Executive Summary

PNNL Supports Cleaning Up Hanford’s Tanks

In fiscal year 2005, Pacific Northwest National Laboratory provided scientific and technical assistance as requested to support cleanup of Hanford tanks under the management direction of CH2M HILL Hanford Group, Inc. PNNL, a U.S. Department of Energy Office of Science laboratory, solves complex problems in the environment, energy, security, and life sciences. CH2M HILL has responsibility for retrieving and disposing of about 53 million gallons of highly radioactive waste stored in 177 underground tanks on the former plutonium production site in southeastern Washington State.

New Methods Provide Accurate Measurements

In the complex and chemically harsh tank waste, traditional sampling and analysis methods can be time-consuming, disruptive, and costly. In addition, these methods supply only a snapshot of the waste’s constituents. So, PNNL researchers developed a new density, flow, temperature, and Raman spectrometer for real-time, at-tank measurements. This compact system is rugged, accurate, and inexpensive.

In the vadose zone and groundwater at Hanford and other sites, radioactive iodine (iodine-129) is of interest. Researchers at PNNL defined and tested a fusion method using inductively coupled plasma mass spectrometry that produces a highly accurate measurement of iodine in solid matrixes from glass to soil.

Supporting Supplemental Treatment

CH2M HILL staff are evaluating bulk vitrification to immobilize some of the radioactive tank waste. In bulk vitrification, waste, Hanford soil, and glass-forming chemicals are mixed, dried, and placed in a large metal container. The materials are then heated, turning them into glass. Once cooled, the container and vitrified waste are buried in a permitted disposal facility. Researchers from PNNL helped demonstrate the vitrification process with actual Hanford waste and answered questions about the behavior of the bulk vitrification waste form.

Understanding Past and Future Behavior of Tanks and the Environment

PNNL scientists investigated contaminated soil samples to more accurately predict waste movement during retrieval from the C Tank Farm single-shell tanks. With this information, CH2M HILL staff can better predict and respond to the movement of these waste plumes.

After the waste is retrieved and other closure activities have been completed, the tanks may be filled with a stabilizing material. As part of CH2M HILL’s risk and

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PNNL researchers evaluated vapors at the tank farms to protect workers from possible health effects.

performance assessments, PNNL scientists developed models that describe the release of contaminants as water infiltrates and contacts the fill material.

While waste retrieval and closure continue, the double-shell tanks will be in service longer than expected. PNNL researchers completed a three-year study of these tanks, including their behavior during an earthquake. CH2M HILL will use this study to show that these tanks are fit for continued service.

**Estimating Future Long-Term Environmental and Human Health Impacts**

To comply with regulations and to evaluate engineering options, CH2M HILL performs assessments of long-term impacts to the environment and human health from remediation activities. PNNL has played an important role in assessments of the Hanford tanks and tank farms, Integrated Disposal Facility, and bulk vitrification. Using expertise in computer modeling, materials, geochemistry, and engineering, PNNL experts provided extensive information on the behavior of contaminants of concern in tank residuals, subsurface sediments, and waste forms.

**Protecting Tank Farm Workers**

Currently, employees taking samples or performing other work around the tanks must use supplied air because of concerns regarding the health effects of vapors emitted by the tank wastes. Researchers at PNNL helped CH2M HILL conduct engineering evaluations of tank vapor sources, releases, and dispersion.

In addition, PNNL toxicologists established screening levels for about 600 vapors that could be given off by the tanks. More thorough toxicological evaluations are being conducted to establish occupational exposure limits.
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Introduction

CH2M HILL Hanford Group, Inc. is the U.S. Department of Energy Office of River Protection’s prime contractor with responsibility for storing and retrieving approximately 53 million gallons of highly radioactive and hazardous waste stored in 177 underground tanks on the Hanford Site. These concrete tanks are categorized into two basic designs: single shell tanks, which have one steel liner, and double-shell tanks, which have two steel liners.

This waste is the byproduct of plutonium production and other missions at Hanford. It contains approximately 200 million curies of radioactivity and is present in a variety of forms. The waste must be retrieved from the tanks and turned into a safe form that immobilizes the radionuclides and chemicals of concern. The tank waste will first be separated into two streams based on its associated radioactivity. The waste will then be vitrified; that is, turned into a glass form. CH2M HILL is responsible for storing the highly radioactive vitrified waste until shipped to a final repository. The less radioactive waste will be vitrified and disposed at Hanford.

Pacific Northwest National Laboratory, under the management direction of CH2M HILL, provided scientific and technical solutions in support of the Hanford tank farm clean-up mission.

