TANK WASTE OPERATIONS and WASTE PROCESSING PLATFORM

Pacific Northwest
NATIONAL LABORATORY

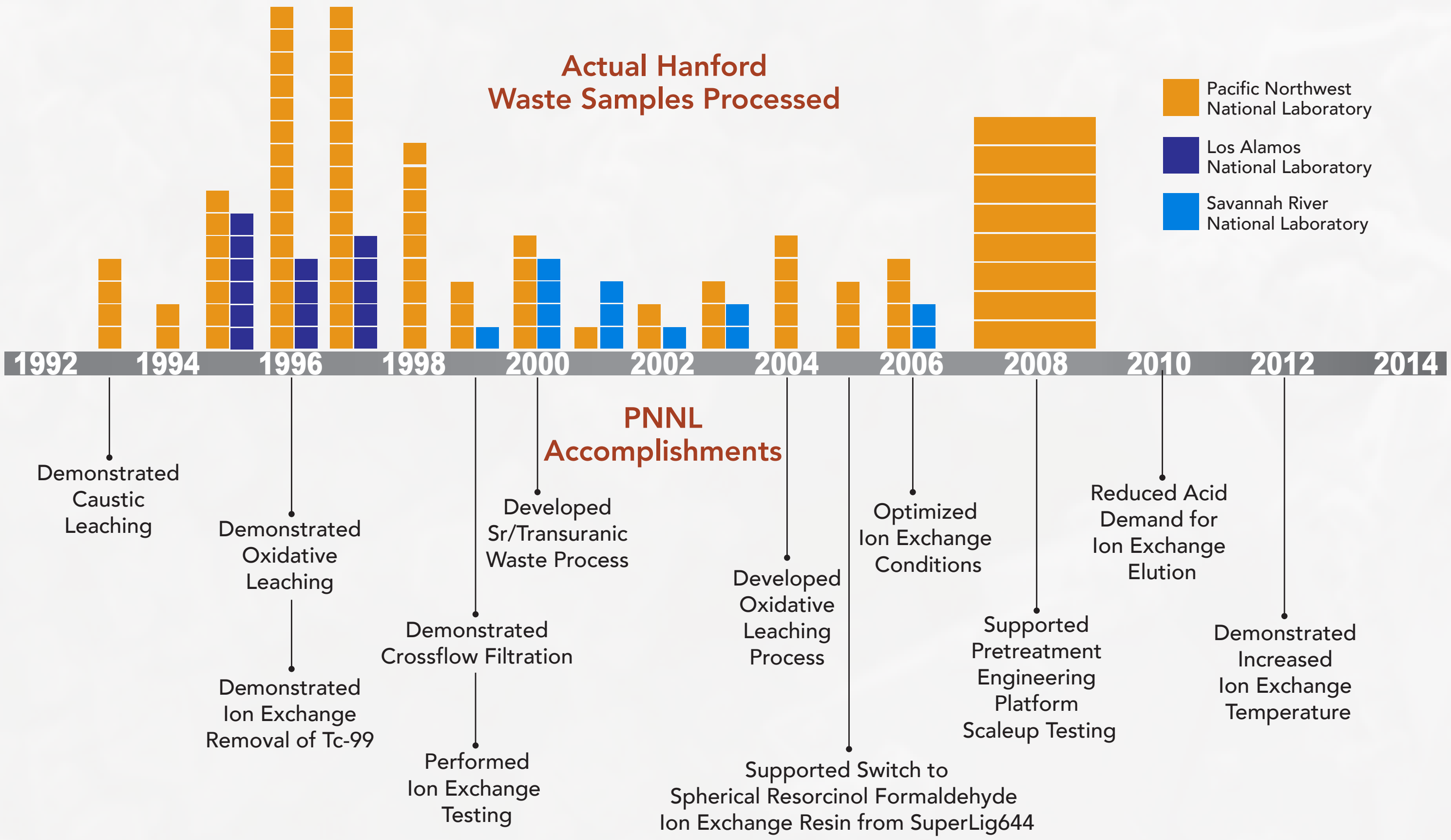


Figure 1. History of Development of the WTP Pretreatment Facility

Tank Waste Operations and Waste Processing Platform

PNNL – A HISTORY OF NUCLEAR PROCESS SCIENCE

Pacific Northwest National Laboratory (PNNL) was created as the nuclear process science laboratory to serve the Hanford mission and has continued to provide continuity of scientific expertise, technical defensibility, and integration across the Hanford Tank Waste Remediation mission. Our scientists and engineers performed the research that underpins the current pretreatment and vitrification flowsheets at Hanford, Savannah River, and West Valley. This includes development of the Hanford Waste Treatment and Immobilization Plant (WTP) baseline processes.

