

Near-Tank Treatment of Hanford Tank Waste: Pilot-Scale Testing - 12107

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ABSTRACT

In order to reduce the number of high level waste canisters that will have to be produced by the Hanford Tank Waste Treatment and Immobilization Plant, supplemental waste treatment technologies are being investigated. One such technology is the Near-Tank Treatment System, which uses continuous sludge leaching, filtration, and ion exchange to process the waste in a simple, compact system. The Near Tank Treatment System is ideally suited for handling Hanford tanks with large amounts of boehmite, a difficult aluminum phase to dissolve. A pilot-scale Near Tank Treatment System was constructed and tested with a boehmite and iron oxyhydroxide waste simulant to evaluate the robustness and effectiveness of the system. The data from the pilot-scale tests were also used to assess scale-up from previously performed bench-scale tests.

INTRODUCTION

To reduce the number of high-level waste (HLW) canisters that must be processed by the Hanford Tank Waste Treatment and Immobilization Plant (WTP), supplementary waste treatment technologies are being investigated as part of the Department of Energy Office of Environmental Management's Advanced Remediation Technologies Program. One such technology, the Near-Tank Treatment System (NTTS), has been studied, developed, and tested at bench-scale by Parsons Infrastructure and Technology Group, Inc., and Battelle-Pacific Northwest Division. A recently completed technology readiness assessment (Josephson et al. (2010)) recommended a fully integrated pilot-scale test of the NTTS. The pilot-scale testing of the NTTS technology is described in this paper.

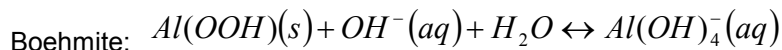
The pilot-scale NTTS demonstration unit was tested with a non-radioactive HLW simulant. The demonstration unit included all necessary equipment for demonstrating the NTTS process, from feed tanks through product tanks. The results from the demonstration unit can be used to develop a conceptual design and rough, order-of-magnitude cost and schedule for deployment of a full-scale system. In this section, the basic technologies for the various components of the NTTS are briefly described. This is followed by a summary of the objectives for the pilot-scale testing and the matrix of tests conducted to demonstrate these technologies at the pilot scale.

Continuous Sludge Leaching

Recent work by the WTP project at Richland, Washington, has indicated that vitrification of approximately one half of the waste is projected to be limited by Al concentration, despite processing to remove it from the vitrification feed. The baseline WTP flowsheet is currently designed to target effective removal of Al in the gibbsite form. However, because a significant quantity of Al is in the more intractable boehmite form, a significant fraction of the Al will remain in the Hanford HLW sludge after being processed via the current baseline approach. Dissolving and separating this more-difficult-to-process Al stream (boehmite) from the HLW sludge would reduce the quantity of HLW canisters produced by approximately one half and improve the canister production rate (Russell et al. (2008)). The primary driver for the continuous sludge leaching (CSL) process is to reduce the number of HLW canisters by one-third to one-half and improve canister production rates at the Hanford Site WTP.

At the Hanford Site, sludge washing/leaching programs have been undertaken to reduce the amount of several species in the HLW sludge. A caustic leaching step has been developed to target the removal

of Al from the HLW sludge. The caustic leaching reactions for gibbsite, $Al(OH)_3$, and boehmite, $AlOOH$, are shown below.



The WTP baseline caustic leaching process has been developed to operate at relatively low temperatures (approximately 85°C, or 185°F) with a short residence time on the order of 8 h. Unfortunately, the time required to dissolve a significant fraction of boehmite is much greater than that for gibbsite. Consequently, the current leaching processes that target gibbsite cannot efficiently remove Al in the boehmite form.

The CSL process will use a continuous stirred-tank reactor operating at 100°C (212°F) to target the leaching of boehmite at a nominal temperature of 100°C (212°F) with a residence time of about 300 h. With this much longer residence time, both gibbsite and boehmite will be effectively removed with an overall target conversion of 70% to 90% for boehmite.

Cross-flow filtration will then be used to separate the reduced volume of HLW sludge from the Al-laden liquid stream (typically called the permeate). The same separation technique is being used to separate waste streams in the WTP.

Raman Spectroscopy

Periodic determination of various ionic species in the CSL permeate is required to sufficiently assess the effectiveness of sludge treatment operations during CSL processing. The current laboratory analytical method, inductively coupled plasma mass spectroscopy, requires a significant turnaround time, during which species of interest could potentially precipitate. A much more rapid and frequent analysis is required to better understand, optimize, and potentially monitor sludge processing operations. Raman spectroscopy was chosen as the rapid analytical technology for this application. Raman spectroscopic data and temperature inputs were used to provide a real-time chemometric analysis to yield a quantitative analytical measurement of the process stream.

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light (typically a laser) which is used to study vibrational, rotational, and other low-frequency modes in a system. The laser light interacts with molecular vibrations or other excitations in the system, resulting in the energy of the laser photons being shifted up or down in comparison with the original monochromatic frequency.

The Raman laser beam was coupled to the sample through a fiber-optic cable and probe assembly that focused the excitation beam 5 mm beyond the tip of the probe and directly into the waste stream. Data was then collected over a range of 200 to 4000 cm^{-1} Stokes shift with a 1 cm^{-1} spectral resolution. Molecue[®] acquisition software was used to collect the data and a stand-alone MatLab[®] program developed by Eigenvector Research, Inc., applied the chemometric analysis and provided a data interface.

Near-Tank Cesium Removal

The HLW stored in the tanks at the Hanford Site consists of a mixture of sludge, saltcake, and supernatant liquids. The insoluble sludge fraction consists of metal oxides and hydroxides and contains many of the radionuclides. The saltcake, generated by extensive evaporation of aqueous solutions,

consists primarily of dried sodium salts. The supernatant liquids consist of concentrated (5- to 15-M) aqueous solutions of sodium and potassium salts. The bulk of the water-soluble radionuclides, such as ^{137}Cs and ^{99}Tc , are contained in the saltcake and supernate. Separation technologies are being developed to pretreat these wastes by removing the water-soluble radionuclides, with the objective of reducing the overall cost of disposal while satisfying regulatory and environmental considerations. This is generally accomplished by separating a large low-activity waste fraction from the remaining HLW. The remaining HLW contains most of the radioactive and hazardous components that are incorporated into a relatively high-quality waste form such as borosilicate glass. The Low Activity Waste fraction contains smaller amounts of radioactive and hazardous components and the majority of the bulk constituents of the waste.