PNNL provides CH2M HILL with science and technologies to assist in retrieving and storing tank waste at Hanford.

The 53 million gallons of tank waste contain over half of the elements on the periodic chart. Pacific Northwest National Laboratory is assisting CH2M HILL in safely storing, retrieving, treating, and disposing of tank waste.
Processing the Waste

New Process Monitor Reduces Operational Downtime

At CH2M HILL’s request, PNNL researchers developed and tested a chemical species monitor for assessing retrieval of saltcake from single-shell tanks. Consisting of a meter to measure density, flow, and temperature as well as a conductivity probe and a Raman spectrometer, this system quickly provides the data needed for timely response to the dynamic characteristics of the waste stream.

Workers at the tank farms will use the information provided by the monitoring system to do the following:

- Make sure the waste added to the double-shell tanks from the single-shell tanks conforms to corrosion specifications
- Minimize the addition of water to prevent saturation of sodium nitrate and sodium phosphate in the tank waste
- Evaluate the effectiveness of retrieval strategies.

In developing the new monitor, the research team calibrated and tested the performance of the system to measure the concentration of sodium salts qualitatively and quantitatively over the concentration ranges anticipated during waste retrieval.

The Raman technology measures multiple analyte concentrations, e.g., nitrate, nitrite, sulfate, carbonate, phosphate, chromate, hydroxide, and cyanide, at the same time.

PNNL developed a compact Raman-based process monitoring system that rapidly quantifies multiple constituents in chemically harsh aqueous streams in support of saltcake retrieval activities for Hanford tanks.

The Raman system provides the first real-time monitoring of tank waste composition and cumulative status during processing. The radiation-hardened sensor is compact, rugged, and accurate.
from Tank S-109. The team independently measured sodium concentration (based on density and conductivity) and the specific salts (based on spectrometry results). In addition, they tested the effects of temperature, flow rate, bubbles and solids, and analyte matrix dependence. The effort also included close coordination with CH2M HILL’s S-109 Retrieval Project to design, fabricate, and test the Raman probe system for incorporation into the S-109 retrieval system.

Two significant tests were completed successfully, a system acceptance test and a manifold validation test. The acceptance test verified that the actual measured accuracy for each analyte of interest met the expected accuracy. The manifold validation test showed that the chemical species monitor, once integrated into the larger system, would operate as intended.

Supplemental Processes for Vitrifying Low-Activity Waste

The U.S. Department of Energy and CH2M HILL are investigating supplemental technologies to immobilize low-activity tank waste. In bulk vitrification the liquid tank waste, Hanford soil, and glass-forming chemicals are mixed, dried, and added to a large metal container that is lined with castable refractory blocks that act as a large crucible to contain the molten glass. Graphite electrodes are used to resistively heat the materials, turning the dried feed into a glass waste form. After the material has cooled, the container and the vitrified waste will be disposed in the Integrated Disposal Facility, an environmentally compliant burial ground being constructed on the Hanford Site.

PNNL supported engineering-scale testing and conducted research to help CH2M HILL and their bulk vitrification contractor, AMEC Earth and Environmental, Inc., evaluate the process and product performance of the supplemental treatment technology. The first engineering-scale test with actual radioactive tank waste was completed. Further laboratory testing with radioactive and nonradioactive spiked simulants was performed to evaluate process performance. A key objective was to evaluate the ability to effectively immobilize the radioactive waste with bulk vitrification. Technetium-99, a long-lived radioisotope in the waste, is particularly important because long-term performance of the disposal facility is sensitive to the behavior of technetium in the immobilized waste form. A small fraction of the technetium in a readily leachable form outside of the glass can affect overall waste form performance.

Demonstrating Bulk Vitrification Performance with Engineering-Scale Radiological Tests

To test the bulk vitrification process and evaluate product performance, PNNL and AMEC jointly performed engineering-scale tests in the Radiochemical Processing Laboratory. These radioactive tests used a combination of simulant and actual tank waste to determine whether the actual waste behaved like the simulant in the vitrification process. Both technetium-99 and rhenium, a nonradioactive surrogate
for technetium, were used in the tests to aid in comparing previous and future nonradioactive tests. The tests showed that a high-quality vitrified product could be produced, that the process behaved similarly with actual waste and with simulants, and that rhenium is a good nonradioactive surrogate for technetium. The results were incorporated by CH2M HILL’s project team as they proceeded with large-scale nonradioactive testing with rhenium to help predict future technetium behavior at full-scale.

