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PILOT-SCALE HYDRAULIC TESTING OF RESORCINOL FORMALDEHYDE ION EXCHANGE RESIN

SUMMARY

Savannah River National Laboratory (SRNL) performed pilot-scale hydraulic/chemical testing of spherical resorcinol formaldehyde (RF) ion exchange (IX) resin for the River Protection Project–Hanford Tank Waste Treatment & Immobilization Plant (WTP) Project. The RF resin cycle testing was conducted in two pilot-scale IX columns, ¼ and ½ scale. A total of twenty-three hydraulic/chemical cycles were successfully completed on the spherical RF resin. Seven of the cycles were completed in the 12" IX Column and sixteen cycles were completed in the 24" IX Column.

Hydraulic testing showed that the permeability of the RF resin remained essentially constant, with no observed trend in the reduction of the permeability as the number of cycles increased. The permeability during the pilot–scale testing was 2 $^{1}/_{2}$ times better than the design requirements of the WTP full-scale system. The permeability of the resin bed was uniform with respect to changes in bed depth. Upflow Regeneration and Simulant Introduction in the IX columns revealed another RF resin benefit; negligible radial pressures to the column walls from the swelling of resin beads. In downflow of the Regeneration and Simulant Introduction steps, the resin bed particles pack tightly together and produce higher hydraulic pressures than that found in upflow. Also, upflow Simulant Introduction produced an ideal level bed for the twenty cycles completed using upflow Simulant Introduction. Conversely, the three cycles conducted using downflow Simulant Introduction produced an uneven bed surface with erosion around the thermowells.

The RF resin bed in both columns showed no tendency to form fissures or pack more densely as the number of cycles increased. Particle size measurements of the RF resin showed no indication of particle size change (for a given chemical) with cycles and essentially no fines formation. Micrographs comparing representative bead samples before and after testing indicated no change in bead morphology. The skeletal density of the RF resin in the 24" IX Column increased slightly with cycling (in both hydrogen and sodium form). The chemical solutions used in the pilot-scale testing remained clear throughout testing, indicating very little chemical breakdown of the RF resin beads. The RF resin particles did not break down and produce fines, which would have resulted in higher pressure drops across the resin bed.

Three cesium (Cs) loading tests were conducted on the RF resin in pilot-scale IX columns. Laboratory analyses concluded the Cs in the effluent never exceeded the detection limit. Therefore, there was no measurable degradation in cesium removal performance.

Using the pilot-scale systems to add the RF resin to the columns and removing the resin from the columns was found to work well. The resin was added and removed from the

columns three times with no operational concerns. Whether the resin was in sodium or hydrogen form, the resin flowed well and resulted in an ideal resin bed formation during each Resin Addition. During Resin Removal, 99+ % of the resin was easily sluiced out of the IX column.

The hydraulic performance of the spherical RF resin during cycle testing was found to be superior to all other tested IX resins, and SRNL testing indicates that the resin should hold up to many cycles in actual radioactive Cs separation. The RF resin was found to be durable in the long term cycle testing and should result in a cost saving in actual operations when compared to other IX resins.

INTRODUCTION

Savannah River National Laboratory (SRNL) contracted with Bechtel National Incorporated on the River Protection Project–Hanford Tank Waste Treatment & Immobilization Plant project to perform pilot-scale hydraulic testing of spherical resorcinol formaldehyde (RF) ion exchange resin and demonstration of cesium removal from simulated liquid radioactive waste. A total of twenty-three hydraulic/chemical cycles where successfully completed on the spherical RF resin in the pilot-scale ion exchange (IX) column testing at the Savannah River National Laboratory. Seven of the cycles were completed in the 12" IX Column and sixteen cycles were completed in the 24" IX Column. This paper will mainly discuss the testing and results of the 24" IX Column. Details of this testing is documented in WSRC-TR-2005-00570.

TEST FACILITY

The ion exchange (IX) column shown in Figure 1, was constructed from a section of 316L, 24" stainless steel pipe and two sections of 24" clear acrylic pipe. The column has an inside diameter of 59 cm (23.25"), and is a 44%-scale version of the Waste Treatment Plant (WTP) IX column, which will nominally be described as half-scale. An acrylic section was on top of the SST section for observing the RF bed during operation. The other acrylic section was below the SST section for viewing below the bed. The resin was mostly contained within the stainless steel section of the column due to anticipated bed stresses.

