Development and Testing of a Near Tank Cesium Removal Process - 9222

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ABSTRACT

Current estimates indicate that the Hanford tank farm system will run out of available storage space prior to startup of the Pretreatment facility. Deployment of a Near Tank Cesium Removal (NTCR) system could allow LAW processing to begin as soon as WTP LAW Vitrification Facility or supplemental treatment (e.g. bulk vitrification) becomes available, freeing up tank space and beginning waste cleanup several years early. The NTCR will be a mobile, shielded, self-contained system that requires only limited process chemicals and separates the HLW into two process streams. The low activity, Cs-decontaminated waste stream from the NTCR can be vitrified, while the high-activity Cs-rich stream would be stored in the Double Shell Tank system until vitrified by the WTP High Level Waste (HLW) Facility.

The NTCR system will be an elutable ion exchange (IX) system based on the Spherical Resorcinol Formaldehyde (SRF) resin, which uses interim storage vessels, process chemical tanks, two IX columns and a resin digestion system. After multiple load-elute cycles the exhausted resin can be dissolved and digested with nitric acid at elevated temperatures, eliminating the need for a separate resin disposal pathway. Rapid deployment of the modular system is enabled by the use of the SRF resin, a simplified flowsheet, resin lifetime extension using cooled nitric acid as the eluant, and resin digestion. Laboratory scale tests of the NTCR resin dissolution and IX processes were conducted to provide data for the design of a demonstration unit (pilot plant) and to make an initial selection of the process conditions. This paper gives a summary of the NTCR process and results of these tests, which have been published in detail elsewhere [1, 2].

INTRODUCTION

The primary mission of the U.S. Department of Energy's (DOE's) River Protection Project (RPP) at Hanford is to retrieve and treat the Hanford tank waste and close the tank farms. The farms are broadly categorized into those containing tanks with single shells (SSTs) and those with double shells (DSTs). The SST retrieval process involves dissolving the saltcake, mobilizing the sludge, and transferring this waste to one of the 28 DSTs. Available DST space is one of the key factors limiting the RPP mission goal of SST retrieval and closure. Once pumped to the DST tank farms, the tank waste can be provided to the Waste Treatment and Immobilization Plant (WTP) for treatment.

The WTP facilities will be large, complex plants design to process any and all Hanford tank wastes. These facilities have significant budget and schedule requirements; startup of the WTP facilities is currently planned in 2019. The limited available DST space at this time will likely limit near-term progress on the retrieval of the wastes from the SSTs into the DSTs. Current estimates indicate that the tank farm will run out of available storage space before start-up of the Pretreatment Facility (PTF). A recent study at Hanford explored the possibility of start-up of the LAW vitrification facility as early as 2013 [3], well ahead of the startup of the pretreatment and HLW vitrification facilities. This concept was referred to as "Start LAW First." The benefits of Start LAW First cited in the study include freeing up DST space, allowing SST retrieval to proceed, and demonstrating progress on tank treatment. Since the

pretreatment facility will not be started until 2019, a rapidly deployable alternative concept such as the NTCR is needed to remove cesium from the feed to the LAW vitrification facility.

The objective of the Near Tank Cesium Removal (NTCR) project is to provide a simple, compact, effective, and proven process to remove radioactive cesium (Cs) from high-level waste (HLW) liquids. Ion exchange using spherical resorcinol-formaldehyde (SRF) will be used. The NTCR system will be a self-contained, modular, transportable system that requires only limited process chemicals and separates filtered tank waste into two process streams. The Cs decontaminated LAW stream can be immobilized and the Cs-rich stream would be stored in the DST system until vitrified by the WTP HLW Facility. This technology can be sized to feed the WTP LAW melters at the nominal operating capacity (30 metric tons glass per day). Alternatively, it could be sized to feed a supplemental treatment system.

The NTCR system is based on an elutable ion exchange system using the SRF Resin. The system employs a simplified flowsheet and equipment design that enables rapid deployment. Two columns are operated in series in a fixed lead/lag configuration to minimize the number of valves. The loaded resin is eluted using dilute nitric acid at less than ambient temperature, which 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 lifetime. After the resin is exhausted, it can be dissolved and digested with nitric acid at elevated temperatures, neutralized and added to the LAW stream. This eliminates the need for spent resin handling equipment and a separate spent resin disposal pathway. Spent process solutions are used to neutralize the dissolved resin liquor, adjust the cesium eluate to meet the tank farm composition specifications, or vitrified along with the cesium decontaminated waste. The equipment needs include interim storage vessels, process chemical tanks, two ion exchange columns and a resin digestion system.

SRF has shown good performance in the areas of Cs loading and elutability as demonstrated on simulants and actual wastes [4, 5, 6]. It has shown good hydraulic performance [7, 8] and is relatively inexpensive. WTP has adopted SRF as the baseline resin for cesium removal for these reasons, and these considerations also make it the clear choice for the NTCR process.

The preliminary NTCR operations flowsheet begins with batches of clarified LAW at a nominal sodium concentration range of 5 M – 7 M. The LAW is pumped downflow at 3 bed volumes per hour (BV/h) through two ion exchange columns containing beds of SRF. The cesium-depleted LAW enters one of two product tank where it is sampled and then pumped to either continued storage or vitrification. LAW processing is terminated when the product ^{137}Cs concentration becomes unacceptably high. A processed LAW volume of 100 BVs is expected based on the results reported in [4] for cesium separation from actual LAW from tank AN-102. The LAW is flushed from the system with approximately 3 BV of 0.1 M sodium hydroxide at 3 BV/h. Axial mixing is minimized and flush volume is maximized by pumping this solution, lower in density than the LAW, down-flow through the columns.