- PNNL led the development of the caustic leaching process. This process dissolves aluminum from the high-level waste (HLW) solids into the low-activity waste (LAW) liquid phase, reducing the number of costly HLW canisters that must be buried in a deep geologic repository. PNNL refined the Bayer Process, originally applied in the aluminum industry, to accommodate the complexities of tank waste chemistry.
- PNNL developed the chromium removal process. After successful leaching of aluminum, HLW canister counts can be reduced further if chromium can also be removed from the HLW solids. PNNL developed a process using sodium permanganate to oxidize the chromium into solution. Thermodynamic and kinetic studies determined a set of process conditions to prevent dissolution of plutonium and other actinides that could turn the liquid into transuranic waste. The process was demonstrated first with gram-scale quantities of tank waste, then kilogram-scale quantities, and finally at pilot scale with simulants.
- PNNL developed the Sr/TRU removal process. In several tanks with very high organic complexants, the concentration of strontium and/or transuranic isotopes in the liquid phase is sufficient to result in classification as HLW. PNNL pioneered a process using manganese and non-radioactive strontium that in one step destroys some of the organic complexants, displaces much of the remaining radionuclides from the remaining organic complexants, and precipitates these radionuclides into the HLW solids.
- PNNL demonstrated the cross flow filtration process. As the above examples show, WTP relies on solubility as a primary means of separation. Therefore, efficient filtration of the pretreated HLW solids from the LAW liquid phase is a critical unit operation. Cross flow filtration was deployed at West Valley, Savannah River, and most recently Fukushima. However, unlike these cases, Hanford wastes contain very fine suspended solids that can quickly cause fouling deep in the filter media, decreasing filtration rates. PNNL has conducted numerous tests with actual Hanford wastes to the understand fouling and mitigate its effects through physical and chemical cleaning methods.
- PNNL demonstrated the cesium removal processes. When hydraulic performance and contracting issues led WTP to pursue an alternative cesium removal resin, PNNL led the effort to select spherical resorcinol-formaldehyde (sRF), and then conducted all of the performance testing with actual waste to demonstrate the alternative. This sRF has subsequently been adopted by the WTP, significantly reducing projected costs and dramatically improving system hydraulic performance.

In this research and development, testing began with small-scale (gram) quantities to assess the chemical and physical systems and gradually increased in scale to kilogram quantities of actual waste. PNNL has performed tests with more than 40 actual waste samples at scales from grams to multi-liters (Figure 1).

A key asset to the tank waste mission is the Radiochemical Processing Laboratory (RPL)—a Category II nuclear facility located on the Hanford Reservation and run by PNNL. The RPL has a full set of capabilities for receiving and testing HLW. Tank waste characterization and process development research has been performed in the RPL hot cells and in radiological fume hoods and gloveboxes. Over the past ~5 years, PNNL (through U.S. Department of Energy [DOE] and internal funding) has invested over $50 million in facility upgrades, including a new set of four modular hot cells to augment the existing High-Level Radiological Facility and the Shielded Analytical Laboratory (SAL). The RPL hosts a variety of analytical capabilities for determination of elemental composition; physical property; radio isotopic separations and counting for alpha, beta, and gamma emitters; microscopy (optical, scanning electron microscopy [SEM], and transmission electron microscopy [TEM] techniques); and spectroscopy using infrared, auger, x-ray, nuclear magnetic resonance (NMR), and Raman techniques. Over the past year, we have added an additional $5 million in state-of-the-art instrumentation, including a new SEM-focused ion beam (FIB), a thermal ionization mass spectrometer, and a single-crystal x-ray diffractometer. All of these techniques and instruments can be applied to a variety of radioactive sample matrices and can be performed to differing quality requirements as directed by our clients.

TANK WASTE PROCESSING PLATFORM

PNNL has established a platform for the evaluation and demonstration of technologies to support tank waste operations and processing, as well as to gain critical insight into WTP facility operations. The platform builds on PNNL's historical experience as the primary developer of the unit operations for treatment of Hanford tank waste. The platform is being established primarily in the SAL's six hot cells with modular unit operations for demonstrating the Hanford Waste Treatment Process Flowsheet as well as demonstrating alternatives. This platform could also eventually serve as the waste qualification platform for the WTP (Arm and Seidel 2011), or for specific units operations needed to support either direct feed options or normal WTP operations. A waste qualification platform is required to ensure stable operation of the WTP and to resolve processing issues with challenging wastes before they reach WTP.