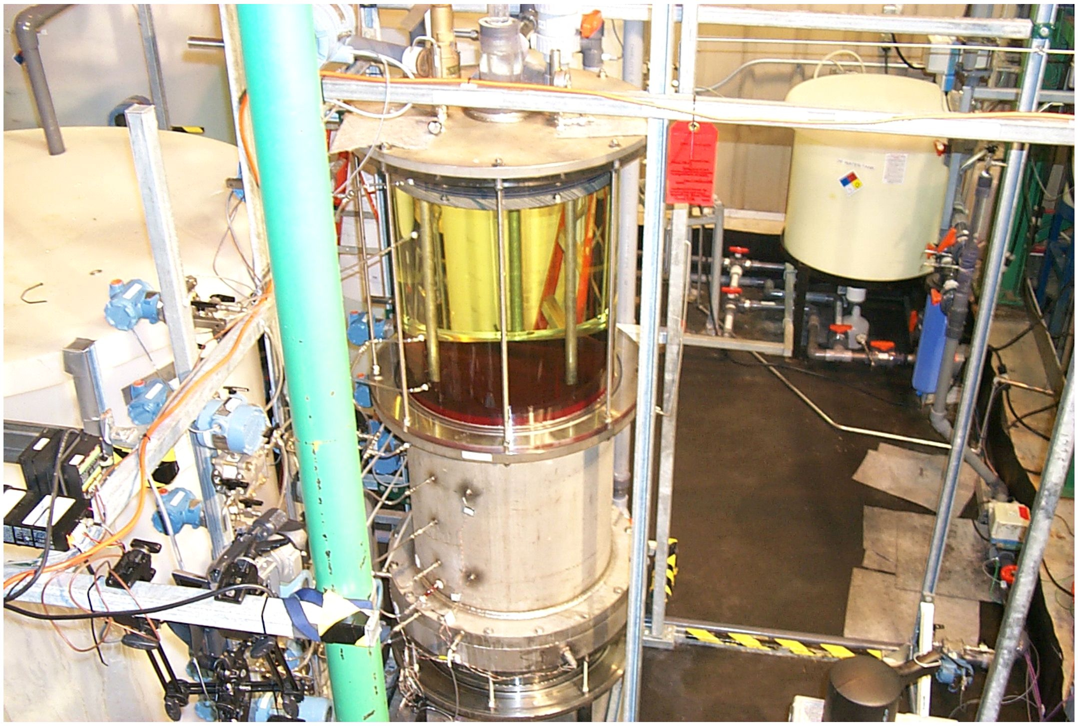

Figure 1. 24" IX Column, RF Resin Test

The overall height of the IX column was approximately 218 cm (86"). The lower section (below the resin support screen) was 17.8 cm (7") high to produce a volume of about 80 liters (2.8 ft^3) or 0.4 BV. The upper section was 75.4 cm (29.7") high to produce a volume of 195.7 L (6.9 ft^3) above the bed, providing for 85% fluidization (volume between sodium form bed and upper impingement plate).

Two 1" diameter stainless steel tubes (with caps) were used to simulate thermowells in the WTP column design. The tubes were inserted into the area above the resin support screen through aligned holes in the upper flange, the upper distributor plate and the upper impingement plate. The tubes were spaced 135º apart. The ends of the thermowells were inserted to 24.1 cm (9.5") above the resin support screen, which corresponds to a 50% insertion depth in a 600-gallon equivalent bed in the WTP. The interior finish of the stainless steel wall where the resin bed resided was approximately 63 micro-inches, mimic the full-scale design.

Non-radioactive cesium was injected into the simulant supply during some simulant loading steps of the 24" RF Test (as specified by the test matrix). The cesium was injected as a solution of cesium nitrate and simulant. The injection system consisted of a 60-gallon supply tank, a peristaltic pump, and a magnetic flow meter. 104.5 grams of cesium nitrate was added to 55 gallons of simulant and injected at a rate of 96.6 ml/min (0.255 gpm) for 32.5 hours to produce a cesium injection rate of 6.7 mg/liter (simulant flow rate was 1.3 gpm).

Figure 2 is a P&ID drawing of the 24" IX Test System.

