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ABSTRACT
The Low Activity Waste Pretreatment System (LAWPS) is being designed to enable the direct feed of waste to the Hanford Tank Waste Treatment and Immobilization Plant (WTP) Low Activity Waste (LAW) facility to be immobilized. Prior to construction of the LAWPS, pilot-scale integrated testing of the key unit operations (crossflow filtration, ion exchange using spherical resorcinol-formaldehyde (sRF) resin) will be conducted by a team led by Washington River Protection Solutions (WRPS) to increase the technology maturation level of the facility’s critical technology elements. As a part of this effort, Pacific Northwest National Laboratory (PNNL) has conducted a series of tests to perform two major objectives: (1) support pilot-scale integrated testing of the LAWPS by supplying information or performance data in advance of operating the pilot-scale facility (1/9th scale); and (2) collect data needed to establish or confirm assumptions/approaches planned for implementation in the LAWPS safety basis. The first objective was focused in two technical areas: developing simulants that are representative of expected waste feed and can be produced at larger scales, and using these simulants in a bench-scale crossflow filter to establish expected solid-liquid separation performance. The crossflow filter was also used to observe the efficacy (with respect to filter production rate) of selected operational strategies. The second objective also included two technical areas: measuring the effect of sRF resin on hydrogen generation rate under irradiation, and demonstrating that the planned hydrogen management approach is effective and robust. The hydrogen management strategy involves fluidization of the sRF resin bed in the ion exchange columns and recirculating the liquid, a scenario that is planned for testing at full column height. The full height tests at PNNL also supported full-scale IX column testing conducted as part of the technology maturation plan. The experimental approaches used at PNNL in these four technical areas are summarized and selected key preliminary results are provided.

INTRODUCTION
The primary mission of the Department of Energy Office of River Protection (DOE-ORP) is to retrieve and process the radioactive waste from 177 underground tanks located on the Hanford site (containing approximately 56 million gallons). The Hanford waste tanks are currently operated and managed by Washington River Protection Solutions, LLC (WRPS). As part of tank farm operations, WRPS supports DOE-ORP’s waste retrieval mission. An important element of the DOE-ORP mission is the construction and operation of the (WTP. The WTP is tasked with separating the waste into low activity waste (LAW) and high level waste (HLW) fractions and immobilizing these fractions by vitrification.
In order to support early production of immobilized LAW, the Direct Feed Low Activity Waste (DFLAW) flowsheet has been proposed. In the DFLAW process, LAW is sent to the LAWPS and the resultant treated waste is delivered to the WTP LAW facility for immobilization by vitrification. Prior to the transfer of treated feed to the WTP LAW facility, decanted tank waste will be pretreated in the LAWPS to meet the WTP LAW facility waste acceptance criteria. The key process operations for treating the waste include solids separation (by crossflow filtration) and cesium removal (by ion exchange). A general schematic of the anticipated process streams and unit operations is shown in Fig. 1.

Fig. 1. General Conceptual Schematic of the LAWPS Facility Unit Operations and Process Streams.

To support the LAWPS design before the end of CD-2 (preliminary design) and to improve the technology maturation level of the LAWPS, both an integrated engineering-scale test facility (1/9th scale) using prototypic equipment and a full-scale test apparatus for the ion exchange columns have been constructed. To support these larger-scale facilities, five technical tasks were identified to be performed by PNNL. These tasks are distinct from the larger-scale test facilities and are planned to be used to accomplish the following objectives:

- Provide technical information or data that
  - supports refinements or simplifications of larger-scale test facilities; or
  - provides expected performance of unit operations (guiding larger-scale operation or providing scale-up data).
- Support the safety basis of the planned hydrogen management strategy of the LAWPS facility.

The four PNNL technical tasks are comprised of the following focus areas:

1) Development of LAW waste simulants;
2) Bench-scale crossflow filter (CFF) testing with simulants;
3) Gas generation measurements in the presence of spherical resorcinol-formaldehyde (sRF) resin; and
4) Gas retention/release dynamics and fluidization of sRF.

Tasks 1 and 2 are focused on providing technical information to inform the larger-scale test facilities, whereas the Tasks 3 and 4 support the LAWPS facility safety basis.

This paper presents an overview of the technical approaches being used at PNNL to address the four technical tasks in the order given in preceding paragraph. Initial experimental results, if available, are also presented. Finally, the preliminary conclusions of the experimental work are summarized.