Based on our experience in testing wastes and alternative technologies for the Hanford flowsheet, a modular system, as presented in Figure 2, enables integrated testing of new process conditions and chemistries as well as rapid incorporation of alternative unit operations into the workflow. The modular system provides flexibility to change out or by-pass certain unit operations, if they are not needed to support waste qualification for specific flowsheets (e.g., direct feed LAW or normal WTP operations). Two hot cells will be dedicated to the pretreatment processes, including filtration, caustic leaching, oxidative leaching, and ion exchange. This equipment is shown in more detail in Figure 3 and Figure 4, and will include two test stands, one referred to as the cross flow ultrafiltration unit (CUF), and an ion exchange unit. The CUF includes a large mixing vessel, pump, and filtration element, as well as sensors, valves, and process controls. This unit is a bench-scale version of the WTP Pretreatment Facility head-end containing unit operations for filtration and leaching. It is designed for flexible operations, a wide range of chemical compatibility, and rapid reconfiguration. The ion exchange unit (Figure 4) includes vessels for numerous solutions, such as feeds, effluents, and eluates. The ion exchange columns can be quickly sized to process up to ~20 L

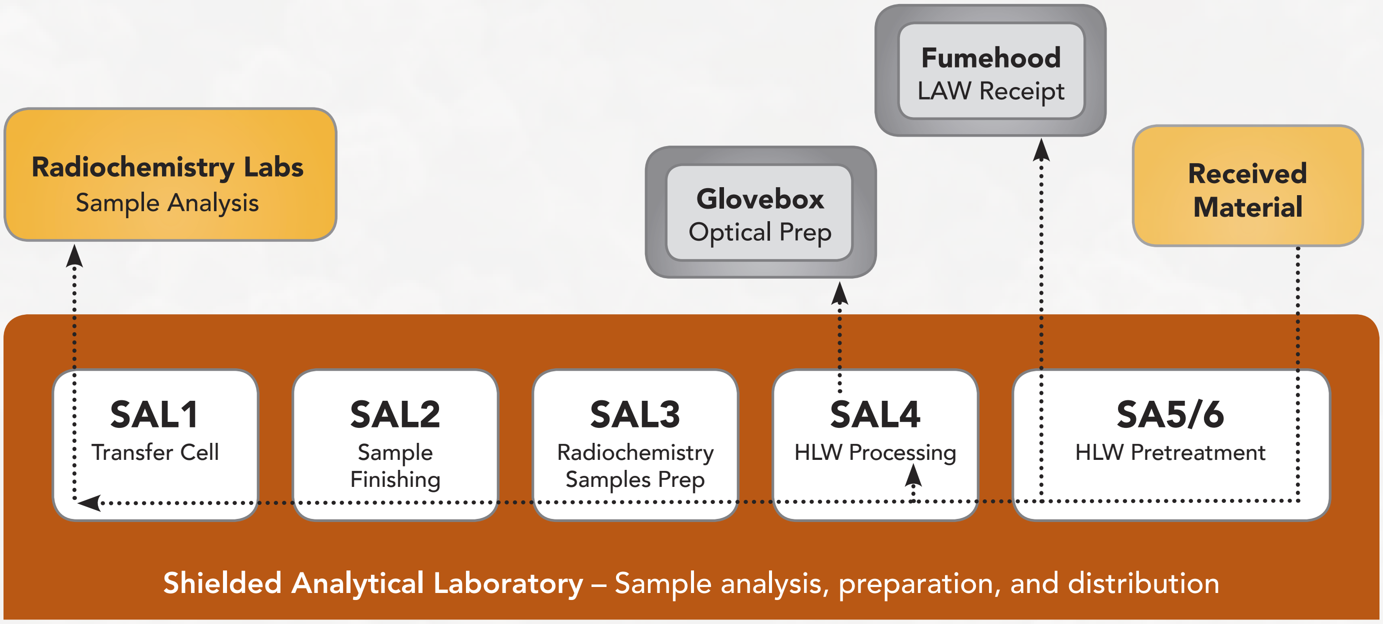


Figure 2. Proposed Configuration of Tank Waste Process Modular Unit Operations

of tank waste, loaded with any exchanger of interest, and would include sufficient flexibility to replicate systems comparable to, for example, tank farm pretreatment. The volume of tank waste processed would depend on the objectives of the specific demonstration and would be established in associated test protocols necessary to evaluate technologies of interest. Treated HLW would be transferred to cell 4 for immobilization while treated LAW would be removed from the hot cell for further processing in fume hoods.