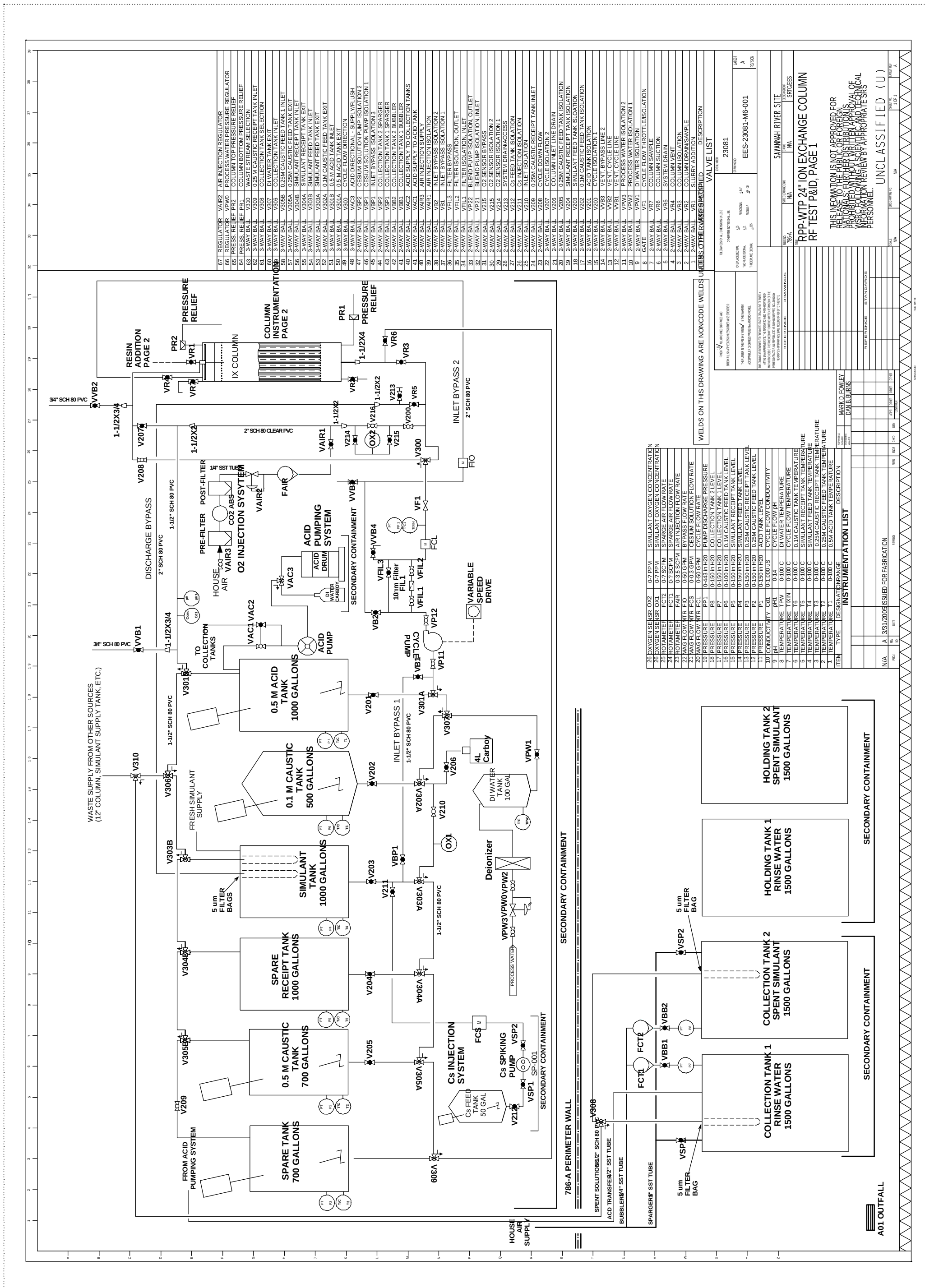

Figure 2: 24" Ion Exchange Column Test System P&ID

The ion exchange column was fully instrumented to include diaphragm pressure transducers, differential pressure transducers, gauge pressure transducers, and a thermocouple.

The electronic output of the M&TE was logged by a PC based Data Acquisition System (DAS) consisting of a DELL OptiPlex GX300 PC with National Instruments LabView® for Windows software, version 6i. The DAS was calibrated before and after the tests using Washington Savannah River Company (WSRC)-approved calibration procedures and NIST traceable standards to assure the quality of the data. Data files were renamed at the start of each cycle. There were seven bed pressure measurements (load-cells) in the column using diaphragm pressure transducers mounted flush to either the column wall or resin support screen. Axial bed pressure was measured in two locations on the resin support screen; in the center and approximately 7.6 cm (3”) from the column wall. These locations were inaccessible and therefore, redundant instruments were installed to account for instrument failure. Radial bed pressure was measured in three locations in the column wall at 0, 15.2, and 45.7 cm (0, 6”, and 18”) above the resin support screen.

Differential pressure transducers to measure axial pressure gradient were spaced every 7.6 cm (3”) for the first 15.2 cm (6”) above the resin support screen, then every 15.2 cm (6”) up to an elevation of 91.4 cm (36”) above the screen. Another pressure transducer measured the differential pressure from 91.4 cm (36”) to 124.2 cm (48.9”), which is just below the impingement plate, to capture bed pressure drop during fluidization. There were redundant pressure tap locations at 7.6, 15.2, 30.5, 45.7, and 61 cm (3”, 6”, 12”, 18”, and 24”) above the screen, 180º away from the primary pressure tap locations. Differential pressure was measured across the resin support screen and across the lower column internals (resin support screen, the lower impingement plate and the lower diffuser plate). Differential pressure was also measured across the upper distributor and impingement plates. Differential pressure transducers to measure radial pressure gradients (cross-bed differential pressure, taps located 180º apart at the same height) were located 7.6 cm (3”) and 45.7 cm (18”) from the resin support screen. Each piece of instrumentation was calibrated before and after the tests.

The layout and capacity of the supply tanks and other support vessels relative to the IX column is shown in Figure3. Polyethylene, open-top storage tanks were used to contain the ion exchange cycle solutions. Each tank was covered with a polyethylene lid to reduce evaporation, fume emissions, and prevent foreign objects from entering the tanks

