faces complex problems," says Ashutosh Goel, a materials scientist at Rutgers University. The plan at Hanford, for example, calls for entombing nuclear waste in

borosilicate glass and encasing the glass in stainless-steel canisters. Yet the exact formulation of the glass, or glasses, is still under investigation.

Open questions include the following: What glass compositions will lead to the highest uptake of nuclear waste? How suited are those glasses to vitrification? And how well will they resist corrosion after being interned for eons in a repository environment?

After 1,000 years or so, Goel says, the steel canister surrounding the glass will likely corrode, and groundwater may seep in and interact directly with the glass, degrading it. “The stability of the glass in the presence of groundwater represents the last line of defense against release of radionuclides” into our environment, he adds.

So scientists would like to better understand how and if glass might leach any radioactive materials locked inside. Whether groundwater degrades the glass enough to cause it to release its radioactive cargo depends on several processes, experiments have shown. For alkali-borosilicate glasses, a well-studied family, the degradation steps would include ion exchange between ionic species in the water and alkali ions in the glass; hydrolysis of silica, boria, and other chemical groups that compose the glass network; and dissolution and release of glass components into solution or onto the surface of the reacting glass.

Goel and colleagues in the US and the Czech Republic tackled the complex relationship between these and other processes and ways to model them in a recently published study (*J. Non-Cryst. Solids: X* 2019, DOI: 10.1016/j.nocx.2019.100033). The authors recommend that to better understand the long-term fate of vitrified materials, researchers in this field should focus on experiments that help determine the rate-limiting mechanisms of glass change over time—especially during long periods of very slow change—and help explain how composition affects the rate at which glass changes.

Related: Radioactive Waste Safety

Some models for predicting how vitrified waste will corrode over millennia in a geological repository assume that the stainless-steel canister eventually disintegrates, leaving groundwater, if present, to react with the glass. Others consider water’s reactions with steel and glass independently.

A new study, however, shows that water-based solutions can trigger unexpected corrosion chemistry that occurs only at the wet steel-glass interface (*Nat. Mater.* 2020, DOI: 10.1038/s41563-019-0579-x). The idea for the study came from Xiaolei Guo and coworkers, who reasoned that if water seeps through cracks in the steel canister, penetrating the microscopic gap between the glass and steel, it could set off reactions in the confined space that would not occur in a more open setting. So Guo, a corrosion researcher at Ohio State who works with Frankel, teamed up with PNNL’s Vienna,

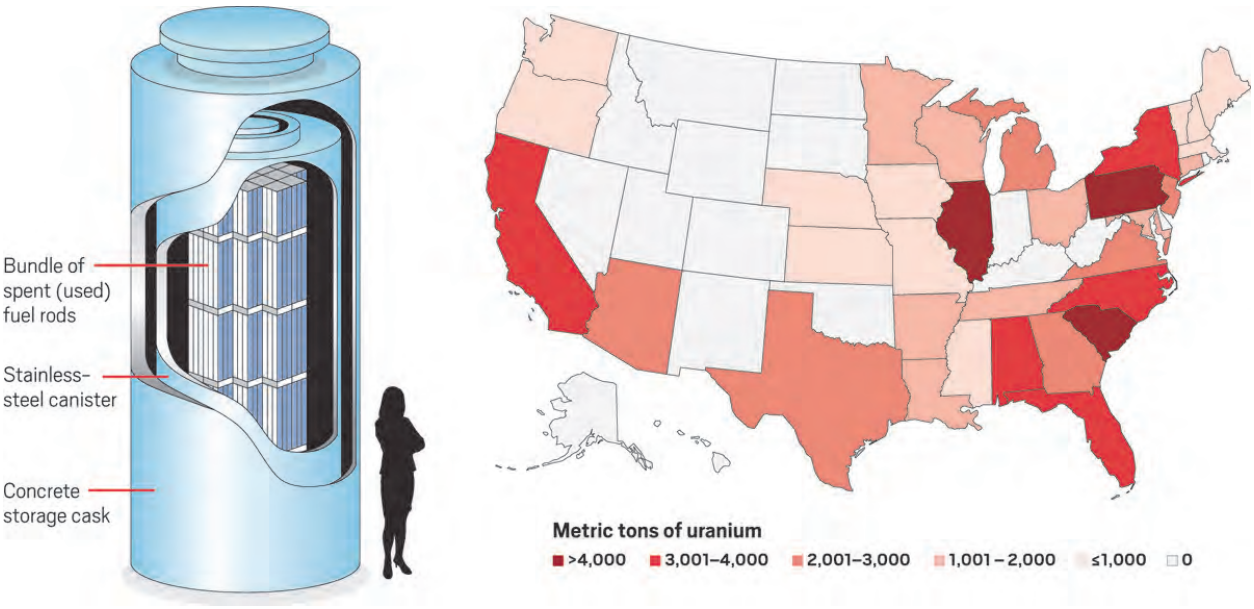
Stéphane Gin of the French Alternative Energies and Atomic Energy Commission (CEA), and others to test the hypothesis.

To simulate damp repository conditions, the researchers pressed glass and steel together tightly and set it in a salt solution held at 90 °C. The temperature was chosen to accelerate the normally slow corrosion process and to mimic conditions caused by ongoing radioactivity. After a month, they found accelerated pitting and corrosion of the glass and steel compared with control samples in which glass and steel were not held in intimate contact. Analyses showed that reactions between metal ions and the water acidified the solution. The acidity corroded the steel and glass, releasing additional ions, thereby accelerating the corrosion process.