A laboratory-scale melter (LSM) will be positioned in cell 4 (Figure 5). PNNL developed the LSM specifically to process small amounts of actual or simulated waste while complete cold-cap processes are studied in detail and prototypic glass and off-gases are generated. We are not aware of another system of this size that allows this level of mission-critical information to be collected. The LSM contains two ports to allow feed to the melter concurrent with off-gas capture. The melter body is between 3 and 4.5 inches in diameter, and, prototypic to WTP, it is slurry fed. Recent studies with simulants have benchmarked this melter with the scaled WTP melters operated at the Catholic University of America (Kim et al. 2012). Critical to off-gas recycle options studies such as technetium-99 management, the LSM can collect off-gas samples for analyses or further treatment processes.

RPL possesses the necessary suite of analytical capabilities. Cells 2 and 3 house the wet chemistry processing needed to perform sample preparations, including fusions and dilutions. Once prepared for analysis, samples can be transferred from the SAL to the analytical services in the RPL or other facilities as appropriate. In-house characterization methods include particle size distribution and density, x-ray diffraction, SEM/TEM, chemical and radiochemical analysis, NMR, Raman, and uv-vis spectroscopy. Additionally, a state-of-the-art dual beam FIB is available to prepare low-volume samples for characterization in RPL or other facilities inside or outside of PNNL. These services are provided by the Analytical Services Organization within PNNL, which maintains these capabilities to an NQA-1 and HASQARD- compliant quality assurance program.

In addition to chemical and radiological characterization, understanding the physical and rheological behavior of the waste before, during, and after each set in processing is critical to design and optimization of new technologies. As noted by numerous reviews of the WTP, in addition to highly variable feed, feed properties can change drastically as waste moves through the flowsheet, and therefore process control requires accurate projections. PNNL has led the development of methods to quantify these properties and authored the associated ASTM standard (ASTM C1752–11). To support testing, a rheometer (Figure 6), modified for operation in a high radiation field, will be installed in cell 3 to allow direct measurement of characteristics including viscosity, shear strength, and thixotropy.

The platform will use existing hot cell equipment designs for filtration, leaching, evaporation, and ion exchange systems. We will work with the Hanford Site contractors to ensure the system design meets the anticipated needs for waste feed qualification and that testing and data generated using the modular unit operations are of the greatest use to current and future mission needs.

Additional details on modular unit operations are provided on the following pages.

Cross Flow Filtration Unit

The CUF has four main parts: (1) slurry reservoir tank, (2) slurry recirculation loop, (3) permeate flow loop, and (4) permeate back pulse chamber.

The *slurry reservoir* is a cylindrical, 304 stainless steel tank with a 4 L capacity. All other major components of the CUF system are also 304 stainless steel. Agitation in the tank is provided by an overhead mixer using a 2-inch diameter, three-blade marine propeller. To allow the system to be easily drained, the bottom of the vessel is sloped at a 15° angle. Baffles are also installed on the tank wall to verify that the slurry mixing is homogenous. Heat tape is installed around the walls of the tank for leaching at elevated temperatures.

The *slurry recirculation loop* directs slurry flow from the slurry reservoir, through the filter, and back into the reservoir for filtration operations. The bottom of the slurry reservoir is connected to the suction side of the slurry recirculation pump—a positive displacement rotary lobe pump. The pump is driven with an air motor, supplied with compressed air from an exterior air compressor. An exterior chiller circulates chiller fluid (water/anti-freeze mixture) through the exterior shell of the heat exchanger to remove heat from the circulating slurry on the tube side of the heat exchanger.

The *permeate flow loop* starts at the center of the filter assembly, where a poly-line connects the filter to a manifold of 0.25-inch stainless steel piping that directs the filter permeate through a series of measurement devices. Permeate exits through a three-way valve connected to the slurry reservoir tank. This valve directs permeate either back to the slurry reservoir tank to be mixed back into the slurry or to a sampling hose used to collect permeate into sample containers.