The resin in the lead or both columns, depending on the operation mode, is then eluted with 0.5 M nitric acid cooled to nominally 10ºC. Cooling is expected to reduce chemical oxidation and nitration and prolong resin operational life. A volume of 7 BV is considered nominally sufficient to elute the resin in either the lead column or both lead and guard columns such that its performance is adequate for processing LAW, provided breakthrough on the column eluted is limited to approximately 1%. An elution flow rate of 1.5 BV/h is baselined for the NTCR. The eluant has a higher density than the 0.1 M sodium hydroxide flush, and so it is pumped up-flow through the columns to minimize mixing with the caustic flush solution and reducing elution efficiency. Up-flow elution also avoids contaminating process lines and equipment that contact decontaminated LAW. The eluate is mixed with the initial volume of regeneration effluent (described below) and sufficient sodium hydroxide and sodium nitrite that it satisfies the chemical composition requirements for interim storage in a DST (described in [9]).

The ion exchange resin is then regenerated with a solution of 3 M sodium nitrate, 3 M sodium nitrite, and 1 M sodium hydroxide to prepare it to process further batches of LAW. A volume of 6 BV per column is considered sufficient for this operation. Regeneration is conducted up-flow to minimize axial mixing of the sodium hydroxide and resident nitric acid that would otherwise occur due to the former being heavier, leading to a reduction in regeneration efficiency.

Experimental work has shown that down-flow introduction of LAW into a regenerated column containing a lighter regeneration solution initiates axial mixing that causes the bed surface to become unleveled. An unleveled bed surface may lead to premature cesium breakthrough in subsequent LAW processing. The proposed regenerant provides a density greater than the LAW to avoid axial mixing and promote plug-flow. The NTCR processes LAW approximately 78% of the time it is operating while it undergoes elution and regeneration during the remaining time.

This paper documents the bench scale resin dissolution and destruction tests and ion exchange tests that were conducted to make the initial selection of the process conditions for the NTCR demonstration unit (pilot plant). The resin dissolution and destruction testing scope included batch tests to investigate the resin destruction kinetics and the minimum temperatures and nitric acid concentrations necessary to achieve dissolution. Some characterization of the final dissolved resin liquor and of the off-gases generated during resin dissolution/destruction was conducted. The IX testing scope included seven small column tests using simulants and a radioactive tracer to monitor the IX performance. Two of the elutions conducted during the tests were run at reduced temperatures (10°C and 15°C).

OBJECTIVES

The objectives of the resin dissolution and destruction tests were to:

- Determine the optimum process conditions for safe execution of the NTCR pilot plant (NTCR-PP) resin destruction process tests.

- Obtain reaction-rate data with nitric acid to define the reaction kinetics for input to the design and operation of the NTCR pilot plant.

- Provide initial characterization information for an initial assessment of disposal options for spent resin destruction process solutions.

- Assess the feasibility of using the caustic resin regeneration solution to neutralize the post-resin-destruction nitric acid solution to provide an initial assessment of disposal options for nitric acid resin destruction residues.

- Provide initial characterization information for the off-gas from the resin dissolution and destruction process.

The specific objectives of the ion exchange tests were to:

- Demonstrate satisfactory Cs decontamination of 100 BV or more of an appropriate simulant.

- Assess the effect of the following process conditions on SRF cesium ion exchange performance: a) abbreviated low-activity waste (LAW) displacement, b) short upflow elution, and c) upflow resin conversion to sodium (Na) form with high-density solution.

- Evaluate the impact of feed variability on the SRF resin performance.

- Determine the effect of lower-than-ambient temperature on Cs elution from the SRF resin beds.

RESIN DISSOLUTION AND DESTRUCTION TEST SUMMARY

Experimental

All bench-scale batch dissolution and destructions tests were carried out in Pyrex Erlenmeyer flasks that were available in various sizes: 500 mL, 250 mL, 100 mL and 50 mL. The flask size was selected for each test based on the total volume of acid-resin used for the test. Typically, four to six batch tests were conducted at the same time except for the single large batch test. The test temperature was controlled independently by using an individual hotplate/stirrer for each batch. Detailed information on batch resin dissolution and destruction experimental setup has been reported elsewhere [1].

Fourteen kinetics tests were selected and conducted in two series. The first series consisted of nine tests in which the initial nitric acid molar excess was approximately 23 to 35 times of the minimum theoretical quantity of nitric acid needed for complete resin destruction, assuming 100% efficiency. The second series consisted of five tests in which the initial nitric acid molar excess was approximately 22 times of the minimum theoretical quantity of nitric acid needed for complete resin destruction. A large excess of nitric acid was used to hold the nitric acid concentration relatively constant so that the effect of TOC concentration could be isolated. Kinetics tests were carried out in 3 M, 5 M and 7 M nitric acid solutions and at 70°C, 80°C, and 90°C for approximately 50 hours and 13 hours for the first and the second series, respectively.

Twelve conditions were selected for minimum condition tests based on the test objectives, the minimum theoretical acid quantity calculations and best technical judgment. The initial nitric acid molar excess for these minimum condition tests varied from 0.3 to 1.1 times the minimum theoretical quantity of nitric acid needed for complete resin destruction. Minimum condition tests were done in 3 M and 5 M nitric acid solutions and at temperatures ranging from 40°C to 70°C for approximately 24 hours.

A large batch resin dissolution and destruction test was run with 5 M nitric acid at an acid volume to resin mass ratio of 100 mL:1 g, which gave an initial acid molar excess of 10 times the minimum theoretical quantity. The test was carried out at 65°C for 9 hours.