The NTTS will process primarily single-shell-tank sludges, and any saltcake retrieved with the sludge. It is expected to remove primarily Al and soluble nitrate and nitrite salts from the solid phase into solution, leaving the majority of the actinides and strontium (Sr) in the sludge, to be immobilized as the HLW fraction. Cesium is very soluble in aqueous solutions, so any present in the sludge and saltcake will be transferred to solution during leaching. It is anticipated that removal of Cs from the CSL permeate will therefore be needed to render it acceptable for immobilization as Low Activity Waste. A rapidly deployable, modular concept such as the near-tank cesium removal (NTCR) can be easily integrated with CSL for this purpose by simply locating the NTCR modular unit where it can process the CSL permeate.

The NTCR system is based on an elutable ion exchange system using the spherical resorcinol-formaldehyde (SRF) resin. It has been demonstrated at the bench scale, as described in Blanchard et al. (2008). The system employs a simplified flowsheet and equipment design, compared to WTP, which enables rapid deployment and efficient operation. Two columns operated in series are employed in a fixed lead/lag position to minimize the number of valves. The lead column acts as the working resin bed, with repeated load and elute cycles. The lag column acts as a guard to ensure Cs in the NTCR effluent never exceeds the permissible level, and is rarely eluted.

The loaded resin is eluted using dilute (0.5 M) nitric acid at approximately 15°C (59°F) that can be neutralized and returned to the HLW tanks (preferably segregated from future feed streams). Eluting the resin at reduced temperature is expected to extend the resin life; lower elution temperatures slow degradation of the resin by oxidation (see Blanchard et al. (2008)). After the resin is exhausted, it will be eluted, transferred from the column to a High Integrity Containment vessel and disposed of as Low Activity Waste. Resin dissolution and destruction has also been considered as a disposal pathway; see Tran et al. (2008). Spent “process” solutions (i.e., solutions used in regenerating or washing the columns) are either used to adjust the Cs eluate to meet the tank farm composition specifications or are vitrified along with the Cs-decontaminated waste. The equipment needs include interim storage vessels, process chemical tanks, two ion exchange columns and a resin loading and removal system.

METHOD

The NTTS testing that was performed to address the objectives listed above comprised five parts:

1. Inhibited-Water Run of the CSL: a shakedown to verify equipment functionality
2. Inhibited-Water Run of the NTCR: a shakedown to verify equipment functionality
3. CSL Optimization, which had a start-up period, demonstration of steady-state operation, and a series of parametric tests (parameters varied were feed and removal flow rates)
4. NTCR Optimization, in which flow rates to the columns were varied to assess column stability

5. NTTS Demonstration, in which the CSL and NTCR were run concurrently at previously established optimum conditions.

System Description

The NTTS may be viewed as two distinct and separate processes operating in series:

1. the CSL process for removal of aluminum (Al) from the HLW slurry via cross-flow filtration, and
2. the NTCR process for removal of cesium (Cs) from the CSL filtration permeate using ion exchange.

CSL Process Description

Figure 1 presents a simplified flow diagram of the CSL pilot-scale demonstration unit process equipment (i.e., without start-up pumps, valves, and instrumentation) for removal of Al from HLW simulant.

The primary functions of the CSL process are to: 1) dissolve boehmite to facilitate removal of 70% - 90% of Al present in HLW to produce a nominal 10 wt% undissolved solids slurry stream for HLW processing; and 2) produce a solids-free permeate stream as feed to the NTCR process for Cs removal. The first function is accomplished by inline mixing of the HLW simulant feed stream containing boehmite with a 30-wt% (10-M) NaOH feed stream to a concentration of about 3-M hydroxide, then completing dissolution of the boehmite in the continuously stirred reactor operating at a temperature of about 100°C (212°F). The second function is accomplished by continuous removal of the liquid phase (permeate) from the slurry via cross-flow filtration.

The CSL process is divided into five major subsystems: 1) Feed Storage & Delivery; 2) Reactor Vessel; 3) Cross-Flow Filtration and Permeate Removal; 4) Leached Slurry Removal and Storage; and 5) Flush Waste System.