The *permeate back pulse chamber* is located to the right of the permeate flow loop and is connected to the filter at the same location as the permeate pressure gauge. The chamber is a ~500 mL steel vessel with a sight-glass to monitor the volume inside the chamber. The vessel has three entry ports: (1) a two-way toggle valve on the bottom connecting the vessel to the permeate side of the filter, (2) a two-way valve

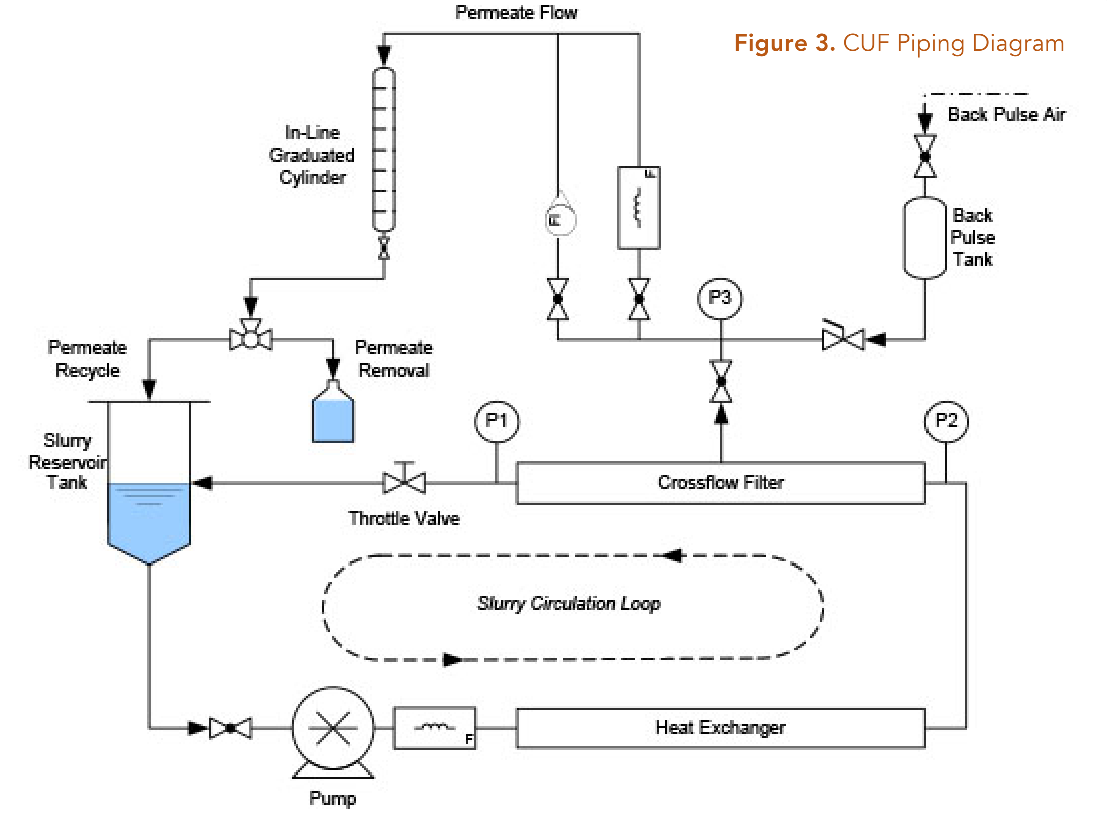


Figure 3. CUF Piping Diagram

connecting the top of the vessel to a funnel, and (3) a three-way valve connecting the top of the vessel to a compressed air line and vent line connected to the top of the slurry reservoir tank.

