Ion Exchange Temperature Testing with SRF Resin-12088

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ABSTRACT

Ion exchange using the Spherical Resorcinol-Formaldehyde (SRF) resin has been selected by the U.S. Department of Energy's Office of River Protection for use in the Pretreatment Facility of the Hanford Tank Waste Treatment and Immobilization Plant (WTP) and for potential application in an at-tank deployment for removing Cs-137. Recent proposed changes to the WTP ion exchange process baseline indicate that higher temperatures (50°C) to alleviate post-filtration precipitation issues prior to reaching the ion exchange columns may be required. Therefore, it is important to understand the behavior of SRF resin performance under the conditions expected with the new equipment and process changes. This research examined the impact of elevated temperature on resin loading and resin degradation during extended solution flow at elevated temperature (45°, 50°, 55°, 60°, 65°, 75°C). Testing for extended times at elevated temperatures showed that the resin does degrade and loading capacity is reduced at and above 45°C. Above 60°C the resin appears to not load at all.

INTRODUCTION

Ion exchange using the Spherical Resorcinol-Formaldehyde (SRF) resin has been selected by Bechtel National, Inc. (BNI) and approved by the Office of River Protection (ORP) for use in the Pretreatment Facility (PTF) of the Hanford Tank Waste Treatment and Immobilization Plant (WTP). SRF is an engineered spherical form of the older Ground Gel Resorcinol-Formaldehyde (GGRF) resin, also termed Resorcinol-Formaldehyde (RF), characterized in previous work [1].

The SRF resin has been shown to be effective for removal of Cs-137 from Hanford AP-101 and AN-102 actual tank waste supernatants [2,3] and for achieving the proposed spent waste classification criteria of <100 nCi transuranic (TRU) and <60 μCi Cs-137 per gram of spent resin [4,5]. The SRF resin was also shown to exhibit excellent kinetic [6,7] and hydraulic behavior [8] compared to GGRF. Therefore, BNI has designated SRF as the baseline resin for cesium removal due to its good performance in these areas (loading, elutability, kinetic and hydraulic behavior) and relatively low cost.

Prior work has focused primarily on loading behavior for 5 $\underline{M}$ sodium (Na) solutions at 25°C. Recent proposed changes indicate that higher temperatures (50°C) to alleviate post-filtration precipitation issues prior to reaching the ion exchange columns may be required. Therefore, it is important to understand the behavior of SRF resin performance under the conditions expected with the new equipment and process changes.

EXPERIMENTAL

The experimental setup for ion exchange kinetics is based upon a differential column concept described in detail previously [9]. This concept uses a thin resin bed exposed to a feed solution with nearly uniform uptake throughout the bed. In essence, this setup is designed to determine resin adsorption properties of a differential cross-section of an ion exchange column. Implementation requires a controlled flow of liquid through the resin bed, a controlled temperature throughout the system, and continuous homogenization of the liquid phase. A schematic of the kinetics experimental setup is shown in Fig. 1.

Resin test samples were placed in the containment reservoir held in place between stainless steel screens. Void space within the apparatus was minimized using resin supports. The simulant was fed through the column in an up-flow manner to minimize the amount of air initially in the system. The system remained closed with the exception of a small vent/sampling port. The resin bed path length and diameter were ~10.1 mm and ~15.0 mm respectively, giving a resin bed volume of 1.8 mL.
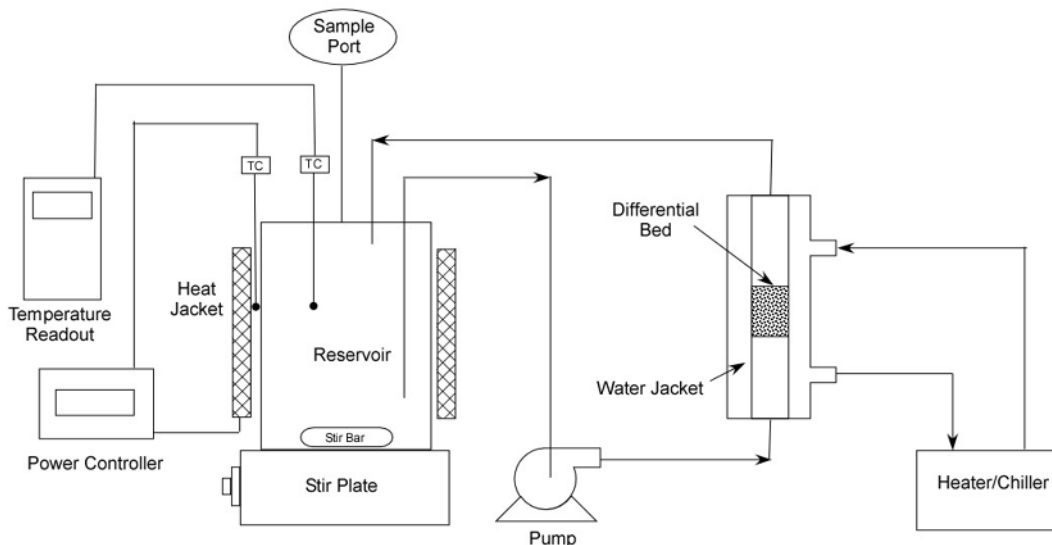