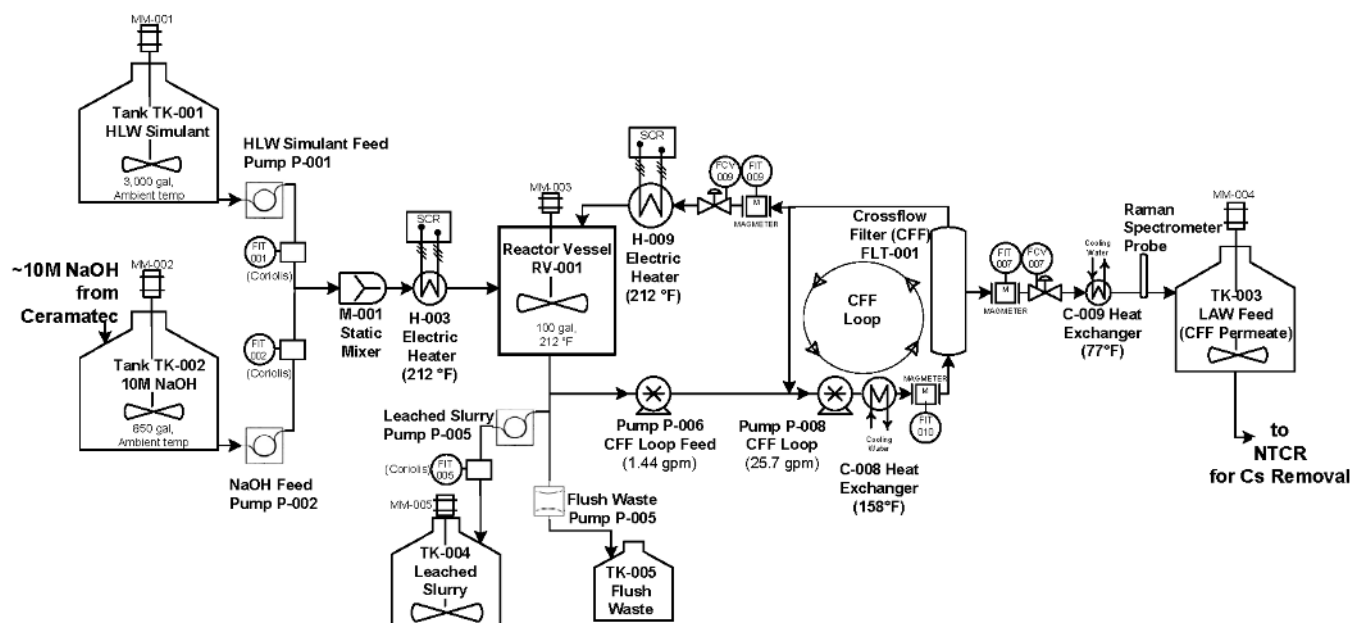


Figure 1. Simplified CSL Pilot-Scale Demonstration Unit Process Equipment and Flow Diagram. Typical flow rates and temperatures are given in parentheses.

NTCR Process Description

The primary objective of the NTCR system is to remove Cs from the cross-flow filtration permeate exiting the CSL system by ion exchange using SRF resin. The pilot-scale system is described by five major subsystems: 1) Low Activity Waste Feed System; 2) Ion Exchange Columns and Low Activity Waste Receiver Tank; 3) Resin Regeneration and Process Tanks; 4) Resin Loading and Unloading System; and, 5) Flush Water System.

Unlike the CSL, the NTCR operates in different modes. Table below outlines the operation cycles for the system, feed solution descriptions, process volumes in terms of gallons and bed volume (BV) (1 BV = 16.7 L or 4.4 gal), and the process time for each cycle in hours. The total cycle of the system is just over 10 days of operations, with the ion exchange process occurring for 8.3 days. The feed system for the ion exchange runs at a higher rate than the designed output from the CSL. For this reason, the lag storage of the NTCR needs to be high enough (minimum of 620 liters or 164 gal) to run the ion exchange cycle continuously without running out of process feed. An estimated 34-h processing delay is required after regeneration is completed prior to processing feed through the ion exchange columns.

Table 1. NTCR Operation Cycles

Operation Cycle	Process Solution Description	Process Volume (BV)	Process Volume (gal)	Time (hr)
Ion Exchange Processing	CSL Feed (190 BV)	200	880	200
Displacement of Low Activity Waste	0.1 M NaOH	4	17.6	1.3
Cs Elution	0.5 M HNO ₃	8	35.2	5.3
Regeneration Cycle 1	1 M NaOH	3	13.2	1
Regeneration Cycle 2	2 M NaOH/3 M NaNO ₃	3	13.2	1
Delay for Permeate Production	N.A.	N.A.	N.A.	34

Test Simulant

A non-radioactive waste simulant was used for the testing described in this report. The simulant recipe was developed to be similar to the simulant being used in other pilot-scale waste processing facilities, e.g., the Pretreatment Engineering Platform operated by Pacific Northwest National Laboratory in 2008-2009 (see Kurath et al. (2009)). The waste simulant used in the testing was developed based on the composite reduction/oxidation (REDOX) sludge characterized in Fiskum et al. (2008). The simulant has the following general characteristics:

- Undissolved solids content of 7.0 wt%;
- Solid components are 80% (by mass) boehmite (AlOOH) and 20% iron hydroxide (Fe(OH)₃);
- Supernatant with approximately 1 M Na concentration.

See Table below for concentration of other ions.

Table 2. Ion Concentration in the Simulant Supernate Used in the Tests

Species	Target Concentrations (mol/L)	Measured Concentrations (mol/L)
Sodium	1.07	0.83
Cesium	3.3×10^{-6}	2.7×10^{-6}
Potassium	4.0×10^{-3}	1.7×10^{-2}
Nitrate	0.65	0.69
Nitrite	0.35	0.42
Aluminate	0	0.03
Free Hydroxide	0.067	0.059

Iron hydroxide is an inert solid with respect to the leaching reaction and is prevalent in tank waste. Air sparging was utilized to mix the contents prior to transferring them to the waste feed tank. Based on the simulant recipe, the initial Al concentration in the solid phase was 2.72×10^4 mg/L.

NTTS Demonstration Results

This section presents the results of the testing, focused on the general process operations and controls.

The NTTS Demonstration test was conducted using the optimum process parameters from prior CSL and NTCR tests to demonstrate safe and successful operation of the integrated system. Instrument data was being collected every second, but the data presented here has been filtered into 1-h averages to make data analysis tractable.

Table presents the target and observed flow rates for both runs. The permeate removal rate was subject to the highest amount of variability.

Table 3. Average Flow Rates for Run 1 and Run 2 during the NTTS Optimization Test. The uncertainty range given with the actual values is the standard deviation (1σ).

Test	Waste Feed (gpm)		Caustic Feed (gpm)		Leached Slurry Removal (gpm)		Permeate Removal (gpm)	
	Target	Actual (\pm)	Target	Actual (\pm)	Target	Actual (\pm)	Target	Actual (\pm)
Run 1	0.028	0.0278 ± 0.003	0.028	0.0278 ± 0.003	0.005	0.0049 ± 0.0004	0.051	0.0493 ± 0.0054
Run 2	0.028	0.0269 ± 0.003	0.028	0.0270 ± 0.004	0.005	0.0049 ± 0.0006	0.051	0.0489 ± 0.0063

The information from the average volumetric flow rates was used to estimate the mass flow rates and calculate a mass balance for the CSL. A mass balance was also performed using the level data over a period during which all the levels were changing monotonically. The results of the two mass balance calculations are shown for Runs 1 and 2 in Table . The two methods are in agreement, with the level method generally underestimating the mass flow rates relative to the flow (volumetric) method. The error

in the mass balance from either method is very reasonable, and suggests that the densities assumed in the design calculations (which were used in these calculations) are good estimates of actual densities.¹