Neutralization of the post-resin-destruction nitric acid solution using the caustic resin regeneration solution test was carried out in a 125-mL Erlenmeyer flask. A 73.2 mL aliquot of caustic regeneration solution from the small-column ion exchange test IX4 and a 5 mL aliquot of acidic resin destruction solution from test RKBD-1 were used. The regeneration solution had a hydroxide concentration of approximately 0.43 M. The resin destruction solution had an acid concentration of approximately 3 M. The pH of the regeneration solution and the resin destruction solution was > 14 and 1, respectively. An approximately two-fold (2X) excess of the caustic regeneration solution was used to ensure that a basic (caustic) mixture resulted. Because the combined regeneration solution contained about 1.4 microcurie of Cs-137, the neutralization test was carried out in a radiological fume hood in a radiological laboratory. The test was conducted with the two solutions starting at room temperature, typically 22°C. After combining them the mixture was covered loosely, left at room temperature, and checked intermittently for 24 hours in case of any delayed reactions.

RESULTS

The percentage destruction of SRF resin as a function of time for 3 M, 5 M, and 7 M HNO_3 at various temperatures is presented in Figure 1. The percentage total organic carbon destruction was calculated based on the theoretical maximum concentration of TOC, which was calculated from initial mass of resin used for each test. The time zero was the time when the reaction started. Sample collection was started immediately after the resin beads completely disappeared. Therefore, the first data points shown in Figure 1 (i.e., 0% total organic carbon destruction at time zero) are theoretical values. These results show that resin destruction started during dissolution. Moreover, TOC destruction increases with increasing temperature at the same acid strength (i.e. 5 M nitric acid). These results indicate that the effect of nitric

acid concentration on the destruction of TOC is relatively weak. The TOC destruction at $80^{o}C$ increases very slightly (~ 3% to 5%) with increasing acid strength. The TOC destruction was largely complete after 10 hours. The acid concentrations in the final solutions were the same, within 10%, of the starting concentrations. Final residual TOC concentrations ranged from 500 mg/L to 2000 mg/L.
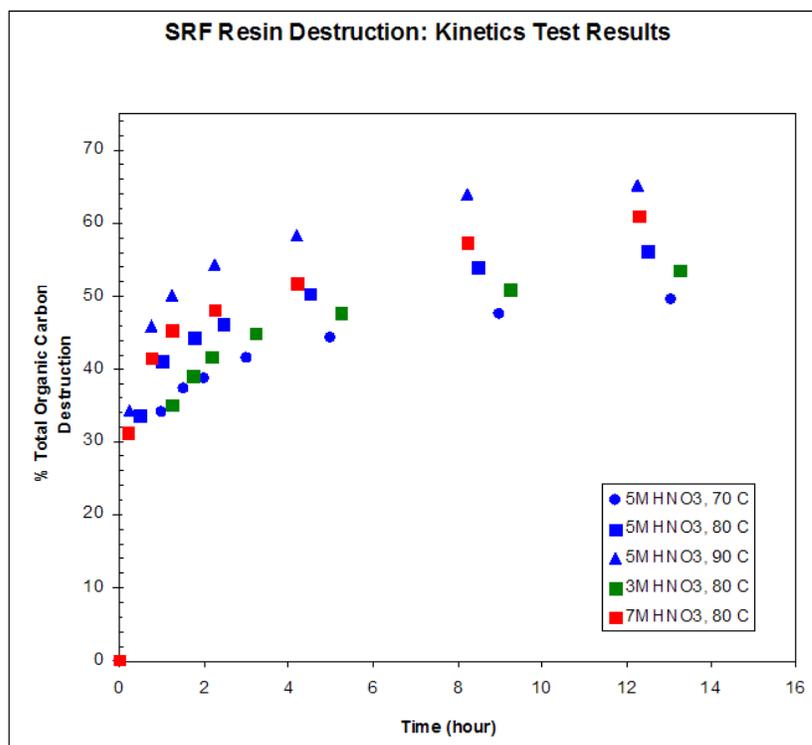
Figure 1. Resin destruction in 3 M, 5 M, and 7 M HNO_3 at various temperatures.

Kinetics data for [TOC] destruction was fitted according to the following empirical rate expression model.

$$Rate = -k \times [TOC]^m \times [acid]^n \qquad \text{(Eq. 1)}$$

where k = reaction rate constant
          [TOC] = concentration of total organic carbon, mol/L
          [acid] = concentration of the nitric acid, mol/L
          m, n, k = constants to be determined by the fit.

    Acid analysis results showed that the acid concentration remained unchanged for all kinetics tests. Therefore, Eq. 1 may be simplified as:

$$Rate = -K \times [TOC]^m \qquad \text{(Eq. 2)}$$

or
$$\ln(rate) = \ln(-\frac{d[TOC]}{dt}) = \ln(K) + m\ln[TOC] \qquad\qquad \text{(Eq. 3)}$$

The constant, K, and reaction order, m, may be determined from the intercept and the slope of $\ln(\frac{d[TOC]}{dt})$ versus ln([TOC]) plot, respectively.

The reaction order and constant K for all 14 kinetics tests are summarized in Table 1. These data show that the TOC reaction order (m), ranges from 4.27 to 11.91. Moreover for each acid concentration, the reaction order varies. These high and varying reaction orders indicate that the TOC destruction reaction may be a very complex reaction system of many series, parallel or independent reactions. Therefore, the calculated reaction order for each test presented in Table 1 is the sum of all individual reaction orders in that particular reaction system. Because the reaction order for each individual reaction may vary from one test to another due to the variation in initial resin mass and other possible experimental variations, the overall reaction order may vary from test to test.