**Reducing the Inventory of Leachable Technetium in the Castable Refractory Block**

CH2M HILL asked PNNL researchers to improve the understanding of technetium migration during bulk vitrification operations and to find ways to reduce any small quantity of leachable technetium species not incorporated into the glass. The team conducted the following activities:

- Quantified the concentration of leachable technetium present in the castable refractory block after processing.
- Determined the feasibility of reducing the oxidation state of technetium to make it less mobile.
- Studied alternatives to prevent technetium migration out of the glass-making area into the castable refractory block.
- Investigated technetium migration/volatilization under different conditions.

*To provide the information needed to make safe, sound decisions, PNNL researchers investigated methodologies to reduce the amount of leachable technetium not incorporated into the glass monolith.*
To elucidate bulk vitrification waste properties, PNNL researchers conducted engineering-scale tests using a waste simulant spiked with actual tank waste.

At the Radiochemical Processing Laboratory, PNNL scientists showed that nonradioactive rhenium was an excellent surrogate for technetium in bulk vitrification contaminant migration studies. This allows researchers to obtain early indication of technetium behavior at the large scale by studying the behavior of rhenium in nonradioactive tests.
The results helped CH2M HILL develop a better understanding of the mechanisms involved in technetium migration. Based on these results, CH2M HILL will make decisions on how to accommodate the leachable technetium or adjust the bulk vitrification process to produce waste forms with less leachable technetium.

**Assessing Bulk Vitrification Long-Term Performance**

Computer modeling experts, geochemists, engineers, and other researchers from PNNL estimated possible radionuclide release rates from the bulk vitrification waste product that is to be disposed in the Integrated Disposal Facility, a shallow, near-surface burial site being constructed in the 200 East Area at Hanford. To calculate how the radionuclide release rates from corrosion of the glass would impact the groundwater at a time far into the future, the Office of River Protection needed to understand how, once the engineered barriers failed, the glass and other materials would react with the water slowly migrating from the surface under changing pH, temperature, and other conditions. This work is part of the broader performance assessment in which the long-term human health and environmental impacts from disposal of the immobilized waste, melters, and other related materials in the Integrated Disposal Facility need to be estimated to address public and regulatory concerns (see page 11).

At PNNL, the research team conducted dissolution tests to examine the corrosion behavior of glass in water over a wide range of conditions. The results were used to develop the parameters needed to conduct performance assessment calculations of the long-term interaction of disposed glass with water. These calculations were carried out with a PNNL reactive transport computer model. Preliminary results suggest that bulk vitrification glass follows dissolution patterns that are very similar to those of the glass being formulated for the Waste Treatment Plant.

Scanning electron microscope images of the glass/block interface help researchers assess how well the waste will lock in certain elements.

The Integrated Disposal Facility is a 60-acre landfill that is being constructed in the 200 East Area of the Hanford Site.
The research team also analyzed for readily leachable technetium-99 and/or rhenium in the castable refractory block from the bulk vitrification engineering-scale tests and developed a best-estimate quantity for use in performance assessment calculations.

For additional information, see Laboratory Testing of Bulk Vitrified Low-Activity Waste Forms to Support the 2005 Integrated Disposal Facility Performance Assessment, PNNL-15126, Revision 1. This report is available on PNNL’s website (http://wwwpnl.gov). Additional information provided by PNNL supporting the Integrated Disposal Facility performance assessment can also be found on the site.

**Closing Tanks and Disposing of the Waste**

**Modeling the Transport of Residual Waste in Tank C-106**

CH2M HILL is producing risk and performance assessments to support the closure of the 149 single-shell tanks at Hanford. To support this effort, staff at PNNL were asked to develop release models for contaminants of concern in the sludge remaining in Tank C-106 after the final retrieval campaign. The primary contaminants of concern are technetium-99, uranium-238, and iodine-129 because of their mobility and long half-lives. Chromium is also a concern because of its mobility.

To produce the release models, PNNL researchers conducted laboratory tests to obtain contaminant release data and a conceptual source release model. The researchers characterized the sludge and identified the water-leachable constituents. Based on the results of these tests, the team performed additional characterization analyses to determine the controlling mechanisms for contaminant release.

The team used the laboratory results of sludge and liquid testing to develop source term release models that describe the release of contaminants as infiltrating water contacts the cementitious material that will be used to fill the tanks at closure. These models simulate the geochemical system under the tank and take into account interactions between the solution phase and the contaminant-containing solids. The researchers determined that greater than 90% of the primary contaminants are not readily leachable from the residual waste. The majority (90%) of the technetium-99 was not leachable under any of the conditions tested.