Fig. 1. Differential Column Ion Exchange Kinetics Apparatus

Stock simulant solutions for kinetics testing were prepared from NaOH (standard concentrated solution), $Al(NO_3)_3 \cdot 9H_2O$ solid, $NaNO_3$ solid, NaCl solid, and $CsNO_3$ solid. The chemicals were blended into de-ionized (DI) water in the order listed, with each chemical being completely dissolved prior to the addition of the next chemical. All stock solutions were analyzed by

inductively coupled plasma-optical emission spectroscopy (ICP-OES), inductively coupled plasma-mass spectroscopy (ICP-MS), and ion chromatography (IC) for cationic and anionic species to confirm proper preparation within ± 20% tolerance.

Small column ion exchange loading tests were performed near prototypic flow conditions with feed recycle until equilibrium loading was achieved in order to evaluate the effect of temperature on cesium uptake. The impact of resin degradation during extended solution flow using elevated temperature (45°, 50°, 55°, 60°, 65°, 75°C) was also examined. Tests performed are shown in Table I.

Table I. Cesium Loading Kinetics Experimental Design

| Run ID[f] | Ion Exchange Kinetic Loading Conditions | | | | | | | | Column Elution Conditions [d] | | | | |
	h [a][b]	T °C	$Cs^{(c)}$ C/C_0	Flow cm/min	Na M	OH M	Initial Cs, M		T °C	BVs	BV $h^{(h)}$	HNO_3 M	Cs M
Test-1-A-4B	720	45	0.52	<0.1[e]	8.0	4.0	5.8E-05		25	25	2.8	0.25	0
Test-1-A-5	10	45	0.52	6	5.0	1.67	2.4E-05		25	25	2.8	0.25	0
Test-1-B-4B	720	65	0.52	<0.1[e]	8.0	4.0	2.9E-05		25	25	2.8	0.25	0
Test-1-B-5	10	50	0.52	6	5.0	1.67	2.4E-05		25	25	2.8	0.25	0
Test-1-C-4B	720	75	0.52	<0.1[e]	8.0	4.0	3.8E-05		25	25	2.8	0.25	0
Test-1-C-5	10	50	0.52	6	5.0	1.67	2.4E-05		25	25	2.8	0.25	0
Test-1-D-1[g]	10	25	0.52	6	5.0	1.67	2.4E-05		25	25	2.8	0.25	0
Test-1-E-4B	720	50	0.52	<0.1[e]	8.0	4.0	5.8E-05		25	25	2.8	0.25	0
Test-1-E-5	10	50	0.52	6	5.0	1.67	2.4E-05		25	25	2.8	0.25	0
Test-1-F-4B	720	55	0.52	<0.1[e]	8.0	4.0	5.8E-05		25	25	2.8	0.25	0
Test-1-F-5	10	55	0.52	6	5.0	1.67	2.4E-05		25	25	2.8	0.25	0
Test-1-G-4B	720	60	0.52	<0.1[e]	8.0	4.0	5.8E-05		25	25	2.8	0.25	0
Test-1-G-5	10	60	0.52	6	5.0	1.67	2.4E-05		25	25	2.8	0.25	0

(a) Resin loading required approximately 10 h to achieve kinetic equilibrium. Samples were collected periodically to define the cesium uptake curve (e.g., 0, 6, 12, 18, 24, 36, 48, 60, 80, 120, 180, 240, 600 min).

(b) The 10 hr kinetics tests were completed at temperatures specified for each run. Six extended duration (720 h) solution flow tests were to be completed at 45°, 50°, 55°, 60°, 65° and 75°C.

(c) The total simulant solution volume was varied to target an expected loading of 0.52 C/C_0.

(d) BV=bed volume. Elution with 0.25 M HNO_3 began after feed displacement (7.5 BV 0.1 M NaOH) and water rinse (7.5 BV DI Water) solutions had been passed through the column. A single elution composite sample was collected and analyzed.

(e)   The actual flow velocity was limited by the pump configuration. The flow velocity was determined at the time of experimentation and was estimated to be approximately 0.08 cm/min.

(f) Each test series (e.g., A, B, C, D, E, F, and G) represented an independent ion exchange column that was loaded and eluted one or more times using the conditions listed. The exact bed volume (BV) of the ion exchange resin depended upon final construction of the apparatus but was ~1 to 2 mL.

