Hanford's vitrification challenge

Thirteen years after the U.S. nuclear weapons complex shut down nearly all production and switched its mission to environmental cleanup of its vast store of radioactive waste, the U.S. Department of Energy (DOE) is finally gearing up to tackle the United States' most problematic nuclear waste. The agency plans to use a special form of vitrification, or glassmaking, when it begins treating the 54 million gallons of mixed radioactive waste stored at its Hanford site in eastern Washington state, which represents 60% of the United States' volume of radioactive waste.

Glassmaking is as old as civilization itself. The vitrification technology adapts the standard glassmaking process of melting silica with added components, which in this case are radioactive waste. The mixture is then poured into steel canisters for storage. Vitrification is already used routinely for nuclear power plant waste in the United Kingdom and France, and it has worked reasonably well with homogeneous U.S. weapons waste. The world's largest running vitrification plant is currently at DOE's Savannah River site in South Carolina, where the technology is sequestering the 34 million gallons of waste stored there.

When the Hanford plant begins treating waste in 2007, the operation will outstrip Savannah River in size. Bechtel National, Inc., the design and construction contractor, has adapted a plant design developed by British Nuclear Fuels, Inc. (BNFL) and now owned by DOE. The ambitious Waste Treatment Project (WTP) now under construction promises to vitrify 99% of Hanford's waste by 2028.

Hanford's waste is so problematic because many of its tanks hold unidentified waste. Four different chemical processes were used at various times to separate out selected nuclear materials, and the agency's recordkeeping is incomplete. In addition, because the resulting waste was highly acidic and would corrode the tanks, millions of gallons of sodium hydroxide were stirred in to alter the pH. Cyanide, nitrate, and chromium compounds also lurk in the tanks along with an alphabet soup of radioisotopes. In fact, Hanford waste now contains nearly every element in the periodic table, says Pacific Northwest National Laboratory chemist John Vienna.

Before and after. **Most of the waste inside Hanford's older single-shell tanks is in the form of saltcake, with the consistency of wet beach sand, and sludge, which looks like fine mud and dries very hard. After being vitrified, it looks far more homogenous (see inset).**

The tank contents are also vertically heterogeneous. At the bottom lies a layer of crusty solids, or salt cake. Above that is a layer of sludge. Because the sludge and salt cake contain the most radioactive substances, they are classified as high-level waste (HLW). Above the sludge is a viscous liquid supernatant termed low-activity waste (LAW). Each waste stream will be processed separately.

The vitrification processes that will be used to treat Hanford's radioactive waste will have to tweak the standard glassmaking formula of melting silica with materials such as soda and limestone because—depending on their concentration and the processing temperature—many of the elements and compounds in the waste can interfere with glassmaking. For example, any chromium, ruthenium, rhodium, and palladium present in the glass melt as oxides, and alloys can precipitate out to agglomerate on the melter bottom, where they can short-circuit the melter electrodes. Chromium, phosphorus oxide, and sodium sulfate dissolve poorly in borosilicate glass, sometimes forming refractory crystalline phases that can corrode the melter lining, clog the outflow of the glass melt to the canisters, and compromise the homogeneity and chemical durability of the finished product. These problems are exacerbated by the need to make any repairs and replacements to the melter by remote operations.

According to a 2001 DOE report, Hanford tank waste fits 89 separate chemical profiles. Given this complexity, it's not surprising that "pretreatment has been the 'Achilles heel' of vitrification in the U.S.," says Alan Dobson, BNFL's representative in Richland, Wash. Pretreatment assumes major importance because the waste is so heterogeneous that it precludes efficient processing, which requires a melter feed with predictable and controllable characteristics.

Another concern is volume, particularly when it comes time to store HLW at the planned Yucca Mountain site in Nevada. Thus, the pretreatment phase is designed to reduce volume by separating out most of the nonradioactive waste components, which comprise the largest percentage of the waste volume. Water is first added to sluice the waste out of the tanks. Then the sludge is washed with either water or a hydroxide solution to remove soluble nonradioactive elements, such as aluminum and phosphorus, which may increase HLW volume by interfering with glass formation. The solid and liquid waste streams diverge, with the latter passing through ion exchangers to wash out the water-soluble radioactive constituents—primarily cesium and technetium; these are sent back to the HLW stream. Some of the water is evaporated before the waste enters the melters, and more escapes as vapor through the melter off-gas system, which is treated before release to the environment.

