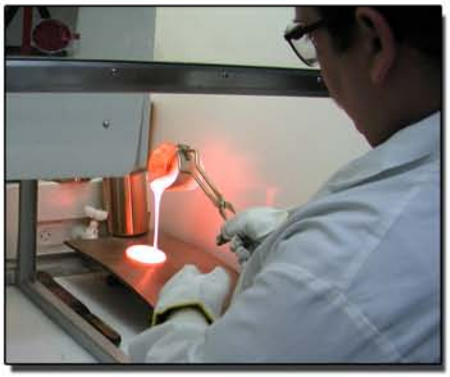
Environmental Solutions

A Summary of Contributions for CY04

PNNL-15072



Battelle Contributions to the Waste Treatment Plant

Battelle
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Executive Summary

Battelle Supports Radioactive Waste Vitrification

In support of the Waste Treatment Plant, Battelle conducted tests on mixing specific wastes within the plant, removing troublesome materials from the waste before treatment, and determining if the final waste forms met the established criteria. In addition, several Battelle experts filled full-time positions in WTP's Research and Testing and Process and Operations departments.

The WTP is a facility designed to turn radioactive liquid and sludge from Hanford's tanks into high-level waste glass logs and a low-activity glass waste form. The high-level waste glass will contain most of the radioactivity, while the low-activity waste glass contains small amounts of radioactivity and most of the nonradioactive liquid waste components. To reduce the cost of disposal while satisfying regulatory and environmental requirements, several separations processes are conducted in a pretreatment facility.

Mixing Thick Wastes with Glass Formers

Tanks at the WTP will contain radioactive slurries and glass-forming materials that need to be mixed. For most of the 300+ tanks, pulse jet mixers are satisfactory. However, some tanks will contain concentrated slurries (high levels of solid particles), which exhibit non-Newtonian rheological properties, that may be difficult to mix. Wastes with these non-Newtonian rheological properties behave more like thick mud than a liquid when sitting still. To resolve the mixing issues the WTP worked with several suppliers, including the prime supplier Battelle, to develop a solution.

Waste Treatment Plant

In support of the Waste Treatment Plant, under construction, Battelle conducted experiments on mixing thick radioactive waste slurries that will be vitrified at the plant.

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A set of bounding properties for the waste that can be reasonably processed at the treatment plant was developed.

Flammable gas may build up in the non-Newtonian waste during mixing. For WTP, Battelle determined the amount of gas buildup under certain conditions, including restarting the mixers after loss of power. Battelle also conducted experiments that demonstrated the removal of the flammable gases from the wastes.

Removing Troublesome Materials

Prior to vitrification, cesium-137 is removed from the liquid fraction of the waste and chromium is separated from the sludge fraction. Cesium-137 is highly radioactive and must be separated from the bulk of the waste and concentrated for disposal in the high-level waste glass. The chromium must be removed from the sludge fraction because it limits the amount of waste that can be incorporated into each glass log. If it was not removed, the number of high-level waste glass logs and the corresponding cost would increase significantly.

The WTP will remove the cesium using ion exchange columns loaded with SuperLig-644® resin. As a cost-saving alternative, WTP is considering resorcinol formaldehyde resins. Battelle demonstrated that these backup resins selectively and effectively removed cesium to meet WTP flowsheet requirements.

In addition, Battelle and WTP examined the effectiveness of oxidative leaching at removing chromium from tank SX-101 and SY-102 sludge wastes. Oxidative leaching uses a chemical additive to change the chromium into a soluble form that can be easily separated from the sludge.

Turning Waste Into Glass

Because the waste in Hanford's tanks varies in chemical composition and physical properties, the composition of the waste streams entering the WTP is expected to vary significantly. To accommodate the variability, Battelle developed a set of bounding properties for the waste that can be reasonably processed and are likely to be encountered at the plant. Ultimately, a set of bounding properties will be used by WTP to design the vitrification equipment. With Battelle's consultation, potential problems can be predicted more accurately.

Storing the Waste

Battelle provided statistical analyses, methods, and expertise to help WTP determine if the vitrified waste met all of the waste acceptance criteria. Waste that does not meet the requirements cannot be stored, resulting in additional expensive and time-consuming processing. In addition, Battelle planned tests to show what would happen if a canister containing glassified waste was dropped accidentally during handling and transport activities. Plans call for these tests to be conducted in 2005.