The study uncovered a previously unknown corrosion mechanism involving dissimilar materials in close contact; some researchers say this process could decrease the durability of glassy nuclear waste. Vienna cautions against drawing that conclusion. This ongoing study turned up “an interesting finding that can be used to improve our models,” he says. He adds that the accelerated process is limited to roughly a 10 μm thick surface region on a standard vitrified waste sample. According to Vienna, the results suggest that less than 1 in 10,000 of the waste packages proposed for storage at Yucca Mountain would fail in 150,000 years.

Widespread storage

Tens of thousands of metric tons of radioactive spent nuclear fuel sit in steel-and-concrete storage casks (cutaway) at nuclear power plants across the US (map) as they await permanent disposal.



Credit: US Nuclear Regulatory Commission (cask)

Source: US Energy Information Administration, 2013 (the most recent year for which data are available).

But what about nuclear waste not slated for vitrification? In the US, about 80,000 metric tons of used, or spent, nuclear fuel sits in casks on-site at power plants around the country. The fuel typically takes the form of 4 m long narrow tubes (~1 cm diameter) filled with small uranium dioxide pellets. Hundreds of these tubes, known as fuel rods, are bundled together to form fuel-rod assemblies. And hundreds of assemblies work together in a commercial nuclear reactor to produce intense heat (and steam)—from splitting uranium nuclei—to drive turbines that generate electricity.

After spending roughly 5 years in a reactor constantly being bombarded with radiation, nuclear fuel stops working efficiently. Reactor operators remove the spent fuel and replace it with fresh fuel. At that point, the spent fuel, which still has roughly 95% of its original uranium, is thermally hot and hazardous because it contains a mix of radioactive plutonium, fission products, and actinides. Several countries separate those components to make new fuel, and along the way, they generate high-level waste by-products that are vitrified.

Credit: Pacific Northwest National Laboratory

At Pacific Northwest National Laboratory, Jodi L. Meline pours a sample of molten glass to study corrosion in vitrified nuclear waste.

The US does not reprocess its fuel. Instead, reactor engineers submerge the assemblies in on-site pools for a few years until the fuel cools and the radioactivity starts to fall. Then they transfer the fuel-rod assemblies to stainless-steel canisters, which are welded shut and packed inside reinforced concrete silos. And there the spent fuel sits for now, accumulating in so-called dry casks above ground at or near power plants, because the US has no permanent repository for this waste.

And the fuel keeps accumulating. About 20% of the electricity in the US comes from 96 commercial nuclear reactors, according to the US Energy Information Administration. And roughly every 2 years, each plant replaces about one-third of its fuel with fresh fuel.

Related: Nuclear Efficiency

The radioactive material in the casks is a controlled solid, not an unruly liquid-sludge combo that's leaking into the ground and warrants vitrification, as is the case for the material in the Hanford tanks. Experts consider dry-cask storage safe in the short term. But because the spent-fuel containers sit in limbo, many of them will remain where they are for decades longer than originally intended. That leaves Eric J. Schindelholz wondering whether environmental factors will eventually take a toll on the stainless-steel canisters' integrity. Schindelholz, who recently joined Ohio State's team of corrosion experts, studies a type of chemically induced damage known as stress corrosion cracking, which can occur in metals at stress points such as weld joints—like the ones used to seal the stainless-steel canisters of spent fuel.

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Ashutosh Goel, *materials scientist, Rutgers University*

He explains that during manufacturing, stress develops at weld seams as they cool and contract. If corrosion sets in at those spots, then some materials can start to crack and fail. The iron-chrome-nickel-based stainless steel used in dry casks is a material prone to fail when corrosion kicks in.

What might cause the corrosion on these concrete-covered casks? Many nuclear power plants in the US were built along coastlines for convenient access to cooling water. Proximity to the coast means exposure to sea-salt aerosol. Because of the cask design, which blocks radiation but allows air flow—for cooling—between the steel cylinders and concrete silos, aerosols can reach the cylinder surfaces. Salt particles, which are

hygroscopic and deliquescent, can settle on canister welds and other stress joints, take up atmospheric water, dissolve, and form chloride-rich corrosive brines. Those conditions could lead to small cracks that breach a cylinder and release harmful material and radiation.

Schindelholz, together with researchers at Ohio State and Sandia National Laboratories, is developing a model that can be used to predict when, how, and where dry-cask cylinders might crack. The model includes input derived from the team's electrochemical and microscopy studies that analyze pitting, crack initiation, and the effects of relative humidity on the morphology and distribution of pits formed in stainless steel exposed to marine atmospheres (*J. Electrochem. Soc.* 2019, DOI: 10.1149/2.0551911jes). These researchers are hoping their efforts will protect the temporarily stored waste until a more permanent solution can be agreed upon in the US.

The tens of thousands of metric tons of radioactive waste that accumulated from commercial power plants and years of national defense operations continue to age at sites around the globe. As the hazardous material and the containers it sits in await permanent disposal, the stockpile keeps growing. Corrosion experts are doing their part to safeguard people and the environment from this danger, but it's still there. "It's a difficult problem, but we need to deal with it now," Frankel says. "Putting it off any longer isn't good for anyone."

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