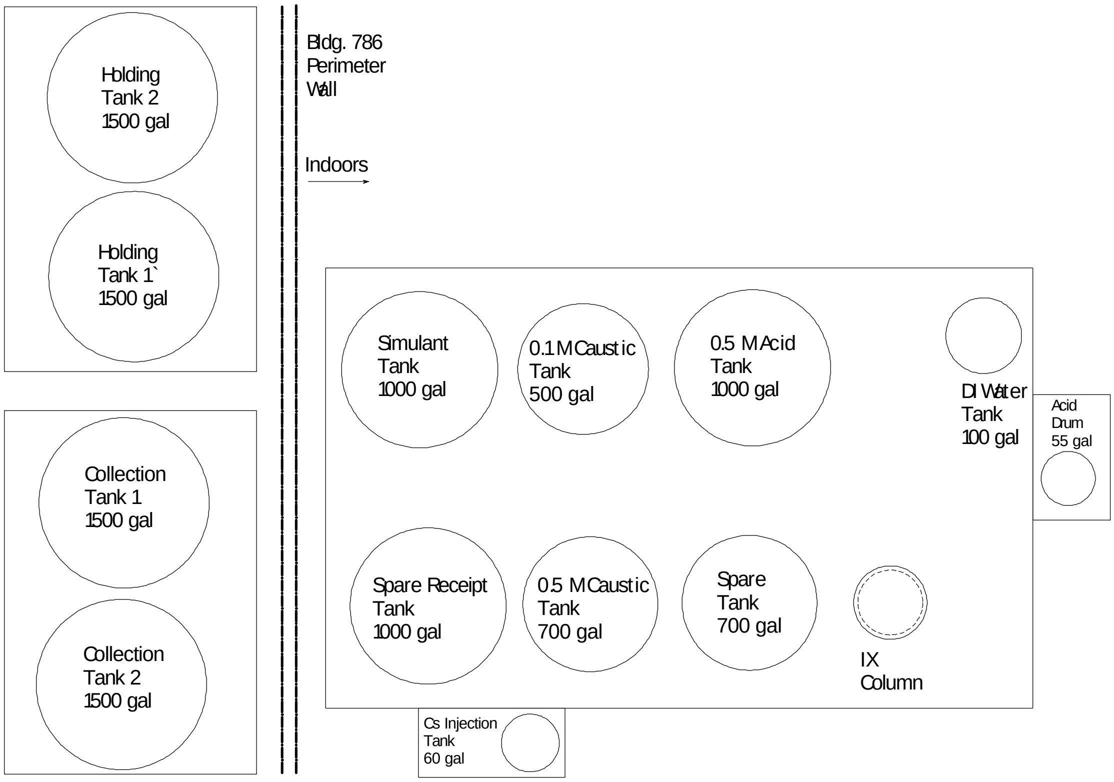

Figure 3. 24" IX Tank Storage Layout

Figure4 is a plan view photograph of the indoor supply tanks and IX column.

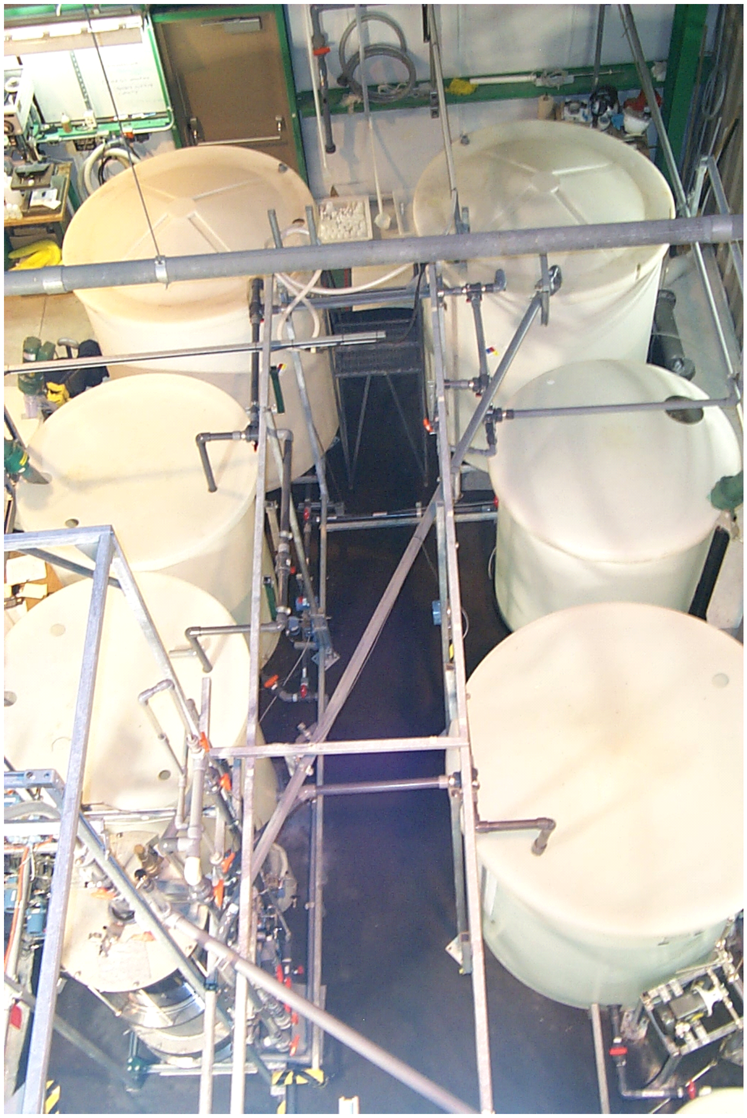

Figure 4. Picture, Plain View of 24" IX Indoor Supply Tanks

TEST MATRIX AND CONDITIONS

Testing included two preliminary chemical cycles, Cycles 0.1 and 0.2 and fourteen formal chemical cycles, Cycles 1 through 14. As with the 12" IX Column testing, flow rates used in testing are multiples of the design basis flow rate of the full-scale column, 22-gpm or a superficial fluid velocity of 5.85 cm/min. Velocities used in the pilot scale testing was in multiples of the design basis flow rate, 5.85x except for upflow Regeneration and upflow Simulant Introduction. To fully cover the potential range of flows in the WTP full-scale column, to allow comparison to the SL-644 resin 24-inch testing, and to allow some measurement of chemical performance, a wide range of Simulant Loading flow rates were covered in this testing. The conditions for the two preliminary cycles and the fourteen formal cycles are listed in Table 1.