Table 4. Mass Balance on the CSL by Two Methods for NTTS Runs 1 and 2

Test	Waste Feed (kg/min)		Caustic Feed (kg/min)		Leached Slurry Removal (kg/min)		Permeate Removal (kg/min)		Mass Balance Error (% residual) [Flow/Level]
	Flow Method	Level Method	Flow Method	Level Method	Flow Method	Level Method	Flow Method	Level Method	
Run 1	0.111	0.093	0.138	0.130	0.024	0.023	0.225	0.194	[0.2/2.8]
Run 2	0.110	0.103	0.136	0.133	0.024	0.025	0.231	0.208	[3.9/0.9]

The temperature control in the CSL system was very successful. The reactor had an average temperature of $99 \pm 3^\circ\text{C}$ ($210 \pm 5^\circ\text{F}$) over the entire run. The slurry entered the cross-flow filtration at an average temperature of 70°C (158°F) and the permeate was, on average, leaving the cross-flow filtration at a temperature of 54°C (129°F). The majority of the deviations from the target temperatures were due to CSL shutdowns, typically for cross-flow filtration cleaning.

The filter performance during Run 1 (and likewise, Run 2) was very consistent. The target permeate rate of 0.051 gpm was maintained over the entire operating time. The transmembrane pressure (TMP) increased gradually over an approximately 50-60 h period from 5 to 40 psig. At this point the cross-flow filtration would be cleaned and the process would begin again with nitric acid. Backpulsing was observed to slow down the rate of TMP increase but it was not determined what the optimal backpulse strategy (in terms of managing TMP and minimizing downtime for cleaning) would be for this system.

The NTCR was operated concurrently with the CSL. Pump P-017 continuously removed permeate from the Low Activity Waste feed tank (TK-003) and delivered it at a flow rate of 0.073 gpm. Operation of the ion exchange columns was very stable, as indicated by the flow rate and near-constant differential pressure. The NTCR is run at ambient temperature (with the exception of the nitric acid elution step), so the temperature data from the NTCR during the NTTS Demonstration Test was trivial and will not be discussed.

The columns were operated throughout the NTTS Demonstration Test without any significant processing problems. This suggests that the ion exchange columns can be scaled directly from the bench scale to full scale, since the pilot-scale columns in the NTTS were designed directly from previous bench-scale experiments. The columns did not experience any issues that would affect the transport phenomena of ion exchange, such as channeling, bed disruption, large thermal variations, precipitated solids or pressure drops of significant magnitude

¹ No density measurements were made during the testing, with the exception of one permeate sample which confirmed that the permeate had a density consistent with expectation: expected = 1.21 kg/L, measured = 1.22 kg/L.

On average, the NTCR feed rate was greater than the permeate rate by approximately 50%. Some consideration of how to prevent idle ion exchange columns will be necessary in future NTTS design. For example, there could be two Low Activity Waste feed tanks (one for lag storage while the other is processed) or the processing capacity of the CSL could be increased.

DISCUSSION

This section discusses the performance of important processing operations in more detail: caustic leaching, filtration, Raman spectroscopy, and ion exchange.

Caustic Leaching

The main objective of the caustic leach is to dissolve a majority (70%–90%) of the Al present as boehmite (AlOOH) and produce a nominal 10 wt% undissolved solids slurry stream for HLW processing and a solid-free permeate stream as Low Activity Waste ready for Cs removal via ion exchange.

The leaching process combines HLW simulant (the composition along with the target concentrations can be seen in Table 5) with a predetermined quantity of concentrated caustic. The values in Table are for the liquid phase. Note that although there were no aluminum or iron solids expected, small amounts are present. This is probably due to some initial leaching and other chemistry that renders Al and Fe soluble in detectable quantities. The solutions are mixed and leached in a reactor near 100°C (212°F), with a residence time on the order of hundreds of hours. Permeate and a small portion of concentrated slurry are continuously removed from the reactor to allow for the introduction of fresh blended caustic and feed material. The reactor solution is pumped through a cross-flow filter where the soluble aluminum leaves with permeate.

Table 5. Target and Actual HLW Simulant Concentrations

	Al (mg/L)	Cs (mg/L)	K (mg/L)	Na (mg/L)	Fe (mg/L)	NO_3 (mg/L)	NO_2 (mg/L)	OH (mg/L)	TSS ^(a) (mg/L)
Target	0	0.44	156	24,599	0	40,300	16,100	1,139	75,600
Actual, CSL Optimization	700	0.36	650	19,000	2,900	43,000	19,400	1,000	86,000
Actual, NTTS Demonstration	700	0.39	630	17,000	2,800	23,900	16,800	250	84,000
(a) TSS = total suspended solids									

The leaching rate (or yield of dissolved boehmite, ξ^{AlOOH}) was calculated using the following equation:

$$\xi^{\text{AlOOH}} = \frac{C^{\text{AlOOH}}}{\left[1 - \frac{C^{\text{AlOOH}}}{\rho_{\text{permeate}}}\right]} \left[\frac{\left(V_{\text{permeate}} + \frac{V_{\text{ls}}^{\text{slurry}} \rho_{\text{ls}}^{\text{slurry}}}{\rho_{\text{permeate}}}\right)}{\left(V_{\text{feed}}^{\text{slurry}} \rho_{\text{feed}}^{\text{slurry}} X_{\text{feed}}^{\text{AlOOH}}\right)} - \frac{X_{\text{feed}}^{\text{Solids}}}{X_{\text{feed}}^{\text{AlOOH}} \rho_{\text{permeate}}} \right], \quad (\text{Eqn 1})$$

where C^{AlOOH} is the concentration of dissolved boehmite in the liquid phase (kg/L), V is the volumetric flow rate of a process stream (L/min), ρ is the density (kg/L), and X^i is the mass fraction of species i . The subscripts *feed*, *permeate*, and *ls* refer to value of the quantity in the waste simulant feed stream, the permeate stream, and the leached slurry stream. Note that there are some assumptions used to generate this equation, namely that the waste simulant feed is well characterized and constant over time, the densities are constant and known, and there are no appreciable solids in the permeate stream.