Contents

Mixing Waste

Assessing Pulse Jet, Steady Jet, and Air Sparging Mixer Performance

Battelle and the Waste Treatment Plant (WTP) Pulsed Jet Mixer team created and implemented a development strategy for assessing the performance of pulse jet mixers, air sparging, and steady jets generated by recirculation pumps on waste with non-Newtonian rheology. Hybrid mixing systems involving these three mixing methods are being considered for mixing radioactive waste, which can have the consistency of mud, in various tanks at the WTP.

Hybrid systems involving pulse jet mixers, steady jets, and air sparging are being considered for mixing radioactive wastes with the consistency of mud.

In 2004, Battelle working with WTP and others completed the following tasks:

- Conducted tests making extensive use of two waste slurry simulants
- Implemented mixing measurement methods
- Developed and implemented scale-up methodology for pulse jet mixers, steady jets, and air sparging
- Conducted near full-scale tests to characterize the mixing and gas release performance of air sparge systems in simulants with a non-Newtonian rheology
- Demonstrated hybrid pulse jet mixer/air sparging system performance on a large scale
- Conducted experiments on retention and release of in situ generated gases and experiments on mass transfer
- Conducted a second set of scaled prototypic vessel tests.

This pulse jet mixer test stand was used to conduct large-scale experiments that provided performance data on mixing and gas retention and release. These results are being used to predict performance in the WTP.

Conducted tests making extensive use of two simulants: In 2004, Battelle and the WTP Pulsed Jet Mixer team made extensive use of a Laponite-based and a kaolin/bentonite clay simulant. These two simulants were developed in 2003. The Laponite-based simulant is a synthetic clay that is transparent in an aqueous slurry. This simulant was extraordinarily useful for testing as it allowed direct visual observation of the mixing behavior. The kaolin/bentonite clay is opaque but provides a closer match to the rheology of particulate tank waste slurries. Both simulants are inexpensive, non-hazardous, and representative of pertinent actual waste rheological properties. The technical basis for the selection of these simulants was published in 2004.

Implemented mixing measurement methods: Battelle implemented methods it developed in 2003 for assessing mixing. These included the use of tracers and radiofrequency tags. The tracer method involves the addition of either dye or sodium chloride to the simulant and monitoring the concentration distribution as a function of mixing time. The radiofrequency tags are added on or below the surface and the location was monitored with antennas placed around and in the tanks. While both methods were developed in 2003, the tracer method was developed further in 2004, and the technical basis and validation of this method was published.

Developed and implemented scale-up methodology: The WTP Pulsed Jet Mixer team and Battelle developed and demonstrated a scale-up methodology for pulse jet mixers applied to slurries with non-Newtonian rheology. The scale-up strategy is based on an extension of turbulent steady jet theory to account for the periodic nature of the jets produced by the pulse jet mixers. The scale-up methodology was demonstrated by conducting simulant tests in three scaled test stands. Each of these test stands contain geometrically scaled pulse jet mixer systems. The working volume of these test stands ranges from about 35 gallons to 10,000 gallons. The final tests were completed in 2004, and the technical basis for the scale-up was documented. The extent of mixing data was used to demonstrate that the mixing results hold at different scales and that scaled prototypes may be used to assess mixing behavior of full-scale mixer systems.

The mixing and gas release of air sparge systems for certain radioactive wastes was characterized.

Characterized the mixing and gas release performance of air sparge systems: Battelle conducted near-full scale tests in an approximately 10,000-gallon tank with single and multi-sparge tube systems to characterize the mixing and gas release performance of air sparge systems in simulants with a non-Newtonian rheology. The tests defined the mixing zone of influence for a single sparge tube and demonstrated the mixing of the tank contents with the multi-sparge tube array. Aerosol measurements were obtained for assessing the impact on the WTP ventilation system. The same test stand was used to determine the gas release characteristics of the air sparge system with the clay simulant. In these tests, oxygen was generated in situ by the decomposition of hydrogen peroxide that was mixed into a kaolin/bentonite clay simulant. The removal of the in situ gas by the air sparging system was determined as a function of mixing time. These large-scale tests allow the sparging system to be designed with minimal scale-up.