Table 1. Test Conditions for 24" RF Ion Exchange Column

	0.5 M NaOH Regeneration (Up-flow)	Simulant Introduction	Simulant Loading (Down-flow)	0.1 M NaOH (Down-flow)	DI H_2O Pre-elution (Down-flow)	0.5 M HNO_3 Elution (Down-flow)	DI H_2O Post-elution (Down-flow)
Cycle 0.1 Regen. Mapping	Up-flow to map bed expansion	Down-flow @ 13.3 cm/min	With Introduction, 72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 Column Volume (CV) @ 13.3 cm/min
Cycle 0.2 Simulant Mapping	12.4 cm/min for 30 minutes No flow for ≥ 4 minutes 2.2 cm/min for 20 minutes Abbreviated bed expansion mapping	Up-flow to map bed expansion	72 BV @ 13.3 cm/min	3.0 BV @ 4.9 cm/min	2.5 BV @ 4.9 cm/min	15.0 BV @ 2.2 cm/min	2.5 BV @ 4.9 cm/min
Cycle 1 Cesium Spiking	12.4 cm/min for 30 minutes No flow for ≥ 4 minutes 2.2 cm/min for 30 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	1 BV @ 13.3 cm/min no Cs 49 BV @ 1.8 cm/min with Cs	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 2 Normal	12.4 cm/min for 30 minutes No flow for ≥ 4 minutes 2.2 cm/min for 2 minutes 2.1 cm/min for 18 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 3 High Flow 2X Normal	12.4 cm/min for 30 minutes No flow for ≥ 4 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	100 BV @ 26.9 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 4 Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 5 Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 6 Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Down-flow @ 13.3 cm/min	With Introduction, 72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 7 Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 8 Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 9 High Flow 2X Normal	13.1 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	100 BV @ 26.9 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 10 High Flow 9.7 psid	11.7 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	100 BV @ Velocity to reach 9.7 psid across resin bed, V= 59.4 cm/min	3.0 BV @ 4.9 cm/min	2.5 BV @ 4.9 cm/min	15.0 BV @ 2.2 cm/min	2.5 BV @ 4.9 cm/min
Cycle 11 Cesium Spiking	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	1 BV @ 13.3 cm/min no Cs 49 BV @ 1.8 cm/min with Cs	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 12 Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min
Cycle 13 High Flow 2X Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV Abbreviated bed expansion mapping	100 BV @ 26.9 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min

	0.5 M NaOH Regeneration (Up-flow)	Simulant Introduction	Simulant Loading (Down-flow)	0.1 M NaOH (Down-flow)	DI H_2O Pre-elution (Down-flow)	0.5 M HNO_3 Elution (Down-flow)	DI H_2O Post-elution (Down-flow)
Cycle 14 Normal	12.4 cm/min for 30 minutes No flow for ≥ 3 minutes 2.0 cm/min for 20 minutes	Up-flow for 1 CV 2.5 cm/min for 52 minutes 4.0 cm/min to finish CV	72 BV @ 13.3 cm/min	3.0 BV @ 8.8 cm/min	2.5 BV @ 13.3 cm/min	15.0 BV @ 6.1 cm/min	1.2 CV @ 13.3 cm/min

Testing was conducted on the 24" IX column using an approved procedure, covering sixteen full cycles; two preliminary cycles, labeled Cycle 0.1 and Cycle 0.2, and fourteen formal cycles. As shown in the table, the sixteen cycles consisted of six steps; regeneration in 0.5 NaOH solution, simulant introduction, 0.1 M NaOH solution for displacement, deionized water wash, 0.5 M nitric acid elution and deionized water final wash.

The sixteen cycles had some common factors.

a. The order of a cycle was always resin regeneration with 0.5 M NaOH solution, simulant introduction, simulant loading, simulant displacement with 0.1 M NaOH solution, resin washing with deionized water, elution with 0.5 M nitric acid solution, and a final washing with deionized water.
b. The flow was always stopped between steps to allow checking of the readings of the differential pressure gages.
c. All of the pressure sensing lines were purged in the direction from the column to the pressure transducer every time the column was filled with a new fluid having a significantly different density from the previous fluid. These two transitions were from 0.5 M NaOH to simulant and from simulant to 0.1 M NaOH.

Some differences existed between the cycles.

a. The regeneration step of Cycle 0.1 was used to map the upflow velocity versus fluidized bed height. The mapping would determine the regeneration protocol for the succeeding cycles.
b. The simulant introduction step of Cycle 0.2 was used to map the upflow velocity versus bed behavior. The mapping would determine the simulant introduction protocol for the succeeding cycles.
c. Simulant was introduced in upflow in most cycles except Cycles 0.1 and 6, where the simulant was introduced in downflow.
d. The resin bed was loaded with non-radioactive cesium in Cycles 1 and 11. A cesium solution was injected into the simulant feed stream to test the hydraulic performance of the bed.
e. The simulant loading superficial velocity was typically 13.3 cm/min. Cycles 3, 9 and 13 had velocities 26.9 cm/min, twice the typical value. Cycle 10 had a velocity much higher than the typical value. The velocity was a set to achieve a pressure drop across the resin bed of 9.7 psig, which would simulate the maximum bed dP in the WTP full scale column.
f. The duration of simulant loading was typically 72 BVs. Simulant loading for the cesium injection cycles was 50 BVs. Simulant loading for the four high flow cycles was 100 BVs.
g. The velocities for simulant displacement, pre-elution wash, elution, and post-

elution wash were lower than typical in Cycles 0.2 and 10 to prepare for the following cesium injection cycles.

The parameters used during the 24" IX Column hydraulic testing of the RF resin is further delineated in Table 2. For example, the table shows that the 1st step of regeneration was at 9.0 gpm, upflow.