Table 1. Summary of Reaction Order and Constant K

Test ID	HNO_3 Conc (M)	Temperature (^{o}C)	Reaction Order, m	Constant K
KBD-1	3 M	70	10.86	1.086E+04
KBD-2	3 M	80	7.96	2.176E+01
RKBD-1	3 M	80	7.34	1.441E+01
KBD-3	3 M	90	7.09	4.863E+00
KBD-4	5 M	70	11.23	2.186E+04
RKBD-2	5 M	70	9.67	8.368E+02
KBD-5	5 M	80	11.25	1.224E+05
RKBD-3	5 M	80	7.99	6.235E+01
KBD-6	5 M	90	7.22	9.953E+00
RKBD-4	5 M	90	6.17	3.596E+00
KBD-7	7 M	70	9.33	3.392E+02
KBD-8	7 M	80	11.91	3.371E+05
RKBD-5	7 M	80	7.35	2.504E+01
KBD-9	7 M	90	4.27	7.430E-03

Neutralization of the post-resin-destruction nitric acid solution with a caustic regeneration solution from the ion exchange tests proceeded smoothly. No precipitation or gas generation was observed in the neutralization mixture, either immediately after mixing or during the subsequent 24 hours. The color of the final mixture was consistent with simple mixing of the yellow acidic resin destruction solution with the clear caustic regeneration solution. The pH was found to be 13 immediately after mixing and also after 24 hours, indicating complete neutralization of the acidic resin destruction solution.

Organic carbon in the form of sugar will be added to the WTP LAW vitrification feed to regulate the redox potential of the melt. The target carbon (C) to nitrogen (N) ratio is 0.75 [10], where the N is from nitrate and nitrite in the waste. A conservative estimate based on residual TOC observed in these tests and typical nitrite and nitrate levels in the target wastes gives a maximum C/N ratio resulting from digested

resin of 0.0076, almost two orders of magnitude below the target for sugar addition. Based on the stability on neutralization and the relatively insignificant amount of organic carbon, addition of the neutralized resin-destruction liquor to the decontaminated tank wastes for vitrification is a feasible method of disposal for this secondary waste stream.

EPA Method 8270C for semi-volatile organic compounds (SVOC) was used to look for 66 analytes of interest. The list of the 66 semi-volatile organic compounds includes a number of compounds that could form on acid oxidation of polymeric resorcinol formaldehyde, including phenol, benzyl alcohol, 2-methylphenol, 4-methylphenol, nitrobenzene, isophorone, 2-nitrophenol, benzoic acid, and 2,6-dinitrotoluene. None of the SVOC analytes of interest were detected in any of the liquid samples. Several other SVOCs were detected and some tentatively identified. In each case, the estimated concentration is less than the method reporting limit but greater than or equal to the method detection limit. Most of these compounds could not be identified, and confirmation analyses were not conducted when a tentative identification was assigned due to the extremely low concentrations.

EPA Method TO-15 for VOCs was used to look for 75 analytes of interest. Useful data could not be obtained because a good sample separation could not be achieved for all samples. This may have been a result of samples that were too concentrated or incompatibility of the GC column with the sample matrices. The standard TO-15 method and the GC column used are, in fact, intended for analyses of air samples with relatively low VOC concentrations.

The percentage NO_x and nitric oxide (NO) in the off-gas as a function of time is presented in Figure 2. The NO_x and NO concentrations were calculated from the NO_x and NO readings from the NO_x analyzer multiplied by an appropriate calculated dilution factor. The time zero was the time when the reaction started. NO_x and NO measurements were started immediately after the reaction was started. The results show that the off-gas NO_x contains mostly NO. There may be other nitrogen oxide compounds in the NO_x mixture (e.g., NO_2, N_2O, N_2O_4, etc.) but they are at much lower concentrations than NO. These results are consistent with the visual observations of the brown color of the off-gases, as nitric oxide is a brown-colored gas. The results also show that the majority of NO_x generation occurs before the completion of resin dissolution. The NO_x increases quickly from the start of reaction, peaks at approximately 75 minutes, then starts to decline. The rate of change in NO_x concentration decreases noticeably after the complete dissolution of resin beads, at approximately 135 minutes. In addition, there is still more than 5% of NO_x after 8.5 hours, which indicates that the resin destruction process continues to generate NO_x at a slow rate.
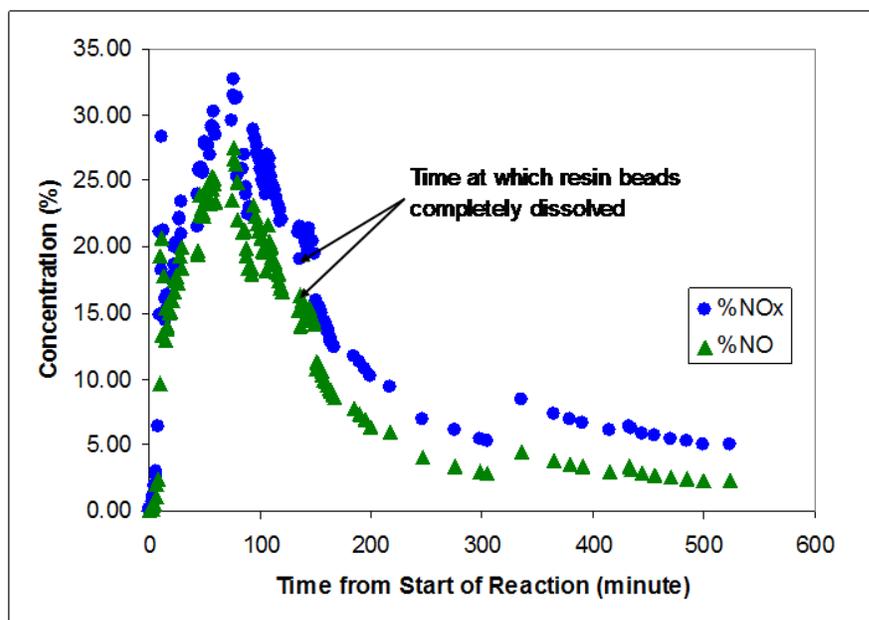
Figure 2. NO$_x$ concentration of the resin dissolution and destruction off-gas.