DEVELOPMENT OF LAWPS SIMULANTS

The objective of the simulant development task was to develop a series of simulants encompassing a wide range of sodium concentrations (4 to 8 M) that are representative of the LAW expected to be processed in the LAWPS facility. Some or all of these simulant recipes are planned to be used during operation of the larger-scale tests (LAWPS engineering-scale integrated test, full-scale IX column test), and all of the simulants have been tested in the bench-scale CFF system. Thus, the simulants are a key element of lending technical defensibility to the data collected from tests at multiple scales. These simulant recipes include four sodium concentrations of 5.6M Na (nominal), 4M Na, 6M Na, and 8M Na (high). The 5.6M simulant represents a “typical” LAW for processing, whereas the 4 and 6M simulants are at the current limits of the LAWPS operating envelope [1]. The 8M simulant is representative of a potential bounding scenario for DFLAW feed.

Simulant Development Approach

The starting basis for the simulant development process was to target the average concentration values of selected chemical species given in Servin (2016) [1], hereafter called the “specification formulation (SF).” Since the SF is approximately 5.6 M sodium, it was used as the basis for the nominal simulant, and the starting point for the other simulants were scaled proportionally with the target sodium concentration. Using the various compositional starting points, test batches were prepared in the laboratory and appraised for dissolution behavior, precipitated solids formation (both quantity and speciation), and physical properties (as practical). A peripheral consideration was to develop simulants that were reasonably straightforward to produce in much greater quantities for both the PNNL CFF and larger scale testing.

To examine if the SF was an appropriate starting point for simulant development, the projected WTP LAW facility feed vector data based on process simulation throughput models, e.g. the Hanford Tank Waste Operation Simulator, were examined (for more details, refer to Mills 2016 [2]). Note that the feed vector represents the “product” stream from the LAWPS and thus differs from the feed to LAWPS in two significant ways:

1. The cesium (Cs) concentration is reduced by a large factor (due to being processed through ion exchange columns) and is effectively negligible.
2. All or nearly all of the solid particles will be separated out during CFF operation in the LAWPS, and are also effectively negligible.
Both of these differences will not meaningfully impact the comparison of the feed vector information to the specification composition, other than negating the usefulness of any comparisons between Cs concentrations.

There are 199 “batches” in total, and they were used to calculate statistical information about the expected concentrations of the same major (generally present at \( \sim 5 \times 10^{-3} \text{M} \) or greater) constituents present in the SF. The maximum, minimum, and median concentrations of the 199 batches were computed; the median feed vector concentrations are compared with the SF in Fig. 2. The proposed starting simulant composition was either very close to the median feed vector values or within the range of minimum and maximum feed vector concentrations (as indicated by error bars in Fig. 2) for all major constituents. This, along with a comparison to other historical LAW simulants in the available literature [3 – 7], established confidence in the approach of using a formulation scaled from the SF as a starting basis.

TABLE I. Final Simulant Recipes for the Four LAWPS Simulants Developed at PNNL.

<table>
<thead>
<tr>
<th>Simulant Component</th>
<th>4.0 M Na Recipe (g species/kg liquid)</th>
<th>5.6 M Na Recipe (g species/kg liquid)</th>
<th>6.0 M Na Recipe (g species/kg liquid)</th>
<th>8.0 M Na Recipe (g species/kg liquid)</th>
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Fig. 2. LAWPS Specification Formulation Species Compared to the Range of Concentrations Projected for WTP LAW Feed Vectors. Error bars indicate the minimum and maximum of each species concentration in the feed vector data.
Results

After iterating on the four simulants recipes in the laboratory, final validation batches (0.5 L in volume) of each simulant were prepared and characterized. The characterization included physical properties such as density, total and undissolved solids (UDS), rheology, and particle size distribution (PSD), as well as chemical analyses of the dissolved species. TABLE I presents the final recipes for each simulant, and TABLE II presents the physical properties that were measured for each simulant. For reference, the physical properties are compared to the expected range of properties contained in the LAWPS specification document [1]. The chemical analyses were conducted to confirm the expected concentration of dissolved species for simulants (4, 5.6M) where the dissolved phase was well defined, and used in conjunction with x-ray diffraction analysis for simulants (6, 8M) with precipitated solids to establish the composition of the solid and dissolved phases.

TABLE II. Physical Properties of LAWPS Simulants Compared with Expected LAWPS Property Range.