Table 2. 24" Summary of Parameters, IX Column Hydraulic Test Matrix

cycle #	type	regen, Upflow 1st step gpm	regen, Upflow 2nd step gpm	upflow simulant intro initial gpm	upflow simulant intro final gpm	simulant load in gpm	displace, gpm	pre-elution rinse, gpm	elute, gpm	post-elution rinse, gpm
0.1	map upflow regen,			1.81	2.89	9.65 downflow	6.34	9.65	4.39	9.65
0.2	max, 5 M + chem prep	9.00	1.42	1.81	2.89	9.65	3.54	3.54	1.61	3.54
1	chemical	9.00	1.42	1.81	2.89	1.30	6.34	9.65	4.39	9.65
2	max, 5 M	9.00	1.42	1.81	2.89	9.65	6.34	9.65	4.39	9.65
3	max, 5 cp	9.00	1.42	1.81	2.89	19.30	6.34	9.65	4.39	9.65
4	max, 5 M	9.00	1.42	1.81	2.89	9.65	6.34	9.65	4.39	9.65
5	max, 5 M	9.00	1.42	1.81	2.89	9.65	6.34	9.65	4.39	9.65
6	max, 5 M	9.00	1.42	1.81	2.89	9.65 downflow	6.34	9.65	4.39	9.65
7	max, 5 M	9.00	1.42	1.81	2.89	9.65	6.34	9.65	4.39	9.65
8	max, 5 M	9.00	1.42	1.81	2.89	9.65	6.34	9.65	4.39	9.65
9	max, 5 cp	9.00	1.42	1.81	2.89	19.30	6.34	9.65	4.39	9.65
10	9.7 psi + chem prep	9.00	1.42	1.81	2.89	43.00	3.54	3.54	1.61	3.54
11	chemical	9.00	1.42	1.81	2.89	1.30	6.34	9.65	4.39	9.65
12	max, 5 M	9.00	1.42	1.81	2.89	9.65	6.34	9.65	4.39	9.65
13	max, 5 cp	9.00	1.42	1.81	2.89	19.30	6.34	9.65	4.39	9.65
14	max, 5 M	9.00	1.42	1.81	2.89	9.65	6.34	9.65	4.39	9.65

HYDRAULIC RESULTS FOR 24" IX COLUMN

A summary of the hydraulic data for the tests with the 24" column are shown in Table 3 and Table 4 for simulant and other fluids, respectively. Permeability is plotted in Figure 5. Details of each cycle on the 24" tests are given in Appendix 7. The flowmeter malfunctioned and therefore the readings were suspect for all of Cycle 0.2 and for the regeneration step and simulant upflow step of Cycle 1. Estimated flows based on changes in tank levels are listed for that period of time. Excluding the two cycles with downflow introduction of simulant and Cycle 0.2 which had a suspect measurement of flow rate, the average adjusted permeability in simulant was 3.40 x 10^{-6} cm^2.

Table 3. Hydraulic Summary with Simulant for 24" Column

	Velocity, cm/min	DP, inch H2O	Resin height, cm	Simulant viscosity, cP	Simulant density, g/mL	Permeability, $cm^2 * 10^{-6}$	Adjusted permeability	Simulant introduction
Cycle 0.1	13.39	61.8	73.0	3.10	1.26	3.28	3.31	downflow
Cycle 0.2	10.39	64.4	71.2	3.01	1.25	2.31	2.33	upflow
Cycle 1	1.81	7.9	72.5	3.05	1.26	3.39	3.40	upflow
Cycle 2	13.41	61.0	73.0	3.00	1.26	3.22	3.25	upflow
Cycle 3	26.95	123.0	72.3	3.04	1.26	3.22	3.28	upflow
Cycle 4	13.42	58.0	73.5	3.01	1.25	3.43	3.45	upflow
Cycle 5	13.39	55.0	73.2	3.05	1.26	3.64	3.67	upflow
Cycle 6	13.39	74.0	73.5	3.00	1.25	2.67	2.69	downflow
Cycle 7	13.41	58.0	73.7	2.98	1.25	3.40	3.43	upflow
Cycle 8	13.42	58.0	73.9	2.81	1.25	3.22	3.24	upflow
Cycle 9	26.95	118.0	73.4	2.96	1.25	3.32	3.38	upflow
Cycle 10	59.05	263.5	73.5	2.86	1.24	3.15	3.27	upflow
Cycle 11	1.80	7.9	73.9	2.85	1.24	3.22	3.22	upflow
Cycle 12	13.42	52.5	74.1	2.85	1.24	3.61	3.64	upflow
Cycle 13	26.95	104.2	74.3	2.85	1.24	3.67	3.73	upflow
Cycle 14	13.41	58.5	74.4	2.84	1.25	3.24	3.27	upflow

It was important to determine if the resin beds were becoming more restrictive hydraulically over the course of testing. Simply comparing pressure drops is insufficient because there are differences in bed thickness, liquid velocity and viscosity. Permeability is a convenient property for comparison.

$$K = \frac{V\mu L}{\Delta P}$$

Where:
K – Permeability
V – Velocity of liquid flowing through the resin bed
μ - Viscosity of the liquid
L – Resin bed height or thickness
• P – Differential Pressure across the resin bed

Permeability has units of cm^2 or m^2. Permeability assumes laminar flow through the resin bed, which is good assumption for the pilot-scale testing. Turbulence increases the pressure drop across the resin bed so that the apparent permeability is less than if the flow had been laminar. Therefore, the Ergun equation was used to correct the permeabilities (adjusted permeability) by removing the turbulent contribution to pressure drop. The raw and corrected permeability for each cycle is plotted in Figure 5.