ION EXCHANGE TEST SUMMARY

Experimental

Complete experimental details have been published elsewhere [2] and are summarized here. Three basic DST simulants and one SST dissolved saltcake simulant were used for testing. One of the DST simulants was tested at two different concentrations (total [Na] = 5.4 M and 4.6 M), for a total of five different feeds. The formulations were derived from evaluation of a suite of Hanford DST wastes (241-AN-101, 241-AN-104, 241-AP-104 and 241-AP-108) and a prototypic dissolved saltcake from the S tank farm. Extensive previous testing with simulants and actual wastes has shown that the SRF ion exchange performance is most affected by the total Na$^+$, K$^+$, Cs$^+$ and OH$^-$ concentrations [4, 5, 6, 7]. Therefore the simulant recipes were restricted to just seven components: Al(NO$_3$)$_3$·9H$_2$O, 50% NaOH, NaNO$_3$, KNO$_3$, NaNO$_2$, NaCO$_3$, and CsNO$_3$. The Cs$^+$ and K$^+$ concentrations in the DST simulants were chosen to bound the concentrations found in the DST wastes. The aluminum and carbonate components are prototypic of the waste and also serve as indicators of effectiveness of the process conditions; aluminum precipitation and/or CO$_2$ gas generation in the bed during elution would indicate insufficient simulant feed displacement. The nitrite ion similarly results in NO$_x$ gas generation during elution if displacement is insufficient.

A Cs-137 tracer was added to the feeds to determine Cs concentrations in effluent samples.

The SRF resin was prepared following a method developed previously [5, 7], with cycling through the Na and hydrogen (H) forms in a beaker, then again after loading in the columns. The ion exchange systems

were comprised of small columns (20 cm long by 1.5 cm dia.), low-flow (0.2 to 1.0 mL/min) positive displacement pumps, stainless steel valves and polyethylene tubing. Valved quick-disconnects were installed in-line to allow for switching of fluid flow direction. Two columns were equipped with jackets for temperature control using a water circulator. The resin bed volumes were nominally 10 mL in the Na form.

The generic ion exchange process steps are shown in Table 2. The dense regenerant was reformulated following shakedown testing to eliminate nitrite which caused NOx generation in the resin bed. The regeneration was also divided into two steps, with the first three bed volumes using only 1 M NaOH to prevent bed floating and fluidization. A second 15 BV load cycle was conducted in six tests to gauge elution effectiveness. An overview of the process conditions for the tests is shown in Table 3.

Table 2. Generic Ion Exchange Process Steps

Process step	Feed Solution	Process Volume, BV[a]	Process Flowrate, BV/h	Process Flow Direction
Loading (Cycle 1)	Simulant	200 - 300	3 to 6	Downflow
Feed displacement	0.1 M NaOH	3.6 – 7.0	3 to 4	Downflow
Elution	0.5 M HNO_3	7.6 - 17	1.5 – 2.1	Upflow
Regeneration	1 M NaOH	2.8 – 3.3	2.6 – 3.3	Upflow
Regeneration[b]	1 M NaOH/6 M $NaNO_3$ or 2 M NaOH/3 M $NaNO_3$	3.0 – 4.4	2.6 – 3.3	Upflow
Loading (Cycle 2)	Simulant	15	3	Downflow
(a) BV = bed volume in regeneration solution (10 mL in the Na-form).				
(b) 1 M NaOH/6 M $NaNO_3$ was used for Wave 1 testing, 2 M NaOH/3 M $NaNO_3$ was used for Wave 2 testing.				

Table 3. Overview of Variable Process Conditions

Test	Simulant	Column	Loading Flow Rate (BV/h) 1st/2nd Cycle	Elution Temperature	Elution Volume	Regeneration Volume
				Wave 1		
E1	DST-1 conc.	1	6.3/3.1	15°C	7.8 BV	5.9 BV
IX1	DST-1 conc.	1	5.6/3.2	Ambient[a]	9.4 BV	6.3 BV
IX2	DST-2	1	6.0/NA	Ambient[a]	7.6 BV	6.1 BV
				Wave 2		
E2[c]	DST-1	2	3.0/3.0	10°C[b]	17 BV Lead 12 BV Lag	7.5 BV
IX3	DST-3	1	2.9/3.0	Ambient[a]	10 BV	6.9 BV
IX4	DS	1	3.1/3.0	Ambient[a]	9.1 BV	7.5 BV
IX5[c]	DST-2	1	3.0/3.0	Ambient[a]	12 BV	7.2 BV
(a) Typically 21 °C ± 2 °C						
(b) Lead column only, lag column was eluted at ambient.						
(c) E2 lag column and Test IX5 added to Wave 2 based on results of Wave 1.						
(d) All tests included a second load cycle of nominally 15 BV, except IX2 (no second load cycle).						

