Waste Treatment AT HANFORD

Pacific Northwest NATIONAL LABORATORY

Pacific Northwest National Laboratory Support to Hanford Tank Waste Remediation

Scientists and engineers at Pacific Northwest National Laboratory (PNNL) provide continuity of scientific expertise, technical defensibility, and integration across the Hanford Tank Waste Remediation mission. This started with PNNL leadership in developing the chemical and engineering processes that generated the Hanford and Savannah River tank wastes and moved to development of the waste treatment processing at Hanford, Savannah River, and West Valley. Building off this past and current work, PNNL is well positioned to support 1) the integrated flowsheet; 2) development of alternative processes such as Direct Feed Low-Activity Waste (LAW), the Tank Waste Characterization and Staging Facility, Direct High-Level Waste (HLW), and In-Tank/Near-Tank Pretreatment; and 3) waste feed qualification. We are committed to addressing technical issues to enable technically defensible solutions. To that outcome, we currently steward four core capabilities:

- Tank Waste Chemistry
- Fluid Dynamics and Scaling
- Waste Forms
- Safety Basis

The following sections detail how we are developing these solutions.

TANK WASTE CHEMISTRY

PNNL has performed extensive characterization and process testing on Hanford tank wastes over the last 25 years. This has included receipt and characterization of full core samples under the Tank Waste Remediation System program as well as development work in the 1990s and 2000s that underpins the current pretreatment and vitrification flowsheets. Our experience includes development of the aluminum leaching process, demonstration of cross flow filtration, development of the Sr/TRU removal process, identification and validation of the cesium removal resin, and development of the Cr removal process. PNNL has led these efforts from initial conceptual testing through actual waste demonstration and ultimately to pilot scale demonstration.

Recent and current work includes:

- Tank Waste Integrated Disposition Flowsheet Team
  - Conducting a technical bases analysis of the interface flow parameters in the River Protection Project Mission Reference Integrated Flowsheet and identifying associated gaps, risks, and opportunities.
  - Developing technology roadmaps that include experimentation/physical testing, modeling, and technical reviews, leading to recommendations to close gaps, mitigate risks, and realize opportunities.
- **Direct Feed LAW**
  - Demonstrated near-tank treatment system as part of the Advanced Remediation Technology process funded by the U.S. Department of Energy (DOE). This involved developing an integrated process for continuous aluminum leaching, cross flow filtration, and cesium removal by ion exchange. The pilot-scale system developed in partnership with Parsons demonstrated the viability of at-tank processing to produce decontaminated supernatant to meet Direct Feed LAW requirements.
  - Demonstrated alternative ion exchange conditions to support reduction in nitric acid usage. This work demonstrated that the quantity of nitric acid required for elution could be significantly reduced, thereby improving the performance of cesium removal processes, including those to be used by LAW Pretreatment System (LAW PS).
- **Tc Management**
  - Identification of the chemical forms of Tc in tank waste including speciation of low valent Tc(I) in alkaline solutions to enable Tc removal from LAW streams prior to immobilization.
  - Conducting fundamental studies of the redox chemistry to predict and control Tc solubility.
  - Performed proof of concept demonstration of low valent Tc(I) by fluorescence spectroscopy to enable real-time detection and quantification.
  - Using internal PNNL funding to develop advanced materials for Tc management. Current research has generated a new active ion exchange material that can be applied to tank waste solutions for oxidizing, separating, and immobilizing all chemical forms of Tc in a one-step process.
- **Resolution of WTP Technical issues**
  - Providing technical expertise on optional flowsheet redesign efforts for the Hanford Waste Treatment Plant (WTP) examining a continuous flow processing option that may be done outside the black cells.

Radiochemical Processing Laboratory (RPL, or 325 Building)

Capabilities for characterizing and testing Hanford tank waste resides in the RPL, PNNL's Hazard Category II Non-reactor Nuclear Facility. The RPL is equipped with hot cells for receiving multi-liter quantities of tank waste. Characterization or process testing is then conducted in the hot cells or subsamples can be transferred to laboratories equipped with gloveboxes and fumehoods within the RPL. Over the past 6 years, PNNL has invested over $50M on new hot cells, gloveboxes, seismic and ventilation upgrade, as well as state-of-the-art instrumentation.