Demonstrated hybrid pulse jet mixer/air sparging system performance on a large scale: Battelle and the WTP Pulsed Jet Mixer team designed and constructed a half-scale replica of the lag storage vessel for evaluation of mixing and gas retention and release performance. Working together, the team designed, fabricated, and installed a hybrid pulse jet mixer/air sparging system in an approximately 10,000-gallon tank. The team operated the mixing system in various modes representing 1) normal operation, 2) post-design basis event operation, and 3) near-term accident response operation. By monitoring the gas content of the simulant with the various mixing modes, gas retention and release characteristics were determined. The in situ generation of oxygen gas was provided from the decomposition of hydrogen peroxide that was mixed into the kaolin/bentonite clay simulant. The mixing performance was monitored using the sodium chloride salt tracer method. These tests provide a large-scale demonstration of the lag storage vessel mixing system and provide performance data for management of flammable gases in the WTP.

Using a half-scale tank containing about 10,000 gallons of simulated waste, a Battelle researcher monitors the performance of the pulse jet mixers under a variety of conditions.

A hybrid pulse jet mixer/air sparging system was d fabricated, and installed in an approximately 10,000-gallon tank.

Conducted gas holdup and mass transfer experiments: Experiments with the mixing test stands using flammable gases are not feasible because of technical and safety issues. Battelle conducted a number of small tests in a bubble column contained in a fume hood for safety to characterize the holdup of hydrogen, air, oxygen and argon in water, kaolin/bentonite clay, and a high-level waste slurry simulant. The impact of anti-foam agent and salt content was also investigated. In addition, Battelle investigated the rate of removal of dissolved oxygen with an air sparge system. The results of these experiments are expected to form a correlation between the gas retention and release results that were obtained with in situ generated oxygen in the scaled test stands and the flammable gas behavior projected in the WTP.

Conducted a second set of scaled prototypic vessel tests: Battelle and the Savannah River National Laboratory conducted tests on three scaled prototypic vessels, with volumes ranging from about 200 gallons to about 1,100 gallons. Each of the tanks was made of clear acrylic plastic to allow observation of the mixing behavior. The support structure and the mixing systems were designed to be readily reconfigured so that different designs could be evaluated. The mixing systems evaluated included various combinations of pulse jet mixers, steady jets generated by recirculation pumps, and air spargers. More than 100 individual tests were conducted with the kaolin/bentonite clay simulant. Battelle and Savannah River determined the extent of mixing and the time required for mixing. This information was used to indicate mixing performance. To further characterize the mixing performance of the final mixing system configurations, the team obtained extensive measurements of the simulant velocities. In addition, the team conducted several tests to characterize the gas retention and release performance of the hybrid mixing configurations. These tests provided valuable information on the design and operating parameters needed to achieve mixing in full-scale vessels.

Testing Gas Release in Pulse Jet Mixed Tanks

For the WTP, Battelle is focused on understanding flammable gas (for example, hydrogen) retention and release when pulse jet mixers are used in tanks containing thick non-Newtonian wastes. Battelle conducted gas retention and release testing, including bench-scale development activities and experiments in pulse jet mixed tanks covering a range of configurations and scales, all using non-Newtonian waste simulant. Battelle conducted several tests to assess the volume fraction of gas retained in simulant during continuous gas generation and steady-state pulse jet mixer operation (that is, "gas hold up" tests), and the gas release characteristics (volume and rate) in scenarios representing plant restart after a loss-of-power event (that is, "gas release" tests). Battelle conducted additional proof-of-concept tests to demonstrate gas stripping mass transfer resulting from air sparging, a possible means of mitigating flammable gas buildup in waste contained in pulse jet mixed vessels. One-quarter-scale and one-half-scale tanks were used in the tests.

Preatreating Waste

Removing Cesium with Ion Exchange

The feasibility of using resorcinol formaldehyde resin, which is easily obtainable, as a backup resin was demonstrated.

In the baseline plans for the WTP, cesium-137 must be removed from the tank waste to produce a low-activity waste (LAW) that can be vitrified into LAW glass. The cesium will be removed using ion exchange with SuperLig-644® (SL-644) resin. WTP is also considering the use of an alternate resin, resorcinol formaldehyde (RF). In 2004, Battelle demonstrated that these resins could selectively and effectively remove cesium from Hanford tank waste. Specifically, Battelle:

- Assessed the aging of SL-644 during storage conditions at WTP. The effects of storage time, storage temperature, storage medium, storage cover gas, and resin form were assessed in a reduced factorial test design.
- Determined elution requirements for SL-644 for carousel column operation and for SL-644 spent resin disposal. Variables included eluant flow rate, acid strength and temperature, and initial concentration of cesium on the resin. Speed and completeness of elution and resin degradation were used to compare the effects of the variables in a reduced factorial test design. Results indicate moderately increased temperature provided the most efficient elution with the least resin degradation of the conditions tested.
- Demonstrated the feasibility of RF resin, which is easily obtainable, as a backup resin if issues arise with SL-644. Physical, chemical, and hydraulic properties of different batches and physical forms (that is, spherical and ground gel) of RF, obtained from three different vendors, were compared. SL-644 was tested in parallel for comparison in some cases. Spherical RF displayed particularly rapid, complete elutability and high durability. These results, combined with good capacity and other properties, suggest that spherical RF would be an excellent alternative to SL-644.
- Determined preconditioning and regeneration requirements for ground gel RF Ground gel RF requires approximately 4 times more sodium hydroxide than SL-644, per volume of resin, for conversion to the sodium form from the acid or as-received forms.
- Determined elution requirements for ground gel RF for carousel operation and for ground gel RF spent resin disposal. Battelle verified the rapid, complete elutability of spherical RF with an additional test.
- Began testing variations of spherical RF. Battelle assessed the physical properties, capacity, elutability, and hydraulic properties. These tests are still in-progress.

Removing Chromium with Oxidative Leaching

The effectiveness of oxidative leaching at removing chromium from tank waste was studied.

The chromium content in waste fed to the WTP limits the amount of high-level waste that can be incorporated into each glass log, raising the costs and increasing the number of logs that need to be made. Battelle worked with WTP to set up the studies needed to examine the effectiveness and other parameters involved in using oxidative leaching to remove chromium from the waste stream and transfer it to the LAW stream, where it poses less of a problem.

X-ray diffraction analyses was used as part of Battelle's investigations into oxidative leaching and chromium removal.

Battelle extensively washed actual tank SX-101 and SY-102 waste sludge samples to remove all readily soluble chromium from the tank sludge. Battelle completed the following preliminary examinations:

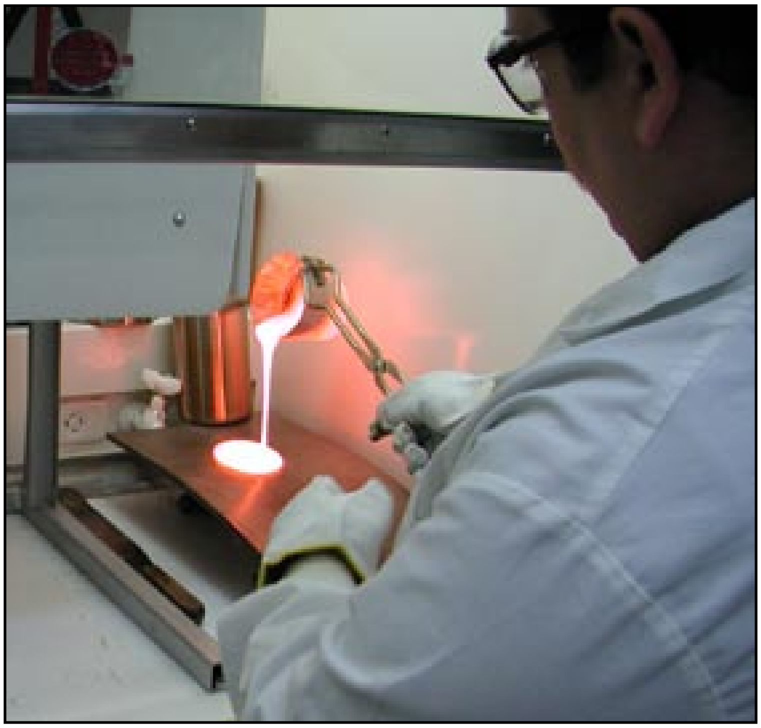
- Scanning electron microscopy electron dispersion spectroscopy
- X-ray diffraction analyses
- Inductively coupled plasma atomic emission spectrometry metals analysis
- Gamma energy analyses
- Alpha energy analyses.

Based on the information from these tests, samples were taken for actual waste testing. The team completed the actual waste testing, and the results have been documented in a final report provided to WTP. To summarize the results:

- Oxidative alkaline leaching can dissolve effectively and selectively major bulk constituents (> 95% removal of bulk aluminum and chromium possible) from alpha-emitting radionuclides.
- The reaction conditions chosen can have a major impact on the effectiveness and selectivity of the process.
- Greater than an order of magnitude reduction in immobilized high-level waste appear possible by employing oxidative alkaline leaching compared to simple sludge washing.