(g) The final column (Test 1-D-1) served as a comparison to prior kinetics testing (Nash et al. 2006).

(h) The flow rate for elution was to be approximately 2.8 BV/h. The flow rate was approximately 5 mL/h and the equivalent BV/h varied slightly with the exact bed volume for each column.

Three small (<10 mL) batches of fresh SRF resin were contacted with 0.5 $\underline{M}$ nitric acid for 70 days. One of the three batches was stored at ~25°C, one was stored at ~45°C, and another was stored at ~55°C. A fourth batch of fresh resin was not exposed to nitric acid and was stored at ~25°C as a control sample. After 70 days, each of the four batches of SRF resin was converted to the sodium form, and then contacted with the cesium loading solution of 5 $\underline{M}$ Na, 1.67 $\underline{M}$ OH, and 2.4E-05 $\underline{M}$ Cs.

RESULTS AND DISCUSSION

Resin was loaded at a very low flow rate (~5 mL/h) for 336 hours at several elevated temperatures. Due to resin degradation and column plugging, the tests were not able to run a full 720 hours as planned. Testing for extended time at elevated temperature showed that the resin degraded above 45°C, and above 60°C it appeared to not load at all. It was observed that the resin disintegrated at 75°C until not much was left and partially disintegrated at 65°C, which caused the column to plug in both tests after ~336 hours. The extended flow test results are shown in Figure 2.
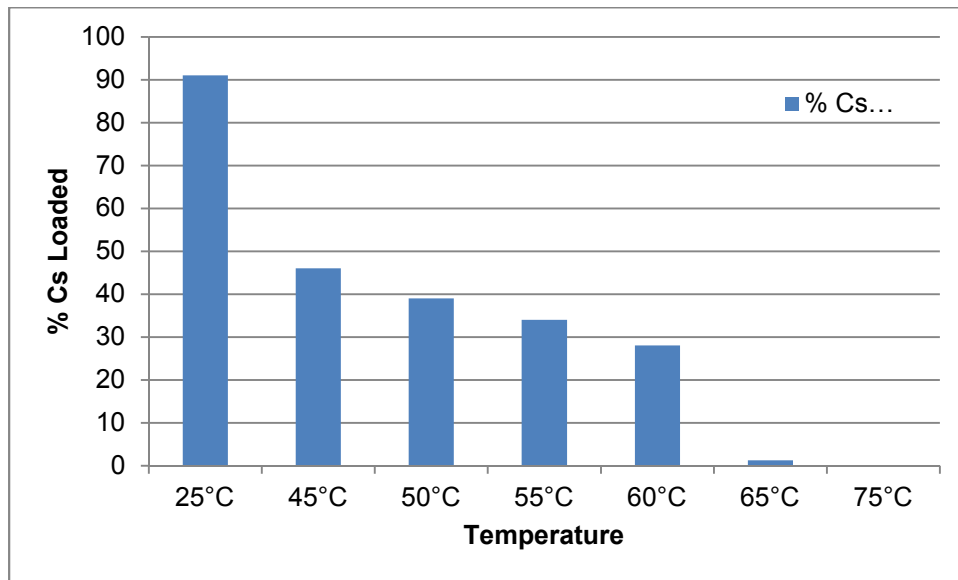

Fig 2. Temperature Effect on Extended Flow Testing

While temperature doesn't appear to affect the initial loading kinetics, it definitely plays a part in the equilibrium loading capacity of the resin, as shown in Figure 3. The 25°C loading had the highest equilibrium loading capacity, and the 60°C loading had significantly reduced capacity. There appeared to be a smaller difference, but regular decrease in loading capacity between 45°C and 55°C.
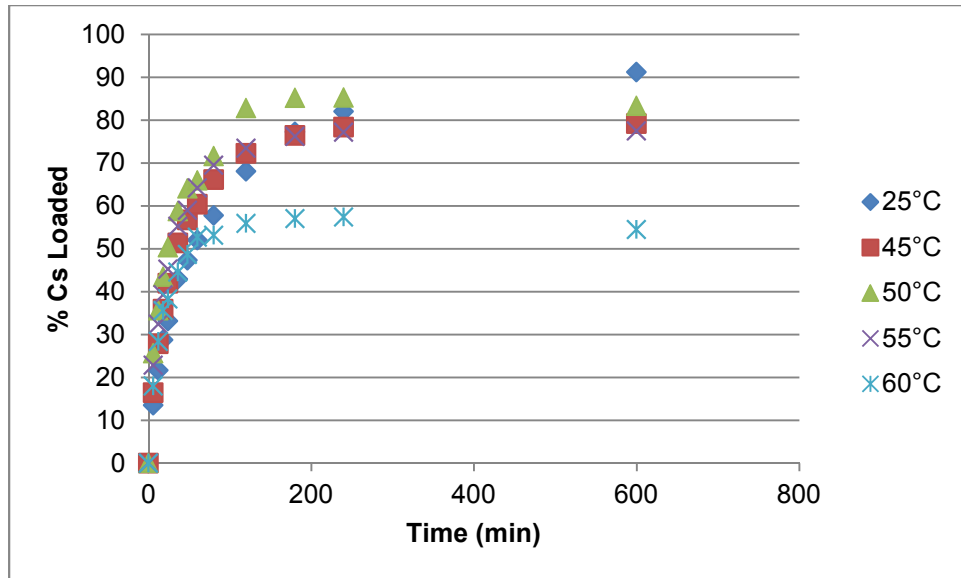
Fig 3. Effect of Temperature on Loading at Equilibrium Conditions