During the NTTS Demonstration Test, the CSL operated at steady state for a prolonged period of time. Therefore, the leach rates estimated from the NTTS Demonstration data should have less variation than the rates calculated from CSL Optimization data. The maximum 24-h leach rates (assuming that the sampled value is representative of the day it was taken) observed during the NTTS Demonstration Test were 62% (Run 1) and 73% (Run 2) with minimum values of 47% (Run 1) and 52% (Run 2); overall, the average leach rate was $59 \pm 5\%$ (**Error! Reference source not found.**). During the test, the observed high for solids in the slurry was 21% and the low was 14% with an average of $17 \pm 2\%$.

The leach rates (yields) calculated from the NTTS Demonstration Test data were, on average, below the objective of leaching 70–90% of the aluminum. However, this calculation contains some assumptions that may lead to an underestimate of the fraction that was leached. The calculation described by Equation 1 is, in particular, very sensitive to the value of the feed mass fraction of boehmite (X_{feed}^{AlOOH}). It is suspected that this value may have been lower than estimated; if the undissolved solids was only 1% lower (e.g., 6 wt% instead of 7 wt%), the calculated leaching yield would be within the target range for the Demonstration Test. The sensitivity of the calculation to undissolved solids is presented graphically in Figure , which illustrates that a undissolved solids on the order of 5.5 to 6.0 wt% places all the leach rates within the target range.

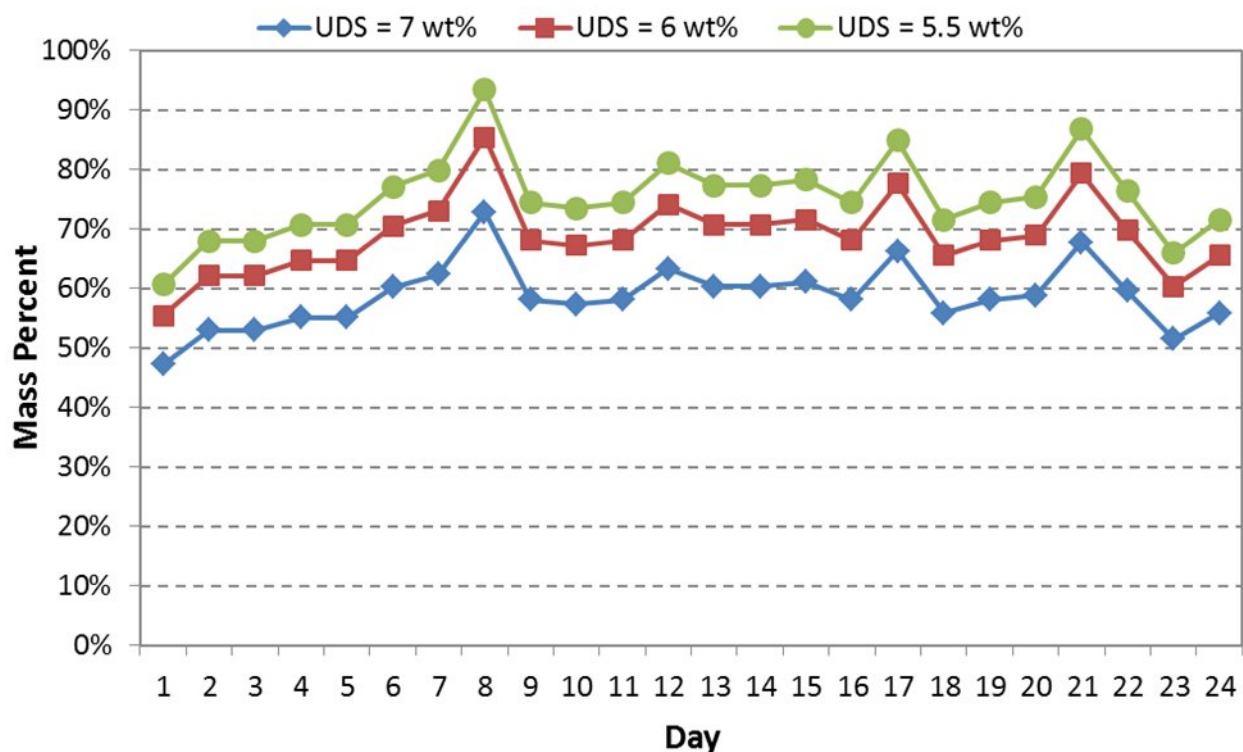


Figure 2. Effect of undissolved solids on the Leaching Rates as Estimated by Equation 5.1

Based on this suspicion, two solid-phase leached-slurry samples were analyzed for aluminum and iron solids. One sample was from the last day of Run 1 of the NTTS Demonstration Test, the other from the last day of Run 2. From these two samples, the leaching yield was calculated to be approximately 90%. By comparison, the undissolved solids of the HLW simulant would have to be around 4.6 wt% for the leaching yields calculated via Equation 1 to average 90%. This data suggests that the undissolved solids actually reaching the reactor was likely below the target of 7 wt%.

Filter Performance

The cross-flow filtration used in the NTTS is effectively identical to the filter module that is intended for use in the WTP and has been tested extensively at the bench scale (e.g., Shimskey et al. (2009a), Shimskey et al. (2009b), Billing et al. (2009)) and demonstrated at the pilot scale (e.g., Daniel et al. (2009a), Daniel et al. (2009b), Kurath et al. (2010)). The inert solid (iron hydroxide) chosen for the waste simulant used in the testing was a challenging component with respect to filtration. It has been demonstrated that $\text{Fe}(\text{OH})_3$ and similar compounds such as FeOOH are significant foulants for this filter type, even when present in small amounts, and adversely affects long-term filtration performance (Daniel et al. (2011)). Based on experimental evidence collected thus far, at long times the filter may cease to remove an appreciable amount of material due to accumulation of foulants both in the pores and in the surface cake.