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>4.0M Na (Nominal)</th>
<th>5.6M Na (Nominal)</th>
<th>6.0M Na (High)</th>
<th>8.0M Na (High)</th>
<th>LAWPS Range [1]</th>
</tr>
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<tbody>
<tr>
<td>Density (g/mL)</td>
<td>1.19</td>
<td>1.26</td>
<td>1.27</td>
<td>1.34</td>
<td>1.0 – 1.35</td>
</tr>
<tr>
<td>Viscosity, 25 °C (cP)</td>
<td>2.26</td>
<td>3.45</td>
<td>3.68</td>
<td>6.59</td>
<td>1 – 15</td>
</tr>
<tr>
<td>UDS (wt%)</td>
<td>0.14</td>
<td>0.45</td>
<td>1.1</td>
<td>0.24</td>
<td>0 – 3.3</td>
</tr>
</tbody>
</table>
CROSSFLOW FILTRATION TESTING
Crossflow filtration is a unit operation that is planned for use in the LAWPS facility. The CFF is a robust and mature industrial separation technology, but there is some remaining uncertainty regarding CFF performance with nuclear waste. The chemical complexity of the Hanford waste creates a large processing parameter space to evaluate (for a set of historical information on this, see Daniel et al. (2010) [8] and Johnson and Duignan (2011) [9]), and even small amounts of solid species can foul a filter (negatively affecting throughput) and/or make it difficult to clean (impacting performance over time). Relevant filtration data collected specifically for Hanford LAW or LAW simulants has, to date, been limited [7, 10]. In particular, the filtration behavior of LAW slurries with low solids loading (<3 wt%) has not been studied extensively and predicting performance is highly uncertain [11]. Nearly all LAW processed in the LAWPS facility will have low solids loading; thus, PNNL’s CFF testing is designed to reduce the uncertainty in performance and demonstrate the robustness of the CFF for LAW waste streams.

Experimental Approach
The crossflow filtration bench-scale testing was performed using PNNL’s Cell Unit Filter (CUF) system. The CUF contains a recirculation loop with a single tubular sintered stainless steel filter element (0.1 grade, Mott Corporation) that is identical to the type planned for use in the LAWPS. The system has been used to filter other waste simulants and additional description is available [11, 12]. An additional capability to backflush the filter element (from shell side to tube side) with various chemical solutions was added to the CUF to conduct the current PNNL testing in order to mimic the proposed cleaning approach for the LAWPS facility.

Crossflow filtration testing was divided into three series, each with a different objective. Series 1 testing was concerned with establishing the performance of the LAWPS simulants, i.e. simulants presented in TABLE I and TABLE II, to provide benchmark data in advance of operating the integrated test facility; the data may also be useful for evaluating filtration scale-up. Series 1 testing has been completed. Series 2 testing, which is on-going, is focused on identifying and testing foulants that could potentially be encountered during processing in the LAWPS. Series 3 testing is an evaluation of the ability to clean the filter and recover CFF performance, and steps were incorporated into both Series 1 and 2 testing to accomplish this objective and collect the greatest amount of relevant cleaning data. Most of the tests in Series 1 and 2 were conducted in a similar way, described by the general schematic of the operating steps shown in Fig. 3.
Fig. 3. Generalized Sequence of CUF Test Steps with Time. Note that CWF = clean water flux, BP = backpulse, the flux response shown is for illustrative purposes only, and the duration of each activity is not scaled.

Results
Each of the simulants described in TABLE I were tested in the CUF system at nominal operating conditions of 20 °C (the LAWPS lower operating limit), a transmembrane pressure (TMP) of approximately 137.9 kPa [20 psid], and an axial velocity of 4.48 m/s [14.7 ft/s]. The permeate flow rates measured in those experiments were converted to a corrected flux by dividing by the surface area of the filter and normalizing for operational deviations from nominal conditions. The normalization process is described in more detail in other recent PNNL CUF work [12]. The comparison of the initial 120-h filtering period for all of the simulants is presented in Fig. 4. For reference, the target production range of the LAWPS facility is given by the two black dotted lines. The simulants filtered were found to achieve or even exceed the target range over the entire 120-h period.