RESULTS

The Cs loading results for tests IX5, E2, IX3 and IX4 are shown in Figure 3. Bed volumes processed are plotted on the x-axis against the Cs effluent concentration on a probability scale on the y-axis. The concentration is taken as the concentration of Cs in the effluent sample, C, relative to that in the feed, C_0, and expressed as a percentage. The probability scale is the inverse of the Gaussian cumulative distribution function, so a plot of this function on this scale appears as a straight line. An ideal breakthrough curve is, to a first approximation, a cumulative Gaussian distribution function. This scale has two advantages: 1) making low C/C_o data easily readable so that the initial load performance is discernable and 2) easily estimating extrapolation to 50% breakthrough in the sigmoidal region.
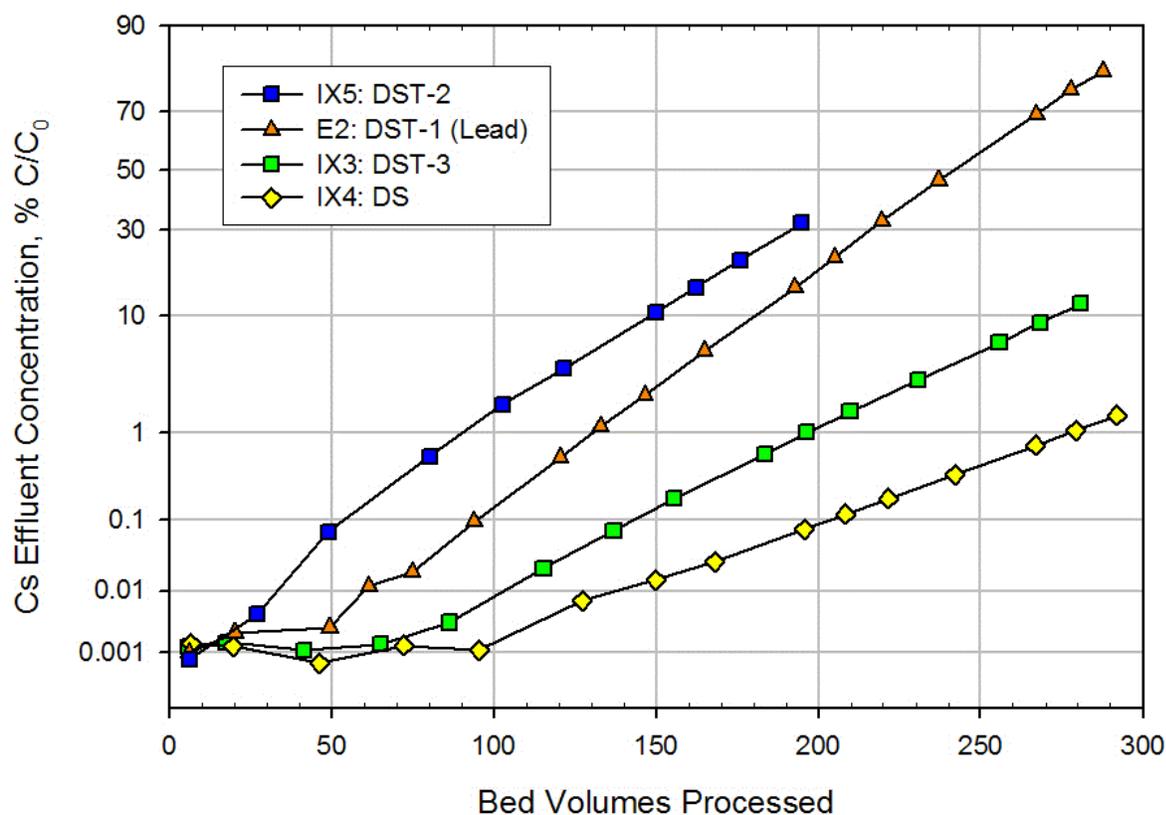
Figure 3. Comparison of four loading curves. The K/Cs ratios in the feeds range from 913 to 2,237. The Na/Cs ratios in the feeds range from 48,583 to 179,533. Flow rates are nominally 3 BV/h and total [Na] is 5.7 M, 4.6 M, 4.7 M, and 4.9 M for DST-2, DST-1, DST-3 and DS, respectively.

The Cs decontamination objective (at least 100 BV processed before 1% breakthrough) is met for the DST-1, DST-3 and DS feeds, and likely would be met for DST-2 at a lower concentration of 5 M total [Na]. The [Cs] and [K] in the DST-1, DST-2, DST-3 and DS simulant feeds span the ranges of [Cs] and [K] found in the five target wastes, AP-104, AP-108, AN-101, AN-104, and dissolved S-saltcake composite. Based on the results presented in Figure 3, performance for the expected waste feeds at 5 M total [Na] and loaded at 3 BV/h flow rate is within the NTCR design basis. Modeling to determine the optimum concentration and flow rate for each actual waste feed is recommended; it is possible that the amount of water and Na added as process chemicals could be reduced by running the wastes with lower

[K] and [Cs] at higher total concentration. The data in this study can be used for validation of such modeling.