Though maintaining filtration rate over long times was anticipated to be challenging, the NTTS cross-flow filtration had an advantage over previous tests, because the filtration occurred at an elevated temperature (60°C (140°F)). In general, the Darcy equation is expected to describe the filtration rate. The equation is written as

$$Q_p = \frac{\Delta P}{\mu R} A_F \quad (\text{Eqn 2})$$

where Q_p is the volumetric flow rate of the permeate, ΔP is the pressure differential across the filter (taken to be the TMP), μ is the permeate viscosity, R is the resistance of the filter, and A_F is the filter cross-sectional area. By Equation 2, a target flow rate will be easier to achieve at lower permeate viscosity. Operating at 60°C (as opposed to previous filter testing, which was almost always conducted under ambient conditions) will help mitigate the expected effect of fouling on the permeate rate.

The resistance term in Equation 2 is the controlling variable for the filtration, but it is not a simple constant. It evolves with time and can be a function of filter cleanliness, use of backpulsing, axial velocity, and the type of material that is being filtered (particle size, density, various colloidal forces). In this case, assuming that the viscosity is held constant, we have the approximate relationship

$$\frac{R_{t+1}}{R_t} \propto \frac{\Delta P_{t+1}}{\Delta P_t}, \quad (\text{Eqn 3})$$

where t and $t+1$ represent two distinct times. The proportionality constant implied by Equation 3 will, in this case, be assumed to be unity. This approach to estimate the change in resistance over time is only correct when the permeate flow rate is constant or nearly so.

These long periods were separated by cleaning events when necessary. Cleaning was performed when the TMP approached 30 psig. Table 6 presents the major segments (periods of operation between filter cleanings) of cross-flow filtration operation from the NTTS Demonstration runs. Based on these seven segments of operation, all of which had a permeate removal rate set point of 0.051 gpm, the cross-

flow filtration can be operated continuously for an average of 53 h before cleaning is required.² During this period, a rise in TMP of approximately 20–25 psig was needed to maintain the permeate rate. This represents an increase in the final resistance (R_f) compared to the initial resistance (R_0) by a factor of five (see Figure 3). On average, the cross-flow filtration cleaning took 4–5 h from start to finish. Thus, the total duration of a cross-flow filtration “cycle” is, on average, approximately 58 h. Over a cycle, the effective average permeate removal rate is 2.75 gal/hr. This rate accounts for the time required to clean the filter.

One operational method that can help delay the onset of increased filter resistance is the application of backpulses. A backpulse forces a volume of permeate back through the filter pores using a high pressure differential. The permeate, as it flows back through the pores, should remove some portion of the fouling particles (either by sweeping out particles in the pores themselves or disrupting the cake on the filter surface). To this point, backpulsing has not been studied extensively enough in operations using this filter type to ascertain an effective backpulse strategy.

Table 6. Major Segments of cross-flow filtration Operation during the NTTS Demonstration Tests

Identifier	Duration (hr)	Volume filtered (gal)	Removal Rate (gal/hr)	□TMP (psig)	□R (R_f/R_0)
<i>NTTS Demonstration, Run 1</i>					
Segment 1	48	142.96	2.98	25.0	5.2
Segment 2	59	178.94	3.03	28.2	6.5
Segment 3	57	172.13	3.02	25.8	4.9
<i>NTTS Demonstration, Run 2</i>					
Segment 1	55	164.65	2.99	19.6	4.2
Segment 2	56	163.63	2.92	21.6	4.3
Segment 3	41	124.54	3.04	18.5	3.2
Segment 4	58	172.42	2.97	23.4	4.9
Averages	53.4	160	2.99	23.2	4.7

² The operational guideline that the cross-flow filtration was cleaned when the TMP approached 30 psig is arbitrary and not binding to future cross-flow filtration operations; however, based on the parameters of the system as-operated, it was a reasonable choice.