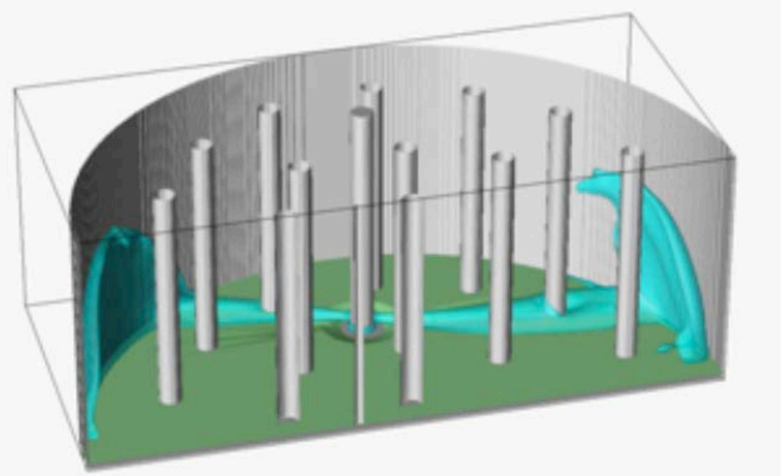
FLUID DYNAMICS AND SCALING

Since the late 1960s, PNNL has demonstrated a robust capability in applied engineering and full-scale, prototypic experimentation in support of process development and commissioning. Our roots reach back to the Hanford Engineering Development Laboratory, and we have supported waste retrieval and feed delivery on the Hanford Site since the early production mission. Major contributions in waste mobilization programs include developing the understanding of mobilization, dissolution, and mixing of salt cake and sludges in waste tanks using rotary jet pumps, jet forces on in-tank components, and slurry transport. PNNL has developed numerical modeling capabilities for turbulent jet mixing of chemically reacting, Newtonian and non-Newtonian slurries. For waste feed delivery (WFD) to the WTP, PNNL has supported the technical basis for the Tank Farm Operating Contractor's (TOC's) understanding of WFD system via analytical and numerical models including prototypic and scaled test results.

Recent and current work includes:

- **Feed Delivery**
  - Resolution of Defense Nuclear Facilities Safety Board concerns regarding isolation valve performance including evaluating full-scale valve performance and durability using slurries with particles matching the abrasiveness of waste slurries.
  - Supported batch transfer scaling behavior through an understanding of the mixing phenomena and data analysis using scaled tank data.
  - Evaluated and recommended statistical methods and tools for tank waste sampling based on advanced sampling theory.
  - Developed PulseEcho instrumentation for measuring critical velocity and demonstrated the PulseEcho ultrasonic method for directly measuring pipeline critical velocity for settling slurries over a broad range of waste conditions, enabling real-time waste certification.
  - Developed Hanford waste simulant design methodology and provided simulant basis documents for small-scale mixing demonstration and double-valve isolation tests.
  - Developed and evaluated dissolution retrieval strategies for single-shell tank (SST) waste in leaking tanks with flammable gas hazards to enable TOC process control plans.
- **Resolution of WTP Technical issues**

  Technical Issue 4 – Vessel Mixing: PNNL is providing senior project managers and technical experts to support issue resolution for the WTP Pretreatment Facility. PNNL staff includes the overall project manager and staff leading test planning as an integrated team with Bechtel National, Inc. (BNI) engineering and URS. These activities include:
  - Design and execution of small-scale testing to determine a preferred vessel design
  - Design of full-scale vessel testing, including simulant selection and instrumentation
  - System development and oversight of pulse-jet mixer (PJM) controller testing



Computational Fluid Dynamics

Computational modeling, working hand in hand with experimental investigations, is a valuable tool for reducing cost and schedule when addressing operational challenges for complex systems. Our scientists and engineers are experts in the development and application of transient computational fluid dynamics techniques to address the conservation of mass, momentum, and energy of multi-phase, chemically reacting mixtures. We have recently applied a new modeling approach (Lattice Kinetics) to DOE Office of Environmental Management waste slurries. The resulting computation tool, ParaFlow, has been benchmarked to several WTP unit operations, including pipeline transport, filter fouling, and rotary turbulent jet mixing.

- Testing alternative solids mixing systems that use AirLift circulation systems to accelerate the development of design features that back up current BNI mixing tests

Previous mixing support activities have included:

- Scaled experiments to support vessel mixing evaluation and verification and validation of models
- Scaled experiments to assess PJM arrays and nozzle designs
- Quarter- and full-scale experiments with non-Newtonian slurries to develop design options for PJM process vessels
- Experiments to guide design of sparging systems in non-Newtonian vessels
- Full-scale experiments and theory of pipeline Newtonian and non-Newtonian slurry transport to establish critical deposition velocities to prevent settling and plugging

WASTE FORMS

PNNL has been a leader in glass technology since the late 1960s, when development focused on vitrifying radioactive wastes. Our scientists and engineers developed and applied the joule-heated, slurry-fed ceramic melter to the treatment and immobilization of DOE's radioactive wastes. This work formed the basis for technologies used at the West Valley Demonstration Project, the Savannah River Defense Waste Processing Facility, and the Hanford Site. PNNL is a recognized international leader in radioactive waste form development and has excelled in this field for nearly half a century. We use a science-based approach to develop innovative materials and melter designs to meet specialized, customized waste form needs.