After the other periods of operation described in Fig. 3, the filter was cleaned using the bench-scale reproduction of the proposed LAWPS cleaning method, which proposes to feed the IX elution/regeneration chemicals (0.1M NaOH, water rinse, 0.45M nitric acid, water rinse) back through the CFF. Immediately following the LAWPS cleaning approach, the same simulant was filtered for approximately 16 h to observe if the filtration rate could be recovered. For the four simulants tested, the post-LAWPS cleaning filter flux measured in the first hour of operation ranged from 80 to 215% of the flux measured in the first hour of the 120-h filtering period. The initial test data suggests that the proposed LAWPS cleaning protocol will effectively restore flux during LAWPS operations.
Corrected Flux Data from the Initial 120-hr CUF Testing Period for All LAWPS Simulants. Flux has been corrected to the nominal operating conditions: 20°C, TMP of 137.9 kPa [20 psid].

**GAS GENERATION TESTING**

Gas generation during LAWPS operations can arise from three main sources: thermal degradation of organic species, radiolytic degradation (both of water and organic species), and corrosion processes. Some of the constituents of tank wastes inhibit both corrosion and radiolytic generation of hydrogen (e.g., NO$_2^-$ and NO$_3^-$). Currently, the estimation of gas generated in Hanford tank wastes is performed using a model derived empirically from a study using a large number of waste simulants and actual tank wastes [13, 14], typically referred to as the Hu model. Within the gas generation model, the waste constituents that affect the generation rate (either inhibiting or enhancing the rate) include total organic carbon (TOC), NO$_2^-$, NO$_3^-$, Na$^+$, and Al$^{3+}$. The effect of sRF resin used in the IX columns on this gas generation is not well understood, as the current state of knowledge in gas generation from spherical resorcinol-formaldehyde ion exchange resin in tank waste simulants is derived from two studies (comprised of a sum total of four tests [15, 16]). Testing was needed to determine the effect of the sRF resin on gas generation and the applicability of the existing gas generation models.

**Experimental Approach**

Gas generation rates were measured for six Hanford tank waste types both with and without external radiation exposure at PNNL in the late 1990s [17 – 22]. A very similar approach, with updated equipment, is being used in these measurements. The basic elements of the approach are to make gas generation rate measurements using reaction vessels and a gas manifold system. The reaction vessels are connected to the gas manifold using small-diameter stainless steel
connecting tubing. Each reaction vessel has its own pressure transducer connected to the vessel’s gas manifold line. A schematic of a vessel is shown in Fig. 5. These vessels were placed in a carousel configuration and housed inside a lead bunker while they were irradiated. A duplicate system was built to perform the measurements in the absence of radiation, i.e. isolating thermally-driven from radiolysis-driven gas generation.

In the hydrogen gas generation experiments conducted using sRF resin, the gas generation vessels shown in Fig. 5 were loaded half full with simulant only or simulant with resin. The vessels (a total of 16) were sealed, with thermocouples installed in both the headspace and the liquid phase. The vessels were sparged with argon gas and leak tested. Half of the 16 vessels were exposed to a radiation field from a Co-60 source. Temperatures and pressures were recorded with a data logger system, and gas samples were taken at approximately 1-week intervals and submitted for mass spectral composition analysis. The irradiation target of each test was to achieve a total radiation dose of ~300 MRad, which required approximately 40 days of operation. Both the thermal and radiolytic systems were operated for the same time period.

**Fig. 5. Schematic of Test Vessel Used in Gas Generation Testing**

**Results**

An example gas generation data set obtained for the radiolytic system is shown in Fig.6 for a test conducted with deionized water and sRF resin. In this case, the presence of the resin produces a noticeable enhancement in the moles of hydrogen produced over time when compared to the water alone. The suspected cause of this difference is the closed nature of the gas measurement system. Pure water, which lacks any species that can prevent back reactions from occurring, reaches equilibrium between hydrogen production and consumption in back reactions. The
resin provides a species that can quench back reactions and thus net hydrogen is generated. Despite this difference, the rate of hydrogen generated is less than what is predicted by the Hu model.

![Graph showing moles of hydrogen gas generated over time at 25 and 45°C in the Radiolytic Test System](image)

**Fig. 6.** Moles of Hydrogen Gas Generated from Water over Time at 25 and 45°C in the Radiolytic Test System. The diamonds represent the vessels containing only water, and the circles represent vessels containing water and sRF resin.

Four other tests either have been or will be conducted using various simulants (the 5.6M simulant, 0.45M nitric acid, 5.6M simulant with a TOC spike) and temperatures (25, 45, and 70°C). The gas generation data will be compiled and used to determine if the Hu model prediction for hydrogen generation in water appears to be bounding of other fluids. The enhancement in hydrogen generation obtained in the presence of sRF resin will also be quantified in the tests in which it is observed.