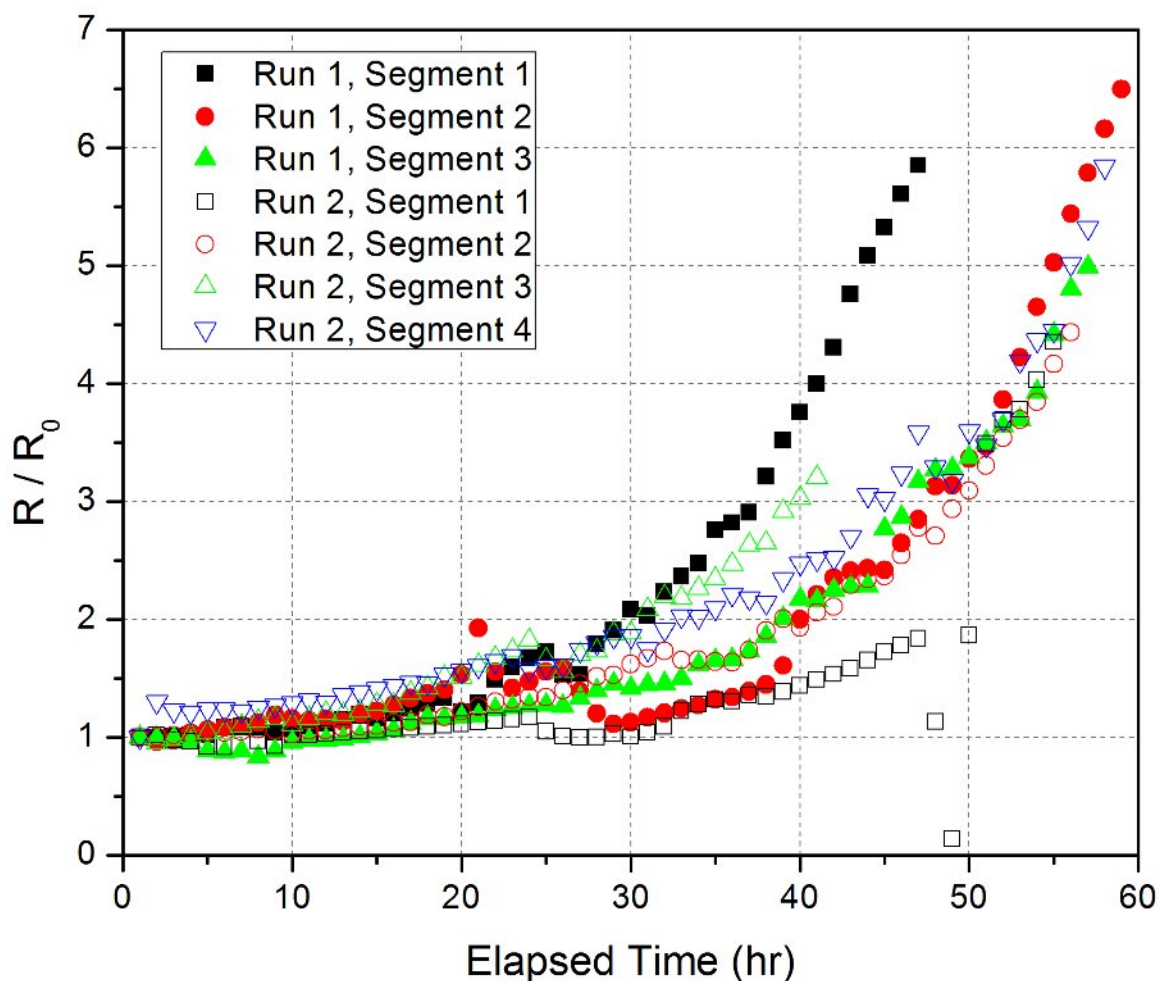


Figure 3. Evolution of cross-flow filtration Resistance for Segments of Operation during the NTTS Demonstration Test

Ion Exchange

The NTCR system is designed to remove cesium from the permeate stream. The permeate removed by the cross-flow filter is pumped through two ion exchange columns loaded with SRF resin arranged in series. The SRF removes the Cs from the alkaline waste stream by cation exchange. After the Cs has been loaded onto the columns it can be removed by elution with nitric acid, where the hydronium ion displaces the Cs and converts the SRF back to the protonated form. The resin is then regenerated by treatment with sodium hydroxide to convert it back to the sodium form for subsequent loading cycles.

All three runs during the NTTS Demonstration Test showed no Cs breakthrough of the lead column with a feed concentration averaging between 0.16 and 0.18 mg/L Cs, depending on the run (see Figure 4). The elution of Cs and regeneration of the columns between NTTS Demonstration Test Runs 1 and 2 and Runs 2 and 3 were successfully demonstrated. Based on the detection limit of the analytical technique (typically 0.005 mg Cs/L), the average Cs removal values for Runs 1, 2 and 3 were > 96.8%, > 97.3%, and > 94.7%, respectively.

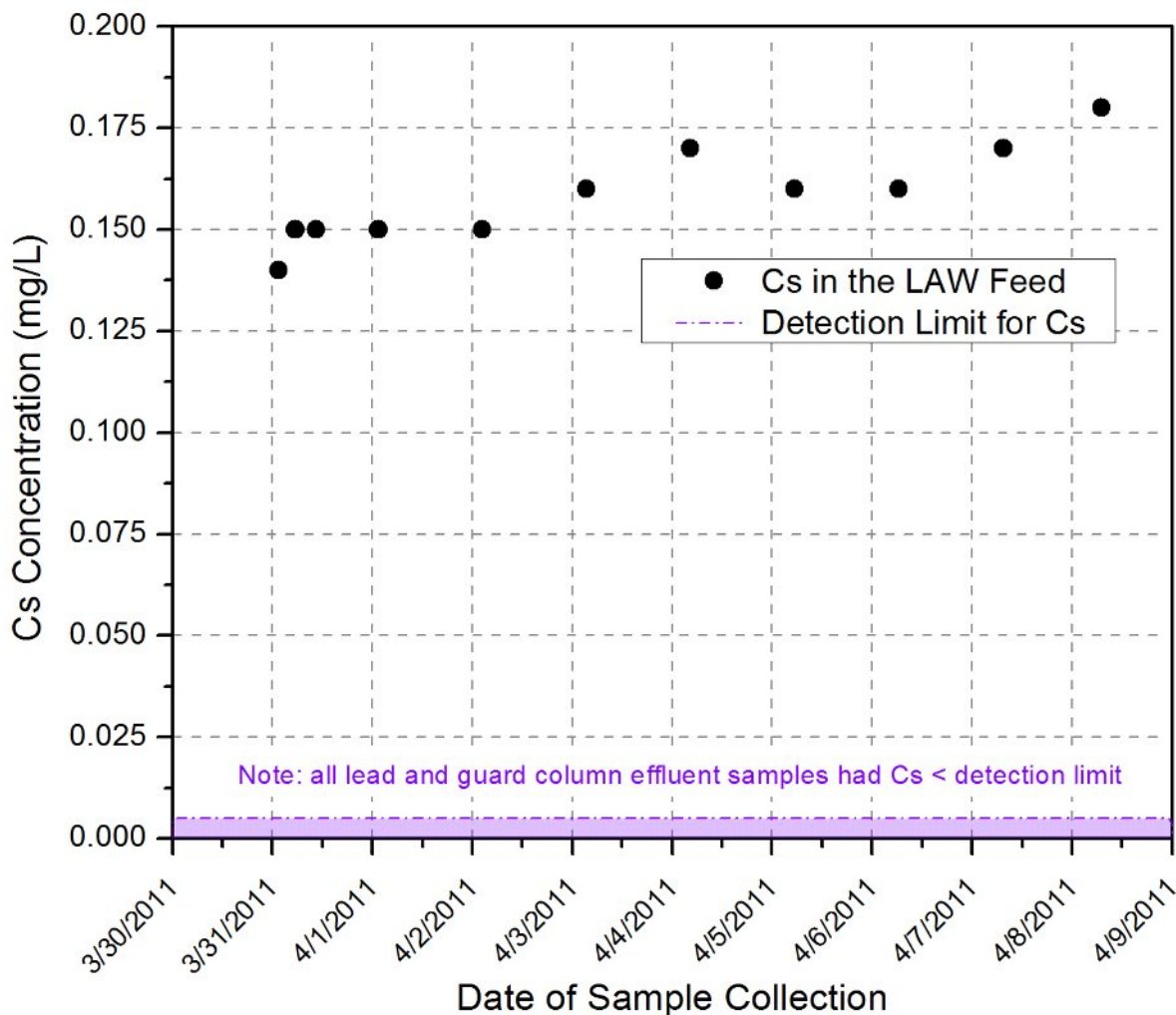


Figure 4. Example Ion Exchange Data – All Effluent Data Below the Detection Limit

CONCLUSIONS

It should be noted that any work involving the use of simulated HLW has inherent limitations. For this work, every attempt was made to ensure that the simulant mimicked the actual waste performance as closely as possible. However, there are always limitations in the ability to

The NTTS Demonstration Test established that all the subsystems could be operated concurrently to process the waste simulant. The NTTS had a stable performance during the Demonstration Test that required very little external manipulation once a steady state was achieved.