Elution curves at 22ºC, 15ºC, and 10ºC are shown in Figure 4, with bed volumes eluted on the x-axis and the eluate sample concentration on a log scale on the y-axis. The concentration is expressed relative to the feed concentration, C_0. The resin beds were loaded comparably prior to elution: 9 – 10 mg Cs/g resin, 70% - 80% Cs breakthrough. There was no major impact on the elution over the temperature range tested. Therefore lower-than-ambient elution appears feasible for NTCR pilot plant operation, and a lower than ambient elution temperature, down to 10ºC, is recommended in order to slow degradation of the resin by oxidation during elution.
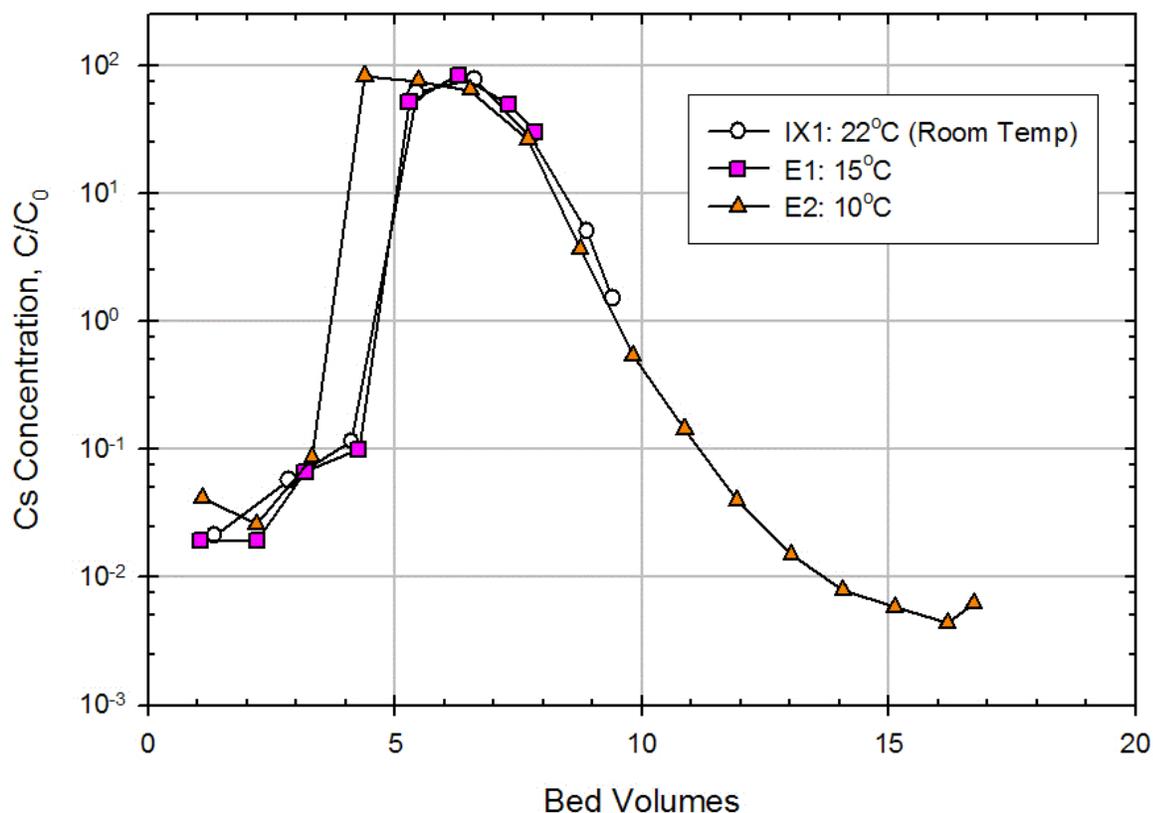
Figure 4. Elution at three different temperatures. Resin beds were comparably loaded prior to elution: 9 – 10 mg Cs/g resin, 70% - 80% Cs breakthrough.

Results of the tests discussed in detail elsewhere [2] also show that the proposed abbreviated LAW displacement is feasible for the NTCR, with some modification. It was found that a four bed volume feed displacement, with no subsequent water rinse, was sufficient to displace the feed prior to elution. The standard WTP protocol for flushing the bed between loading and elution is to use 3 BV of 0.1 M NaOH followed by 3 BV of a water rinse [4]. Reducing this to only 4 BV of 0.1 M NaOH for the NTCR represents a decrease in the flush volume of 33% relative to the WTP flowsheet.

Results presented and discussed in detail in [2] indicate that an upflow elution volume of 8 BV is expected to be sufficient to elute the NTCR <u>lead</u> column. Relatively short elutions used in three tests (8 BV – 10 BV) resulted in Cs breakthroughs on the subsequent loads that could easily be removed to below the Cs removal design basis by a lag column. The highest observed breakthrough on a second load, for example, was only 0.39 % of the feed concentration, and this level of Cs was easily removed by

the lag column in all tests. The Cs breakthrough observed on the second load appears to come from Cs in the resin bed that was not completely removed during elution, and drops over the first 10's of bed volumes. Elution of the lag column can be similarly short if eluted prior to significant loading and breakthrough. A 9 BV lag column elution is expected to be sufficient if the resin is loaded to a maximum of 2 mg Cs per g resin.

Upflow resin conversion with a high density solution was successful after eliminating nitrite (NO_2^-) from the solution composition and implementing a two-solution process. Initial tests with the proposed solution (1M NaOH, 3M $NaNO_2$, 3M $NaNO_3$) resulted in floating of the (H-form) resin bed and severe gas generation in the bed. The gas generation was attributed to nitrite (NO_2^-) in the high density regenerant solution contacting H^+ in the resin bed. The H^+ is present from residual eluant (0.5 M HNO_3), and from conversion of the H-form resin to the Na-form, which releases H^+. The dense regenerant was reformulated to eliminate the nitrite: 1 M NaOH, 6 M $NaNO_3$. This resulted in conversion of the resin to the Na-form with no gas generation, but the resin bed floated in the column when the dense solution was fed upflow to the column. Therefore a two-solution process was implemented: 3 BV of 1 M NaOH followed by 3 BV of 1 M NaOH, 6 M $NaNO_3$. This process converts the resin to the Na form without raising the bed and without gas generation. It also leaves the resin bed immersed in a dense solution prior to introduction of feed on the next load cycle, which prevents disruption of the top surface of the resin bed. Several of the tests were run using simulants at 5 M total [Na] or less to improve performance. The dense conversion solution was reformulated for these tests to 2 M NaOH, 3 M $NaNO_3$. Lowering the total Na in the regenerant reduces the amount of Na added to the waste stream while retaining the benefits of the dense conversion solution. Raising the NaOH/$NaNO_3$ ratio provides more hydroxide for eluate and dissolved resin liquor neutralization.

The feed loading flow rate was varied from 3.0 BV/h to 6.3 BV/hr. The higher flow rates significantly reduced the effectiveness of Cs decontamination. The bed volumes processed to 1% Cs breakthrough, for example, dropped from 90 BV to 50 BV when the flow rate was increased from 3.0 BV/h to 6.0 BV/h for the DST-2 simulant. The ion exchange performance will improve with reduced flow rate as long as the kinetics are limited by diffusion of Cs from the feed solution to the resin beads, so performance may be even better at flow rates below 3 BV/hr. However, this improvement must be balanced against the increased time required to process feed. A loading flow rate of 3 BV/h is recommended for the NTCR pilot plant, but modeling is recommended for optimizing this.