As well, PNNL has extensive experience in testing and evaluating low-temperature waste forms for the solidification of Hanford tank wastes. PNNL provided process design and waste form development support for the Hanford Transportable Grout Facility and the Hanford Grout Disposal Program. More recently, PNNL has conducted waste form development and testing programs leading to the selection of Cast Stone for the solidification of WTP aqueous secondary wastes and supporting the evaluation of Cast Stone as a supplemental immobilization technology for Hanford LAW. Combined with our expertise in tank waste chemistry, PNNL is also developing radionuclide-specific immobilization technologies for separated radionuclides such as ^{99}Tc described above.

Recent and current work includes:

- **ILAW Glass**
  - Developed and defended the technical basis for disposal of immobilized low-activity waste (ILAW) glass in the Integrated Disposal Facility (IDF). This will allow DOE to dispose of a majority of the ^{99}Tc and ^{129}I on site rather than managing it as HLW. PNNL continues developing and defending the technical basis for disposal of a broader range of ILAW glasses with optimized waste loading in the IDF and generating the glass performance data and models to support the IDF Performance Assessment (PA).
  - Developing the eSTOMP water and reactive transport simulator to facilitate near-field modeling activities for the IDF PA.

Glass Development Laboratory

PNNL glass development expertise spans from fundamental chemistry to bench- and engineering- scale fabrication. Our scientists and engineers in the Glass Development Laboratory in the Advanced Process Engineering Laboratory (APEL) use state-of-the-art instrumentation for formulation and characterization of advanced glass compositions. Our expertise and capabilities include basic glass chemistry, glass property, and property-composition testing as well as modeling, batch-to-glass conversion chemistry, and waste form qualification. Our laboratory capabilities are supplemented by bench- and engineering-scale melter testing platforms in APEL and PDL-East, which allows for rapid testing and verification of waste slurry processing flowsheets. We then perform final verification with actual radioactive waste using comparable capabilities in the RPL.

- **Supplemental Treatment** (using low-temperature waste forms)
  - Expanding existing LAW supplemental immobilization Cast Stone testing program to include chemistries relevant to the Effluent Treatment Facility aqueous wastes, including WTP LAW secondary wastes.
  - Extending effective diffusivity measurements in support of the LAW supplemental immobilization testing program to obtain longer-term leach data.
  - Characterizing Tc speciation in Cast Stone waste forms to understand and improve retention.
- **HLW and HLW Direct**
  - Developing methods and algorithms to formulate acceptable and processable waste glasses from abruptly changing waste feed compositions. This includes glass property composition models to enable 1) numerical optimization of glasses in real-time without need for time-consuming experiments and 2) new approaches to formulate glass accounting for all uncertainties with minimal need for "engineering margins," which reduces the processing envelope.
  - Developing crystal-tolerant glass formulations with high loading for roughly half of the Hanford HLW while reducing the risk of melter failure due to crystal accumulation.
  - Developed and issued models that can be used in system planning efforts to understand the impacts of ongoing glass formulation efforts on projected ILAW and immobilized high-level waste glass volumes.
  - Developing fundamental understanding of Tc behavior in glass melting, enabling alternative approaches to increase Tc incorporation in HLW glass.
  - Characterizing and modeling melter feed-to-melt conversion process to predict melting rate and reduce the likelihood of melter process upsets.

SAFETY BASIS

PNNL scientists and engineers are leaders in risk assessment and associated research to evaluate and mitigate potential nuclear safety issues. We currently perform this work for DOE, the Nuclear Regulatory Commission, industry, and international entities. However, this capability is rooted in the needs of the Hanford mission. Examples of our contributions include closure of Hanford tank safety issues such as organic, ferrocyanide, and mitigation of gas release events in SY-101.

In the 1990s and early 2000s, PNNL established a fundamental understanding of gas generation, retention, and release behaviors in tank waste slurries. This work allowed appropriate controls to be incorporated into the Authorization Basis for the tank farms, which was a significant factor underpinning closure of the flammable gas tank safety issue and returned many double-shell tanks (DSTs) to useful service.

We established and executed the Hanford Tank Vapor Program, and once institutionalized, transferred it to the Tank Farm contract. Our contributions included determining the decomposition mechanisms and rates for many of the gases, developing the analytical methods, and providing statistics to support past worker safety programs.