The CSL demonstrated effectively 90% dissolution of the hard to leach boehmite phase. The cross flow filtration system was able to deliver decontaminated salt solution to the NTCR system. The NTCR system exceeded the design basis by providing effluent below the detection limit beyond the design basis required time.

The NTTS system was successfully demonstrated and has shown that leaching and decontamination of the subsequent permeate can be readily achieved using relatively small footprint equipment in an at tank application.

REFERENCES

ASME—American Society of Mechanical Engineers. 2008. ASME NQA-1-2000, Part IV, Subpart 4.2, *Guidance on the Graded Application of Quality Assurance (QA) for Nuclear Related Research and Development*. New York. ISBN: 0791831272.

Billing JM, RC Daniel, DE Kurath, and RA Peterson. 2009. *Bench-Scale Filtration Testing in Support of the Pretreatment Engineering Platform (PEP)*. PNNL-18673, WTP-RPT-203, Pacific Northwest National Laboratory, Richland, Washington.

Blanchard DL, SK Fiskum, JM Peterson, AF Farawila, and DE Kurath. 2008. *Small Column Ion Exchange Testing for the Near Tank Cesium Removal Project*. PNWD-3985, Battelle-Pacific Northwest Division, Richland Washington.

Daniel RC, JM Billing, KJ Cantrell, ML Luna, RA Peterson, ML Bonebrake, RW Shimskey, and LK Jagoda. 2009a. *Characterization of Filtration Scale-Up Performance*. PNNL-18117, WTP-RPT-168, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Daniel RC, JM Billing, JR Bontha, CF Brown, PW Eslinger, BD Hanson, JL Huckaby, NK Karri, ML Kimura, DE Kurath, and MJ Minette. 2009b. *EFRT M-12 Issue Resolution: Comparison of Filter Performance at PEP and CUF Scale*. PNNL-18498, Pacific Northwest National Laboratory, Richland, Washington.

Daniel RC, JM Billing, CA Burns, RA Peterson, RL Russell, PP Schonewill, and RW Shimskey. 2011. *Filtration Understanding: FY10 Testing Results and Filtration Model Update*. PNNL-20299, Pacific Northwest National Laboratory, Richland, Washington.

Fountain MS, DE Kurath, GJ Sevigny, AP Poloski, J Pendleton, S Balagopal, M Quist, and D Clay. 2008. "Caustic Recycle from Hanford Tank Waste Using NaSICON Ceramic Membranes." *Separation Science and Technology* 43 (9–10):2321–2342.

Fountain MS, DE Kurath, GJ Sevigny, AP Poloski, J Pendleton, S Balagopal, M Quist, and D Clay. 2009. *Caustic Recycle from Hanford Tank Waste Using NaSICON Ceramic Membrane Salt Splitting Process*. PNNL-18216, Pacific Northwest National Laboratory, Richland, Washington.

Josephson G, G Lumetta, H. Harmon, J. Young, and B. Knutson. 2010. *Technology Readiness Assessment for the Near-Tank Treatment System*. PNWD-4190, Battelle-Pacific Northwest Division, Richland, Washington.

Kurath DE, BD Hanson, MJ Minette, DL Baldwin, BM Rapko, LA Mahoney, PP Schonewill, RC Daniel, PW Eslinger, JL Huckaby, JM Billing, PS Sundar, GB Josephson, JJ Toth, ST Yokuda, EBK Baer, SM Barnes, EC Golovich, SD Rassat, CF Brown, JGH Geeting, GJ Sevigny, AJ Casella, JR Bontha, RL Aaberg, PM Aker, CE Guzman-Leong, ML Kimura, SK Sundaram, RP Pires, BE Wells, and OP Bredt. 2009. *Pretreatment Engineering Platform Phase 1 Final Test Report*. PNNL-18894; WTP-RPT-197, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

Russell RL, RA Peterson, WC Buchmiller, RW Shimskey, and XY Yu. 2008. *Bench-Scale Testing Results of the Continuous Sludge Leaching Process*. PNWD-3991, Battelle-Pacific Northwest Division, Richland, Washington.

Sevigny GJ, AP Poloski, MS Fountain, and DE Kurath. 2008. *Preconceptual Design Description for Caustic Recycle Facility*. PNNL-17507, Pacific Northwest National Laboratory, Richland, Washington.

Shimskey RW, JM Billing, EC Buck, RC Daniel, KE Draper, MK Edwards, JGH Geeting, RT Hallen, ED Jenson, AE Kozelisky, PJ MacFarlan, RA Peterson, LA Snow, and RG Swoboda. 2009a. *Filtration and Leach Testing for REDOX Sludge and S-Saltcake Actual Waste Sample Composites*. PNNL-17965, Pacific Northwest National Laboratory, Richland, Washington.

Shimskey RW, RC Daniel, AE Kozelisky, JM Billing, K Draper, PJ MacFarlan, EC Buck, MK Edwards, RA Peterson, AJ Casella, RT Hallen, RG Swoboda, and JV Crum. 2009b. *Filtration and Leach Testing for PUREX Cladding Sludge and REDOX Cladding Sludge Actual Waste Sample Composites*. PNNL-18048, Pacific Northwest National Laboratory, Richland, Washington.

Tran DN, JM Peterson, DE Kurath, TL Sams, and DL Blanchard. 2008. *Near Tank Cesium Removal – Phase II Resin Dissolution and Destruction*. PNWD-4011, Battelle-Pacific Northwest Division, Richland Washington.