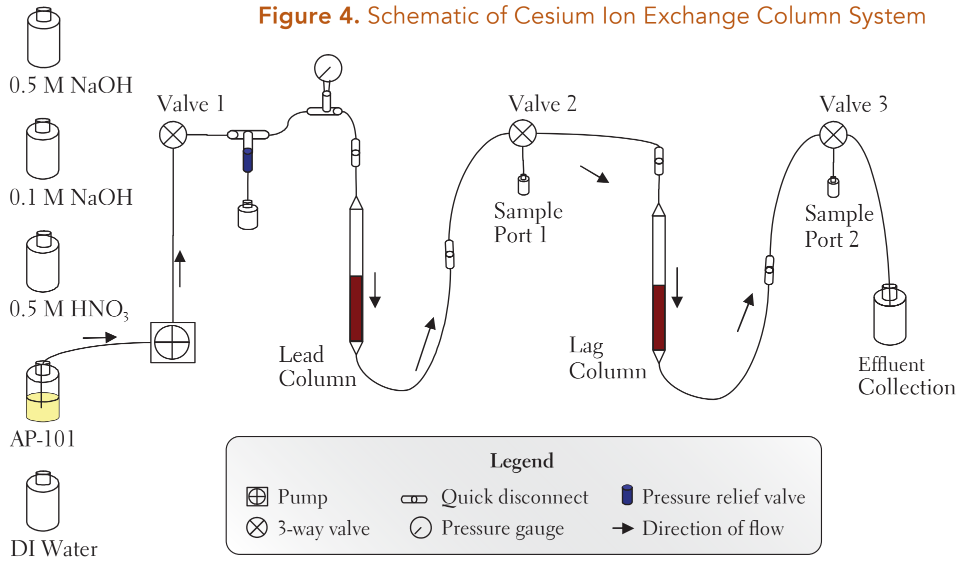
The bottom line is used to direct permeate flow from the chamber to the filter. The funnel on the top of the chamber is used to introduce cleaning and rinse solutions directly to the vessel. The compressed gas line is used to pressurize the fluid in the chamber with compressed gas and to vent the chamber to atmospheric pressure. To back pulse the filter, the vessel is first vented to atmospheric pressure. Next, permeate is allowed to fill the chamber by opening the toggle valve. Once the chamber is half full of permeate (as seen from the sight-glass), the toggle valve is closed. The three-way valve is then positioned to allow compressed gas at 80 psig to fill the chamber and pressurize the fluid. Next, the three-way valve is then positioned to isolate the pressurized chamber. The slurry pressure inside the filter is then brought below the pressure of the compressed gas line (<20 psig). The toggle valve at the bottom of the tank is opened, allowing the pressurized permeate inside the chamber to flow backward through the filter element. The toggle valve is closed when the permeate level is below the area visible through the sight-glass.

Ion Exchange System

The ion exchange column system consists of two small columns containing the ion exchange material, a small metering pump, three valves, a pressure gauge, and a pressure relief valve. Valves 1, 2, and 3 are three-way valves that can be turned to the flow position, sample position, or no-flow position. Valve 1 is placed at the outlet of the pump and is used to eliminate air from the system, purge the initial volume of the system, or isolate the columns from the pump. Valves 2 and 3 are primarily used to obtain samples and can also be used to isolate the columns from the rest of the system. Both the 10-psi trigger pressure relief and the 15-psi pressure gauge are plumbed inline and before the first column.

The two columns are connected in series, with the first column referred to as the lead column and the second column referred to as the lag column. The columns are standard 1.5 cm diameter by 15 cm tall Spectra/Chrom Organic columns. Each resin bed is supported by stainless steel, 200-mesh screens, stabilized with snug-fitting O-rings. The cavity below the screen support is filled with 3 mm diameter glass beads, reducing the fluid-filled volume from 2 mL to 1 mL. The flow rate is controlled with a remotely operated FMI stroke-rate controller.

Figure 4. Schematic of Cesium Ion Exchange Column System



Laboratory Scale Melter

The LSM setup developed at PNNL uses a fused quartz crucible as a small melter, allowing direct observation of cold-cap formation and off-gas evolution during slurry feeding. This method provides many advantages over the traditional crucible method of fabricating radiologic glass, including the ability to observe cold-cap behavior, estimate melt rate, and quantify crystal formation and settling behavior. The single-use fused quartz crucible melter bodies have a 3-inch outside diameter and are 10 inches tall, with two smaller ports (0.75-inch outside diameter). The vertical tube is used as the feed inlet and the slanted tube is used for off-gas collection. To maintain a constant temperature in the cold-cap region of the melter, the hot zone of the crucible is continuously raised as the melt layer height is increased from feed processing. This assembly can collect off-gas samples for chemical analyses or can be connected to gas chromatography-mass spectrometry for evolved gas analyses. A key factor for successful operation is to keep the cold-cap coverage relatively low at about 40% so the steady state cold-cap coverage can be maintained without causing bridging.