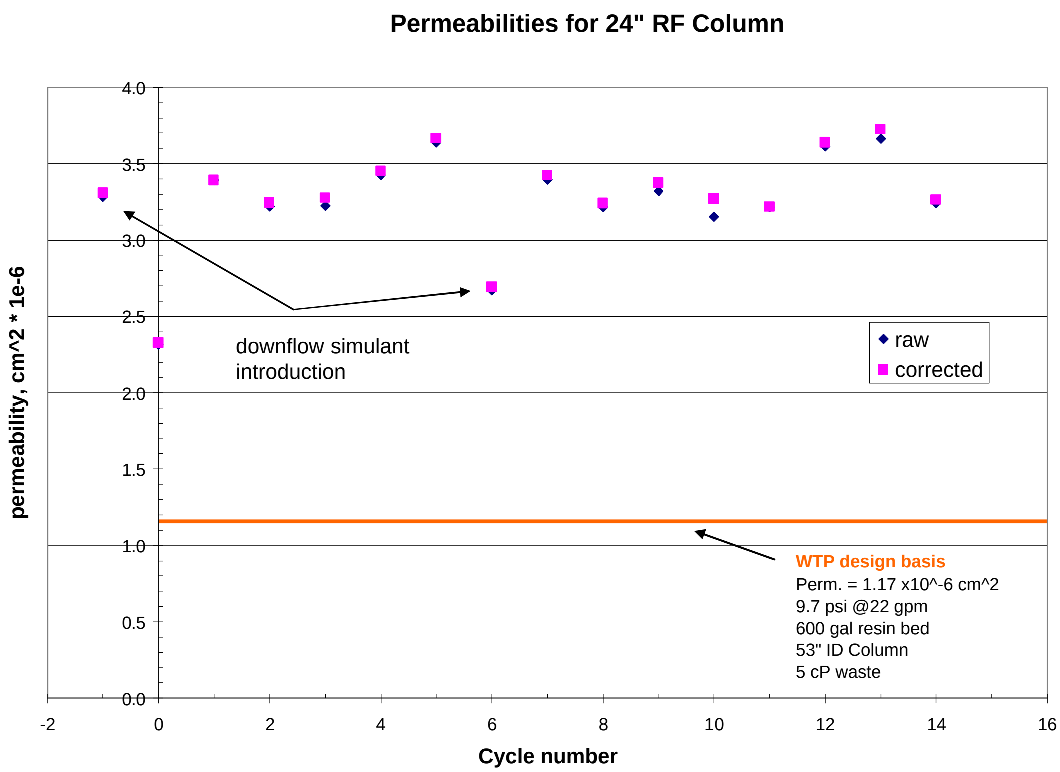

Figure 5. Permeabilities for 24" IX Column, RF Resin

Figure is another plot of the permeability for each of the 16 cycles ran in the 24" IX Column. The plot shows that the permeability essentially remained constant over the ½ scale pilot-scale testing. Over the sixteen total cycles, there were no trends of the permeability increasing or decreasing. The lowest permeability occurred in Cycle 6 (eight total cycles) where the Simulant Introduction step occurred in downflow. Cycle 10 (twelve total cycles, see x in plot) was the worst case scenario for permeability where the flow rate was 43 gpm and the dP across the RF resin bed was 9.7 psi. For this run the permeability was essentially the average of the sixteen cycles at 3.27×10^{-6} cm^2. The plot also depicts that the RF resin bed permeability is approximately three times better than the design bases requirement of 1.17×10^{-6} cm^2. The graph also depicts that the permeability for all 16 cycles is approximately three times better than the full-scale permeability requirement.