Both the mostly solid HLW and the mostly liquid LAW waste streams will be mixed with glass-forming materials just before entering the melter. Unlike other vitrification processes, the Hanford process will use a series of borosilicate mixtures, each tailored to fit the characterization profile of a specific batch of waste, says Todd Wright, WTP research manager.

Glass's random molecular structure is a big plus. Although it would be possible to use crystalline materials whose lattices could incorporate heterogeneous waste molecules, the number of different chemical matrixes required would be prohibitive. "The universality of the glass matrix, the ability of it to tolerate a really broad range of chemistry, is the advantage here," says Vienna.

The Hanford WTP will use a Joule-heated ceramic melter, in which a set of nickel–chromium alloy electrodes heat the waste and glass-forming material to around 1150 °C. The glass–waste mixture will be stirred by convection and by bubbler elements, and then poured into carbon steel canisters to cool. Finally, the canisters will be sealed tightly and their outer surfaces scrubbed to remove residual contamination. Current plans provide for the LAW to be stored on site, while the HLW will go to Yucca Mountain.

In past DOE projects, the Joule melter design has been plagued by corrosion of electrodes by noble metals, failure of seals around bubbler element entry points, cooling of glass in the outflow that resulted in flow stoppages, and unwanted crystallization and foaming. Although the DOE's 2001 Melter Review Report recommended "substantial improvements in the current technology" and said that the vitrification process using borosilicate glass had "not been optimized," it still concluded that use of borosilicate glass and the Joule melter is the best available approach. Hanford's vitrification mavens emphasize that the basic process is firmly understood and ongoing research is for confirmation only.

Vienna adds that the problems are "not issues that would make the plant not work or make the process unsafe or make the product not of high enough quality," but are rather issues of optimizing the speed and quantity of throughput. For example, chromium content limits the amount of HLW waste that can be incorporated into glass. Chromium can be removed by oxidative leaching and transferred to the LAW, where it poses less of a problem.

Recently, DOE has been pushing to resolve its waste problem more quickly and cheaply, and there is a chance that for the LAW, vitrification may be at least partially abandoned for less complex technologies. For example, grouting consists of combining the waste with Portland cement, sand, and other constituents and letting the mixture set like concrete in the tanks themselves, other containers, or large flat fields. Another option is steam reforming, in which high temperatures and added chemicals transform waste into crystallized pellets. However, these treatments won't work for HLW because the matrix materials will decompose long before the radioactivity decays. In addition, they are not specified for HLW in the Tri-Party Agreement between the U.S. EPA, DOE, and the Washington State Department of Ecology, which legally governs Hanford's cleanup processes.

Alternative treatments would require reclassifying some of the waste as lower risk. A pending lawsuit in Idaho federal court against DOE by watchdog groups and Native American tribes challenges DOE's attempt to call some of the tank waste "transuranic" and "low-level" rather than HLW.

DOE also continues to explore variations of vitrification technology, such as using other forms of glass, including aluminosilicates, iron phosphates, and their glass–ceramic derivatives. These alternative glasses "can incorporate a larger fraction of waste," says Vienna, leading to less volume and therefore less expense. But, he adds, "They typically have more processing difficulties" and haven't been as well studied as borosilicate glass. In addition, current repository standards specify borosilicate glass.

DOE is also investigating a new device called the Advanced Cold Crucible Melter (ACCM), which was developed by the French nuclear services company Cogema. The ACCM is a water-cooled melter heated by direct high-frequency induction. Cogema asserts that the ACCM design reduces melter corrosion and allows for higher waste loading. Finally, DOE is contemplating a $30 million investment to investigate the potential of the Advanced Vitrification System (AVS) under development by Radioactive Isolation Consortium, LLC (RIC). In the AVS, an ac coil inductively heats the waste inside a steel storage canister with an inner graphite–alumina module serving as the crucible. RIC Vice President Louis Ventre says the AVS has achieved 50% waste loading, compared with about 30% with the current system, and could finish Hanford vitrification by 2012 rather than the currently expected 2028. However, the DOE Inspector General reported in August that the process has too many unknowns to be considered a serious candidate for waste cleanup.

Todd Martin, an independent consultant who has advised DOE on environmental management issues, would prefer that DOE commit firmly to the current Hanford project and make slow and steady progress rather than push the system to its limits. "The pressure to get more done faster drives them closer to the edge of their technological envelope," says Martin. "In the case of Hanford tank waste, best is oftentimes the enemy of good." —VALERIE BROWN