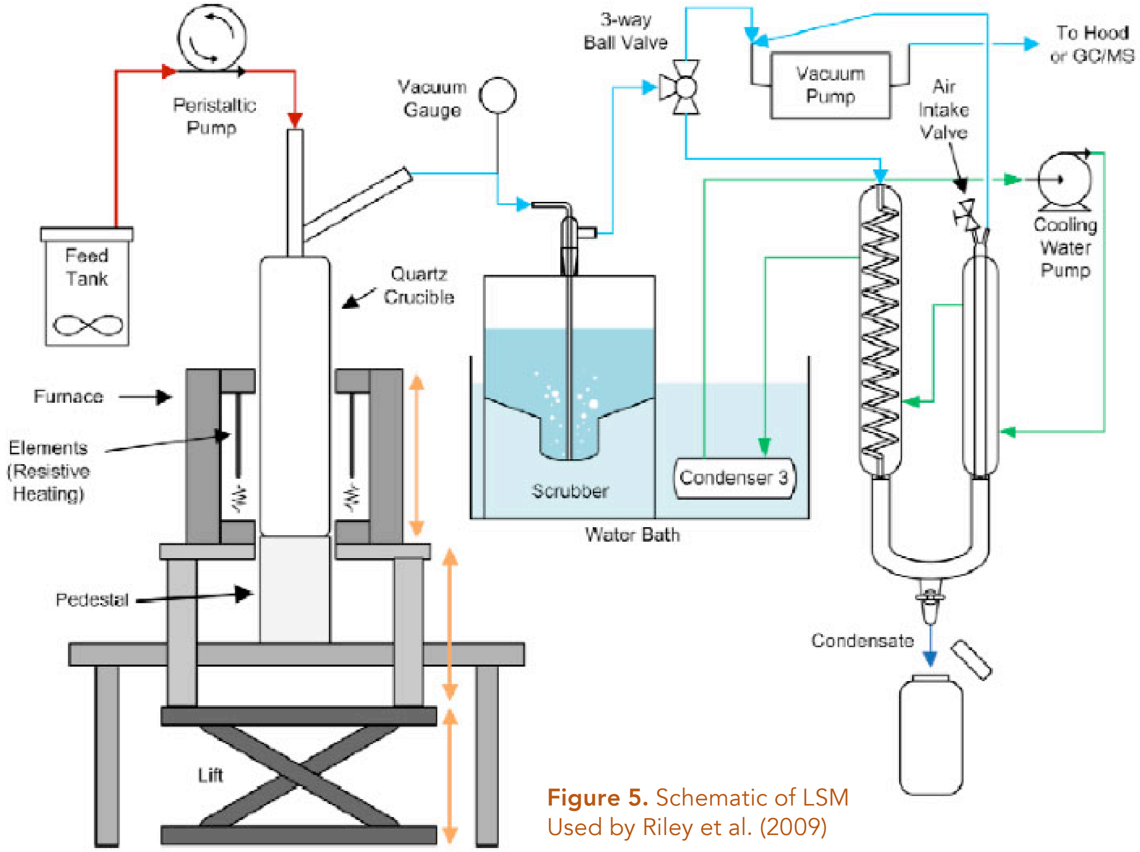


Figure 5. Schematic of LSM Used by Riley et al. (2009)

Rheometer

Rheological characterization is accomplished using a Rotovisco® RV20 Measuring System equipped with an M5 measuring head and RC20 controller manufactured by Thermo Electron Corporation. This system would be installed in cell 5 of the SAL. The M5 measuring head is a "Searle" type viscometer capable of producing rotational speeds up to 500 rpm and measuring torques up to 0.049 N·m. The minimum rotational speed and torque resolution achievable by this measuring head are 0.05 rpm and 0.49 mN·m, respectively. Specific measurement tools such as cup and rotor assemblies and shear vanes are attached to measure selected rheological properties. Shear strength measurements are performed using a 8 mm by 16 mm (R × H) shear vane tool. Flow curve measurements are done using an MV1 stainless steel measuring cup and rotor.

Temperature control is achieved using a combination of the standard measuring system temperature jacket and recirculator, allowing testing from -5° to 80° C. The recirculating unit is located next to, but outside, SAL cell 4. Shear strength measurements are carried out at ambient temperature.

Figure 6. Rotovisco® RV20 Measuring System

Teaming

The platform is being established in partnership with the Hanford cleanup contractors and the DOE waste processing national laboratories to ensure its design and operation provide maximum impact across the entire DOE waste processing mission. It will be run as a user facility to encourage external researchers and students to access its state-of-the-art radioactive material testing capabilities.

Highly trained scientists and engineers are critical to fulfilling DOE's environmental mission. This includes expertise at DOE, national laboratories, and cleanup contractors. To meet this need, we will leverage experts within the national laboratories, the DOE complex, U.S. industry, international partners, and specifically universities to develop the next generation of nuclear professionals.

We are partnering with appropriate universities and Minority Serving Institutions to collaborate with professors in guiding new students into nuclear-related fields of study and to engage postdoctoral, master's, and undergraduate students, allowing them to access and conduct research within operating nuclear facilities. This promotes specific radiological training in the specialties of solution thermodynamics, molecular modeling, synthetic organic and inorganic chemistry, radiation chemistry, analytical chemistry, chemical kinetics, physical properties measurement, and process engineering.