In addition, the team made advances in testing and analytical methods to characterize tank waste material, including

- Inductively coupled plasma mass spectrometry analysis of iodine-129, strontium-90, neptunium-237, plutonium-239, and americium-241
• Scanning electron microscopy/energy dispersive spectroscopy mapping of elements in waste material

• Synchrotron x-ray analysis

• Mössbauer spectroscopic analysis.

These advances improved source term models for residual tank waste.

Additional information can be found in Hanford Tank 241-C-106: Residual Waste Contaminant Release Model and Supporting Data, PNNL-15187. This report is available on PNNL's website (http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15187.pdf).

Creating a Highly Accurate Way to Measure Radioactive Iodine in Soil, Waste, and Glass

Because of its 15.7-million-year half-life and mobility in the subsurface, iodine-129 is a contaminant of interest in the vadose zone and groundwater at the Hanford Site. To understand the long-term risk associated with iodine-129 at Hanford, all possible sources must be examined. The three primary sources of iodine-129 are the tank waste, the vadose zone, and the groundwater system. The ability to assess the iodine-129 contribution quantitatively from these sources requires specialized extraction and analytical techniques that are complicated and uncertain.

Several techniques have been used to extract iodine from solid matrixes; however, all of them rely on two fundamental approaches: liquid extraction or chemical/heat facilitated volatilization. While these methods are typically chosen for their ease of implementation, they do not totally dissolve the solid.

Researchers at PNNL defined a method that produces complete solid dissolution and conducted laboratory tests to assess its efficacy to extract iodine from solid matrixes. Testing consisted of potassium nitrate/potassium hydroxide fusion of the sample followed by sample dissolution in a mixture of sulfuric acid and sodium.

Researchers at PNNL developed a simple and cost-effective method to extract and quantify iodine from solid matrixes. Iodine-129 is a contaminant of interest at the Hanford Site.
Analyses conducted at PNNL help CH2M HILL predict the movement of contaminant plumes from leaking tanks through the vadose zone.

Bisulfite. The fusion extraction method resulted in complete sample dissolution of all solid matrixes tested: standard reference material soil samples, glass samples containing low levels of iodine, and Hanford tank waste material. The greatest benefit of this extraction technique is the total dissolution of the solid sample without volatilization of iodine. In addition, this extraction technique can be applied to other matrixes with little or no adaptation.

This research also showed the applicability of inductively coupled plasma mass spectrometry as a rapid and quantitative technique for analyzing iodine. The primary benefit is the exceptional analytical detection limits. The ability to analyze the fused/extracted solution samples directly, without requiring elaborate and time-consuming separation and preconcentration steps, increases productivity significantly and minimizes the potential for laboratory-induced error. This analytical tool, when coupled with sample preparation via fusion, becomes a simple and cost-effective method to quantitate total iodine (iodine-127 and iodine-129) in solid samples.

For more information on this new technique developed by PNNL, see the article “Extraction and Quantitative Analysis of Iodine in Solid and Solution Matrixes” in Analytical Chemistry, volume 77, number 21, pages 7062-7066.

Answering Questions About Tank C-105 Waste Leaks

PNNL chemists, geologists, hydrologists, and computer modelers conducted a two-tiered investigation of contaminated vadose zone samples collected within the C Tank Farm. Their analyses will help CH2M HILL staff better predict the movement of radioactive and chemical waste plumes from the single-shell tanks through the vadose zone.

Soil samples collected near the single-shell tanks in the C Farm were analyzed to determine the spread of radioactive and chemical waste leaked from the tanks.
Researchers at PNNL analyzed vadose zone sediment to ascertain the cause of accelerated corrosion of the stainless steel casing in two wells used to monitor groundwater contamination near the A-AX Tank Farms.

Based on their findings, the PNNL team recommended using portland cement as an annulus sealing agent in groundwater monitoring wells in areas with high moisture content or where perched water could accumulate. This alternative finishing method should prevent casing failure due to corrosion. For additional information, see Investigation of

Portland cement is recommended as an annulus sealing agent in groundwater wells at risk for rapid corrosion.
Providing a Digest of T, TX, TY Tank Farm Vadose Zone Information

PNRL hydrologists, geologists, and computer modeling experts helped CH2M HILL evaluate how corrective actions would reduce or eliminate the consequences of past leaks from the T, TX, and TY tanks. These 36 single-shell tanks are located in the 200 West Area. Twenty of them are suspected or confirmed to have leaked to the soil.