The elution flow rate was also varied between 1.5 BV/h and 2.1 BV/hr. The fastest rate (2.1 BV/hr) appears to give the sharpest elution curve and highest peak maximum, suggesting the most efficient elution, but experimental uncertainty in the amount of Cs loaded and eluted, and differences in the breakthrough extent prior to the elution, make it difficult to determine which flow rate resulted in the most efficient elution. In the absence of more data, an elution flow rate of 1.5 BV/h is recommended for the NTCR pilot plant, and modeling to optimize this flow rate is recommended.

Elution and regeneration flow rate testing in the pilot plant is also recommended, due to the higher superficial velocity of the eluant in the resin beds at the larger scale. The superficial velocity is the velocity of the fluid flowing past the resin beads. This increases for a given flow rate measured in BV/h as the resin bed size increases. Uneven resin conversion fronts were observed for all elutions and to a lesser extent for the regenerations. This fingering may be amplified by the higher superficial velocity. The increased upward force of the fluid at the higher superficial velocity may also be sufficient to fluidize or float the resin beds.

No loading tests were conducted in this study in which the simulant concentration was the only variable, but comparison of several loading curves [2] suggests that reducing the feed concentration from 5.4M [Na] to 4.6M [Na] improves the performance as much as reducing the flow rate from 6 BV/h to 3 BV/hr. Based on these results a maximum feed concentration to the NTCR of 5.0 M [Na] is recommended. Additional tests of performance versus feed concentration are recommended.

CONCLUSIONS

Bench scale test results support development of an NTCR demonstration unit (pilot plant) for scale-up of testing. The results indicate that a rapidly deployable NTCR unit is feasible and can allow an early start of Hanford tank waste remediation by providing cesium decontaminated feed to the LAW vitrification facility in the interim before the Pretreatment Facility is operational. Specific conclusions are provided below.

Bench Scale Resin Dissolution and Destruction Tests

- Optimum process conditions for safe execution of the NTCR pilot plant (NTCR-PP) resin destruction process tests were determined. The SRF resin can be completely dissolved using moderate nitric acid concentrations (3 M - 5 M) and moderate temperatures (50 ^{o}C - 70 ^{o}C), and 50% or more of the total organic in the SRF resin can be destroyed within 10 hours at higher nitric acid concentrations (5M – 7 M) and higher temperatures (80 ^{o}C - 90 ^{o}C).

- Sufficient data were collected to understand the reaction kinetics for input to the design and operation of the NTCR-PP. However, a common rate expression as a function of the total organic carbon concentration in solution, [TOC], could not be derived. This is attributed to complexity of the organic destruction process, which likely proceeds through many sequential and parallel pathways and results in a high and variable reaction order.

- Initial characterization of the spent resin destruction process solutions was made. The acid concentrations in the final solutions are the same, within 10%, of the starting acid concentrations. Semi-volatile organic compound analytical results show that none of the 66 analytes of interest were detected in any of the nine liquid samples.

- The acidic resin dissolution solution can be neutralized by the caustic resin regeneration solution with no precipitation or gas generation. This will allow this solution to be vitrified along with the decontaminated tank wastes.

- The resin dissolution and destruction off-gas contains a significant amount of NO_x (i.e., ~35% at peak) of which NO is the predominant component. The NTCR design is expected to contain an off-gas scrubbing system to treat the off-gas.

- In-column dissolution and destruction of spent resin is not recommended due to the difficulty in controlling the reaction in the confines of an ion exchange column. However, *in situ* spent-resin dissolution and destruction can be achieved by sluicing the spent resin with nitric acid to a separate vessel for dissolution and destruction.

Implementation of the *in-situ* resin destruction will eliminate the need for a separate resin disposal pathway and associated equipment. Based on these results the process is currently envisioned to involve sluicing the resin from the column to a separate reaction vessel. The nitric acid concentration and temperature will be minimized. It appears that a nitric acid concentration of 3 M - 5 M and a temperature up to 70 ^{o}C will be sufficient. Additional control of the process can be achieved by starting at a relatively low temperature and slowly increasing the temperature to the final target value.

Bench Scale IX Tests

- Satisfactory Cs decontamination of at least 100 BV of three different tank waste simulants was demonstrated. The simulants cover the range of the expected K and Cs concentrations in the candidate feeds.

- An abbreviated LAW displacement, short upflow elution, and upflow resin regeneration using a dense regenerant were successfully demonstrated. The SRF cesium ion exchange performance was within the NTCR design basis. Some adjustments to the proposed process operations parameters were required.

- The NTCR process can tolerate differences in SRF IX performance resulting from feed variability in the range expected. Performance for the expected waste feeds is within the NTCR design basis.

- Reduced temperature elution was successfully demonstrated at both 10^oC and 15^oC.

Recommended NTCR demonstration unit ion exchange process operating parameters were identified based on these results. A summary is provided in Table 4.

Table 4. NTCR Ion Exchange Process Operation Summary (Per Column)

Operation	Process Solution	Volume[a] (BV)	Flow (BV/h)	Duration (h)	Direction
LAW Processing	LAW @ 5M Na	100+ [b]	3	33+	Down
LAW Displacement	0.1M NaOH	4	3	1.3	Down
Lead Column Elution (T ≤ RT)[c]	0.5M HNO_3	8	1.5	5.3	Up
Lag Column Elution[d] (T ≤ RT)[c]	0.5M HNO_3	9	1.5	6	Up
Regeneration	1M NaOH	3	3	1	Up
	2M NaOH, 3M $NaNO_3$	3	3	1	Up

a) Allowances for system holdup may vary with system configuration and processing details (e.g., switching flow direction may increase holdup).
b) To 1% breakthrough on the lead column.
c) Lower than ambient elution temperature, down to 10°C, is recommended.
d) Lag column eluted as soon as breakthrough is observed; multiple load-elute cycles on the lead column are expected before lag column breakthrough.

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