WTP Qualification Laboratory Needs

Once full WTP operation begins, the current waste qualification strategy calls for the testing of each batch of feed, starting 180 days before introduction of that feed to the WTP. This would involve processing a 4 to 20 L sample of the staged feed through all the unit operations for the WTP and performing many analytical characterization methods, such as hydrogen generation rate and organics analysis. A key element of this test is the process performance testing, wherein the leaching, filtration, and melter operation conditions would be identified through process testing of these unit operations. The test bed would be available at the start WTP operations to perform these functions.

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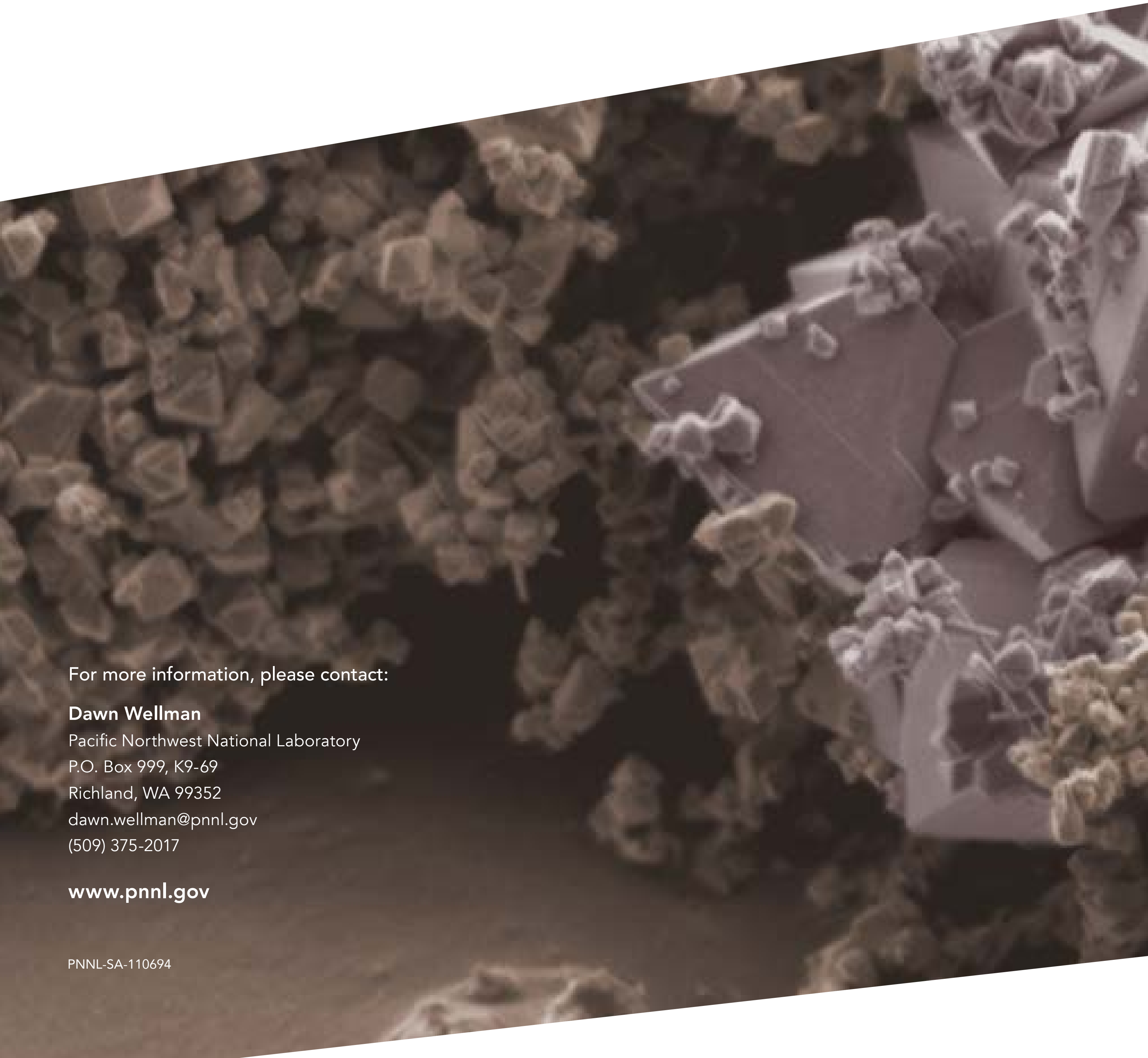

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