Glassifying Waste in Melters

Studying Waste Feed Rheology



PNNL researchers prepare LAW glass for product performance testing.

To help WTP facilitate consensus design parameters among their Research and Testing, Environmental and Nuclear Safety, Design, and Process Engineering functions, Battelle developed a set of bounding physical and rheological properties for waste materials that can be reasonably processed and are likely to be encountered in the WTP vitrification facilities. Ultimately, a set of bounding physical and rheological properties will be used by WTP to design process equipment for WTP vitrification facilities. With these bounding property descriptions, the transfer and processing problems that may be encountered can be predicted more accurately.

Battelle identified physical and chemical parameters that are significant to WTP vitrification-stream processing through the use of dimensional analysis. Battelle compared that data with historical data for actual and simulated process streams. Battelle used the physical and chemical parameters identified to recommend upper and lower physical and rheological bounding ranges that, if exceeded, will likely result in plant performance degradation.

In addition, Battelle developed bounding conditions for two LAW vitrification streams: 1) pretreated LAW and 2) LAW melter feed. The bounding conditions proposed by Battelle were formulated based upon actual waste data, theoretical/empirical correlations, and the need for a reduction in plant operational risk.

Parameters important to WTP vitrification-stream processing were identified through dimensional analysis.

High-Level Waste Canister Testing

To meet the very stringent quality assurance, waste acceptance requirements for the canisters of vitrified high-level waste, WTP is testing how the canisters respond to different scenarios, including falls. As part of this effort, Battelle developed plans and completed an initial task to prepare for drop testing up to three high-level waste canisters. The canisters, filled with nonradioactive glass, were seal welded at the Savannah River National Laboratory and shipped to Hanford in December. Battelle is in the process of developing the plans necessary to conduct a 7-meter drop onto an unyielding surface.

Qualifying Waste Forms

To assist WTP in meeting waste form specifications set in its contract was well as by the U.S. Department of Energy, Battelle provided statistical analyses, methods, and expertise.

Developing Compliance Equations: As part of the immobilized high-level waste and immobilized LAW compliance strategies, WTP Research and Testing, Waste Form Qualification, and Battelle provided input on equations for calculating each required compliance quantity. These equations are a function of the sample, analysis, and other measurements that will be made during production. Battelle worked iteratively with the WTP Waste Form Qualification to develop the equations.

Compliance Over a Waste Type: Battelle developed statistical methods for demonstrating waste acceptance compliance over a wide range of immobilized high-level waste and immobilized LAW compositions. The compliance strategies call for reporting means and standard deviations over a waste type. Battelle developed methods to calculate standard deviations while properly accounting for single-batch uncertainties from simulation calculations and variations over batches or canisters associated with a waste type. Battelle is drafting a report that includes sections on these methods.

In addition, Battelle determined methods for calculating statistical tolerance intervals to demonstrate compliance over a waste type. These methods include the product consistency test for immobilized high-level waste, the product consistency test and the vapor hydration test for immobilized LAW, and some radionuclide characterization for immobilized LAW. These methods must account for compositional variation over batches or canisters, as well as single-batch uncertainty. In the case of the product consistency test and the vapor hydration test, model uncertainties must also be addressed. With the new immobilized high-level waste compliance strategy, the methods and results developed (see PNWD-3099/WTP-RPT-013) are now applicable, which minimizes the amount of new work needed to accommodate the change in compliance strategy. Also, Battelle determined that the methods previously developed can be adapted to the immobilized LAW compliance situation.

Providing Direct Staff Support

Several Battelle staff with special technical expertise provided full-time support to the WTP by filling positions within the WTP Research and Testing and Process Operations Departments. Specific areas of contribution are as follows:

- Glass formulation and waste form qualification: Two Battelle staff members provided technical expertise and direction in the development and execution of activities associated with glass formulation and waste form qualification.
- Ion exchange: Battelle staff provided evidence and technical basis for the process design for cesium removal using an organic elutable ion exchange resin.
- Waste simulant validation: A Battelle staff member serves at the Simulant Coordinator ensuring the development and use of simulants is coordinated, consistent, and defensible. This person is the principal contact for all simulant questions and is involved in resolving all issues that involve the "performance" of a simulant.

In addition, Battelle developed thermodynamic models to determine the present waste composition and model WTP processes. The models are used to determine the required amounts of reagents, estimate volumes of LAW and high-level waste glass, and determine the fate of contaminants in WTP.

Statistical methods for demonstrating waste form compliance were developed.

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