PNNL holds the "Analysis of Record" for all DSTs and SSTs at the Hanford Site. This detailed structural analysis, conducted to the American Concrete Institute Standard, includes numerous elements such as thermal, seismic, and operating load stresses. This understanding enables and establishes limits for work in, around, and on the tanks without risk of structural failure. The work started in 2003 and we anticipate completing the final tank type by fall of 2014.

PNNL led development of several ultrasonic testing (UT) detection technologies in the 1990s and early 2000s to assess tank leak integrity. This included ultrasonic technologies for WFD described earlier in this document. For tank integrity assessment, these technologies included the Remotely Operated Nondestructive Examination system to implement the ultrasonic Synthetic Aperture Focusing Technique (SAFT) for crack detection in the knuckle region of DSTs. Additionally, Tandem SAFT was developed and approved for flaw depth sizing on the knuckle region of the DSTs. PNNL supports the integration and application of future inspection technologies such as Electromagnetic Acoustic Transducer and Phased Array UT to improve detection of wall thinning, pitting, and cracking.

Recent and current work in this area includes:

- **Flammable Gas Safety**
  - Provided the technical basis for closure of the retention and release of flammable gas in "deep waste" layers unresolved safety question and changes to the documented safety analysis (DSA) for certain sludge wastes. This included 1) lab- and full-scale experiments, analysis, and modeling; and 2) modification of the DSA to define criteria for waste characteristics and process behavior that identify specific wastes and tanks that, based on previous operating experience, will have low gas retention and will not exhibit large, spontaneous releases.
- **Chemical Vapor Issue Resolution**
  - Independent Expert Review Panel of Chemical Vapors and Worker Protection: Providing toxicological and exposure assessment.
  - Chemical Vapor Solution Team: Identify, demonstrate, and implement detection, control, analysis, and mitigation technologies to address Hanford tank vapor issues, and conduct analysis of database(s) to 1) develop statistically driven tools to mitigate and/or eliminate tank vapor related risks, and 2) detect trends and develop correlative and predictive models to guide future analyses and operations.
- **Air Dispersion Modeling**
  - Conduct modeling to support the revision/modification of existing air permits to ensure compliance with waste acceptance criteria and federal laws and regulations during retrieval of AY-102.
  - Providing data to support qualification of the current designs for 19 air exhaust stacks against the acceptance criteria of ANSI/HPS N13.1-1999, Sampling and Monitoring Releases of Airborne Radioactive Substances from the Stack and Ducts of Nuclear Facilities.
  - Providing technical support for the design, specification, and procurement of off-gas monitoring systems, and system performance testing.
- **Tank Structural Integrity**
  - Conducted analysis of record for structural integrity of SSTs.
  - Conducted analysis of record for structural integrity of DSTs, including qualification for higher liquid limits in AP farm.
  - Currently preparing an SST summary report and evaluation of the new PSHA (probabilistic seismic hazard analysis) relative to the analyses of record.
- **DST Integrity Project**
  - Reviewing UT inspection results and performing extreme value statistical analysis of each tank examined.
  - Performance demonstration testing of all UT inspectors.
  - Inspector, equipment, and procedure qualification.
  - Evaluating UT system changes and performing requalification.
  - Development of advanced equipment for nondestructive examination and special studies.
- **Resolution of WTP Technical issues**
  - Technical Issue 1 – Flammable Gas: PNNL is providing technical leadership and senior technical staff for the closure of the flammable gas concerns in the Pretreatment Facility. PNNL's nationally recognized experts are working alongside BNI's engineering team to conduct testing and technical resolution.
  - Technical Issue 2 – Criticality: PNNL is providing technical leadership and senior technical staff for the development of a defensible criticality strategy for the operations of the Pretreatment Facility. PNNL's technical experts are leading the PNNL/BNI team to conduct hazard evaluations and develop the new critically operational strategy.
- **WTP Hazards Analysis**
  - Leading Subject Matter Experts team on WTP Analytical Laboratory hazard analysis to identify and evaluate consequences as well as potential candidate controls to prevent or mitigate hazards.

High Bay Facilities

PNNL has had a robust capability in applied engineering and full-scale prototypic experimentation in support of process development and commissioning since the late 1960s. Recently, we have developed numerous large-scale capabilities in support of the Hanford tank waste mission including a WTP prototypic slurry flow loop, a research scale continuous melter, and pilot-scale sludge leaching systems. Our scientists and engineers have employed these systems to support WTP design and contributed to resolution of several recalcitrant nuclear safety concerns.

U.S. DEPARTMENT OF ENERGY

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