The resin that had been aged in an acid environment showed significant effects at elevated temperatures, as can be seen in Figure 4. The resin that was aged at 25°C in acid had very comparable loading results to the resin that was kept in de-ionized water at 25°C. However, the resin that was kept at 45°C in acid showed reduced loading capacity and some degradation. The resin that was kept at 55°C in acid completely dissolved and was unable to be loaded for comparison.
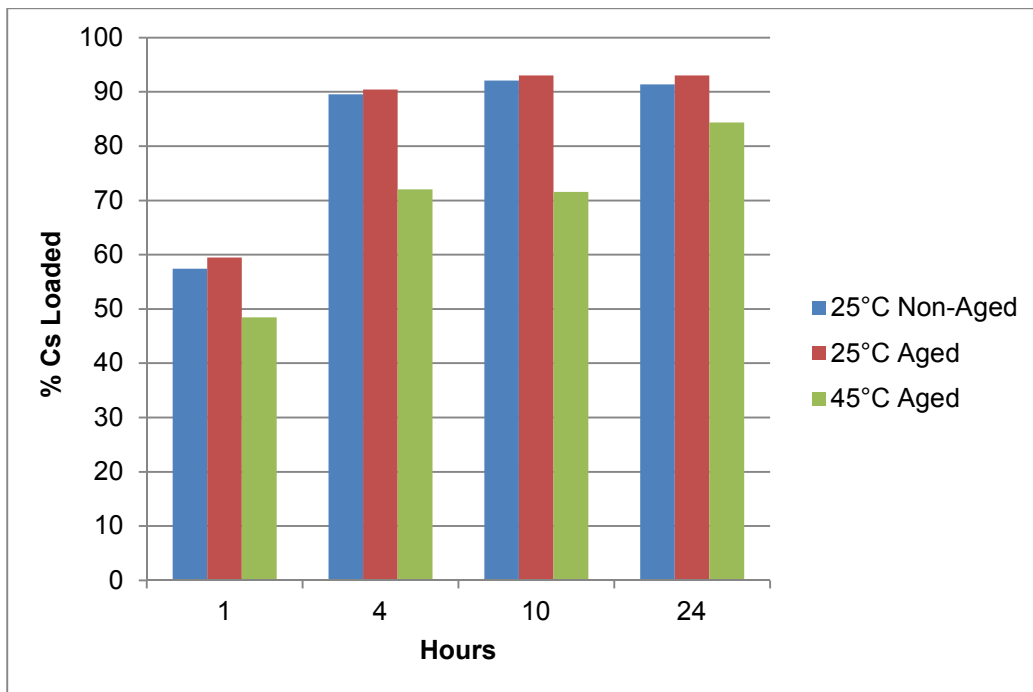

Fig 4. Resin Loading after 70 Days of Acid Aging

CONCLUSIONS

Testing at elevated temperatures showed that the resin degrades and loading capacity is reduced at and above 45°C. The point of noticeable degradation was not determined but appears to occur between 25°C and 45°C. Above 60°C the resin appears to not load at all. It was observed that the resin disintegrated at 75°C until not much was left and partially disintegrated at 65°C, which caused the column to plug in both tests after ~336 hours. The results indicate that WTP will lose resin loading capacity if the ion exchange process is performed above 25°C, and the resin will disintegrate above 65°C.   Therefore, WTP will have a restricted operating range of temperatures to perform the ion exchange process with this resin. PNNL and WTP are currently evaluating the operating limits of the resin in further detail.

Aging in 0.5 $\underline{M}$ HNO$_3$ also caused the resin to lose capacity above 25°C and to completely dissolve at 55°C. Again, WTP will have a restricted operating range of temperatures when eluting the resin with nitric acid in order to maintain resin loading capacity and avoid disintegration of the resin.

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