**GAS RETENTION, RELEASE, AND FLUIDIZATION**

The purpose of gas retention and release experiments at PNNL is to quantify gas release behavior from sRF resin for both spontaneous releases and gas release induced by bed fluidization. The strategy for controlling the potential retention and release of hydrogen gas during an off-normal condition, e.g. loss of flow to the IX columns, is to recirculate fluids upwards through the sRF to fluidize the bed and release the flammable gas. The released gas bubbles then move with the fluid to a vented break tank [23]. The configuration of the process lines for recirculating liquid and moving released gas into the break tank will affect the rate of gas release into the break tank, but the configuration has not yet been specified. Accordingly, the information that can be collected and that will be useful for system design will focus on retention and release inside the IX column itself.

The specific fluidization velocity to induce gas release and manage hydrogen
concentrations has also not yet been specified and needs to be determined during testing. Aguilar (2016) [23] gives fluidization velocities for sRF regeneration for both 1 M NaOH and LAW simulant solutions; these velocities are different for the different fluids but both give bed expansion of about 40% [24] which is appropriate to keep the fluidized bed below the height of exit screen of the IX column and is a suitable target for gas release testing. While this specification provides a basis for selecting 40% bed expansion as a target for a number of gas release tests, another key goal of testing is to determine the minimum fluidization velocity (and associated bed expansion) needed to release gas, which may be lower.

Fig. 7. Schematic Drawing of the 10-in. Diameter Column and Apparatus for Fluidization and Gas Retention and Release Studies (not to scale).

**Experimental Approach**

The experimental method to study retention and release is to build a full-height IX column with a 25.4 cm [10 inch] inner diameter (note that the full-scale IX column has an inner diameter of 106.7 cm [42 inch]). A schematic of the experimental apparatus is given in Fig. 7. Full height in this instance means that the column contains a resin bed height of 1.28 m [50.4 inch] and supernatant liquid height of ~0.86 m [~34 inch]. Complimentary experiments conducted at smaller scales, e.g. column diameters less than 25.4 cm, will be used to verify the selection of gas generation chemistry and column diameter. Hydrogen gas will be generated in-situ to permit observation of gas retention and release behavior, and the gas will be collected from the headspace. Peak retention of gas in the resin bed will be measured, as well as establishing fluidization velocities needed to release the retained gas and continually remove gas as it is generated.

The fluidization apparatus is capable of measuring gas retention and fluidization behavior for a range of simulants (water, LAW salt solution, and physical simulants, i.e. fluids with certain density or viscosity) as well as operating at elevated temperatures up to 55°C. To lend technical defensibility to the safety approach,
PNNL testing will span the range of anticipated operational and off-normal conditions in the LAWPS facility. The testing is expected to determine if a single fluidization velocity is sufficient for all scenarios or if additional refinements are needed.

**Results**

Data from fluidization column testing has yet to be analyzed. However, considerable effort was needed to develop a gas generation agent that was suitable for use in sRF resin. Gas generation methods that have been used in past work [25 – 27] were not found to be effective due to the unique chemistry of the resin. Thus, an investigative study was conducted to identify and select an appropriate gas generation chemistry for the impending testing. Sodium borohydride (NaBH$_4$), which was demonstrated to generate hydrogen gas in-situ in the resin bed, emerged as a good candidate with controllable kinetics. An example of gas bubbles generated using sodium borohydride is given in Fig. 8. It has also been demonstrated to generate sufficient quantities of gas to observe several retention and release events over time; example gas retention data from one such experiment is shown in Fig. 9.

![Image of Hydrogen Gas Bubbles Generated Using Sodium Borohydride and Retained in a Bed of sRF Resin.](image_url)
CONCLUSIONS

Four PNNL tasks supporting the technical maturation of the LAWPS facility were described in this paper. A few preliminary conclusions can be offered, pending the completion of the experimental work and associated analyses. Four simulants were developed to support CFF testing and integrated testing at larger scales that are chemically representative of LAW. CFF testing performed to date suggests LAW filtration can achieve production targets and the proposed LAWPS cleaning approach will be effective. Potential fouling agents that might be found in LAW have yet to be investigated and are the subject of future work. Gas generation testing conducted thus far suggests that water is an appropriate choice for a bounding hydrogen generation value, even in the presence of sRF resin. A gas generation agent was developed that will permit conducting a series of gas retention, release, and fluidization experiments in order to strength the safety basis of the LAWPS facility.

REFERENCES