The PNNL research team developed an exhaustive summary of geochemical and modeling studies on the movement of technetium, nitrate, and uranium in groundwater plumes. The team used the results from the geochemical studies to update the conceptual model of contaminant transport. For more information, see Field Investigation Report for Waste Management Areas T and TX-TY, RPP-23752, Revision 0-A. See http://www.hanford.gov/docs/gpp/fieldwork/vadose/RPP-23752.pdf.

Estimating Waste Form Performance in the Integrated Disposal Facility

Environmental regulations require that analyses be performed to estimate how waste forms will behave over time so that the public and the environment can be protected. So, PNNL analyzed how two major types of immobilized low-activity waste (glass from the Waste Treatment Plant and bulk vitrified glass) would perform in the Integrated Disposal Facility. These analyses included computer simulations that take many days, even on the world’s very fast supercomputers, to estimate how slowly contaminants are released and to indicate the processes and parameters that are important in that release.

PNNL scientists looked at a variety of glass compositions and environmental conditions so that the performance assessment could be robust. For more information, see Waste Form Release Calculations for the 2005 Integrated Disposal Facility Performance Assessment, PNNL-15198. See http://www.pnl.gov/main/publications/external/technical_reports/PNNL-15198.pdf.

Protecting Tank Farm Workers

Concern that vapors emitted by the underground Hanford waste tanks could have adverse health effects on workers resulted in the August 2004 requirement by CH2M HILL that all work in the farms be conducted using supplied air breathing systems until the potential health effects of vapor exposures had been properly evaluated.
PNNL researchers uniquely familiar with efforts conducted in the 1990s to characterize the tank headspace vapors have helped reevaluate existing data, identify data needs, and develop a technical basis for the CH2M HILL Tank Farms Industrial Hygiene Program. The researchers have provided engineering support on headspace dynamics (e.g., mixing, air exchanges, ventilation), estimation of vapor emissions caused by waste-disturbing activities (transfers and retrievals), selection of appropriate sampling methods and media, and interpretation of sampling results. The team modeled the dispersion of released vapors into the workers’ breathing zone to estimate likely exposure levels at various distances from vapor sources under different meteorological conditions and vapor release scenarios.

Researchers at PNNL also conducted chemical and toxicological evaluations to determine which of the hundreds of vapors present in the tank headspaces have been detected at levels of concern, and then assigned acceptable occupational exposure guidelines to many of the vapors of concern that lacked national guidelines. PNNL toxicologists conducted reviews of the available literature and established headspace concentration screening values for about 600 of the vapors. These screening values were then compared with the maximum observed headspace concentrations to identify the chemicals that needed further evaluation. More thorough toxicological evaluations are being conducted to establish acceptable occupational exposure limits that will be incorporated into the industrial hygiene strategy for tank farm worker protection. These engineering efforts helped to bound the vapor problem and allowed the CH2M HILL industrial hygiene staff to develop suitable area monitoring strategies.

Currently, all workers in the tank farms use supplied air. To protect workers from harm without adding unnecessary restrictions, PNNL researchers assisted CH2M HILL in developing occupational exposure limits for tank-related vapors.
Engineers, computer modelers, and other researchers at PNNL completed a three-year comprehensive structural analysis of all the double-shell tank designs.

Safely Storing Tank Waste

Two key studies were performed: a thermal and operating load analysis and a seismic analysis. The thermal and operating load analysis was completed in FY04, and the bulk of the seismic analysis was completed in FY05. The results from the two analyses are being combined to provide a comprehensive and up-to-date analysis of record for the double-shell tanks.

To update the seismic analysis for these tanks, PNNL researchers performed a nonlinear seismic soil structure interaction analysis. This modeling contained the tank structure and the surrounding soil in a single time domain model. This allowed for the inclusion of contact surfaces and potential sliding at several structural interfaces. In addition, the team used hydrodynamic response of the liquid waste in the model, including waste sloshing at the free surface. These features had not been incorporated into earlier tank analyses. Incorporation of these features required that new methodologies be developed.

The data from this work will be part of the documentation sent to the Washington State Department of Ecology to demonstrate that these tanks are fit for continued service. This effort directly supports the Tri-Party Agreement milestone entitled “Submit Written Integrity Report for the Double-Shell Tank System,” due March 31, 2006.

To provide accurate data on the integrity of double-shell tanks if a seismic event should occur, PNNL completed a soil-structure interaction model that incorporated new features and methodologies not previously used on other Hanford tanks.

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