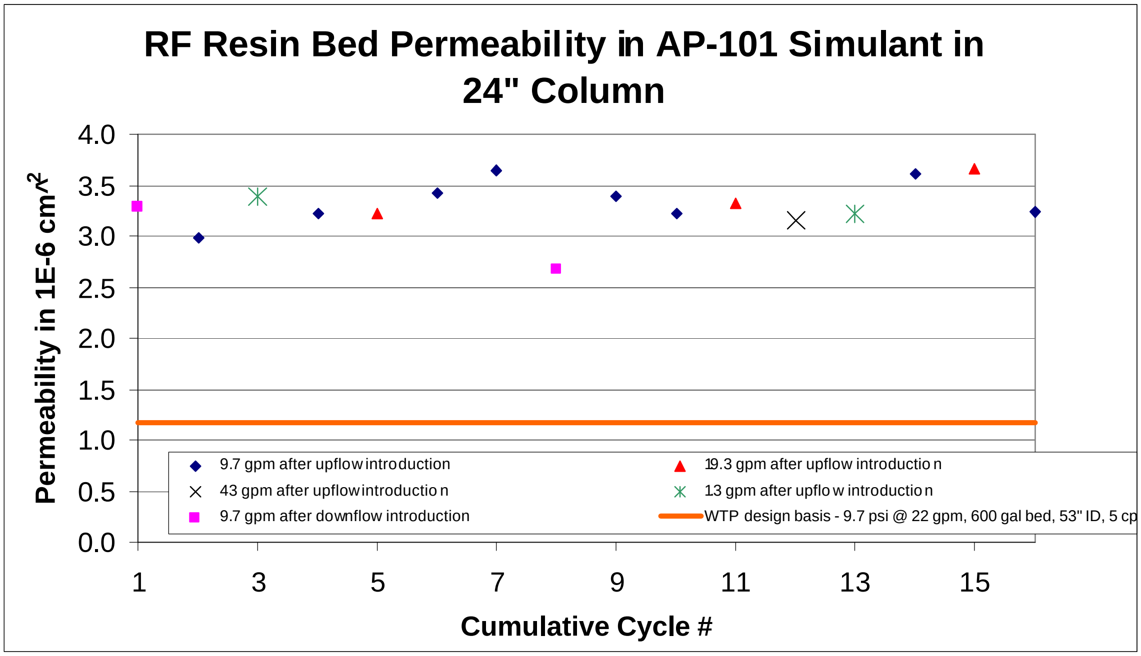

Figure 6. RF Resin Bed Permeability in AP-101 Simulant in 24" Column

Solid Pressures Measured in 24" Column

Solid pressures were measured using load cells during testing of the 24" column, where some of the highest solid pressures were measured for the highest flow cycle. Cycle 10 had a simulant superficial velocity of 59 cm/min. Figure 1 plots the solid pressures. The highest pressures, up to 9 psig, were axial pressures measured at the support screen because hydraulic drag was pressing the plug of resin down. The highest pressure was at the center of the screen. Figure 2 plots solid pressures for downflow simulant introduction in Cycle 6. The highest pressures are also at the screen, but the highest pressure at the screen is located close to the wall because of resin swelling. Figure 3 plots solid pressures for a typical, moderate flow cycle with downflow introduction of simulant. Solid pressures reach only 2.5 psig.

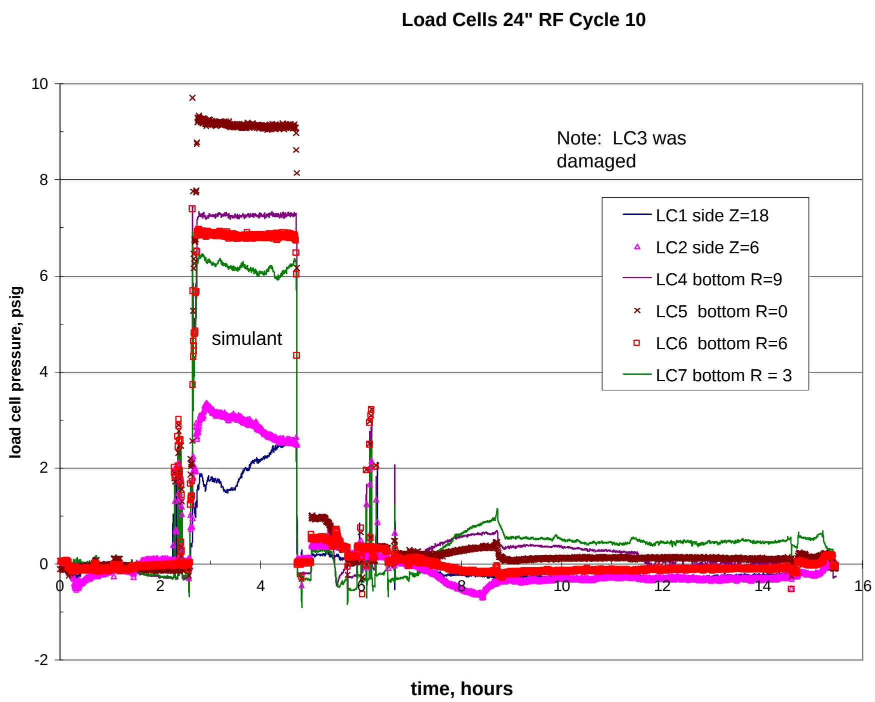

Figure 1. Solid Pressures 24" IX Column Cycle 10, 43 gpm Simulant

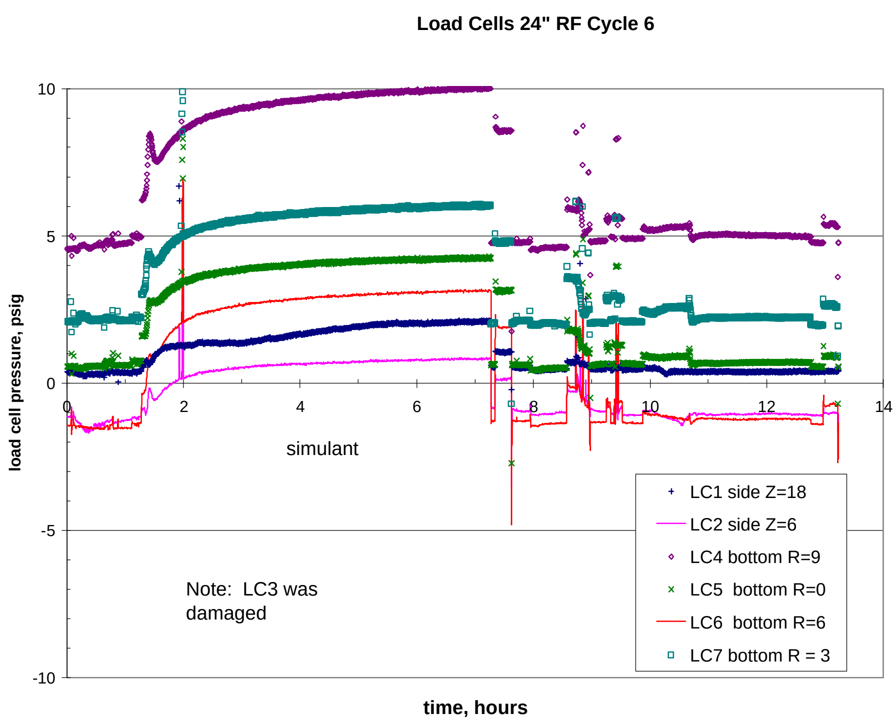

Figure 2. Solid Pressures 24" IX Column, Downflow Simulant Introduction

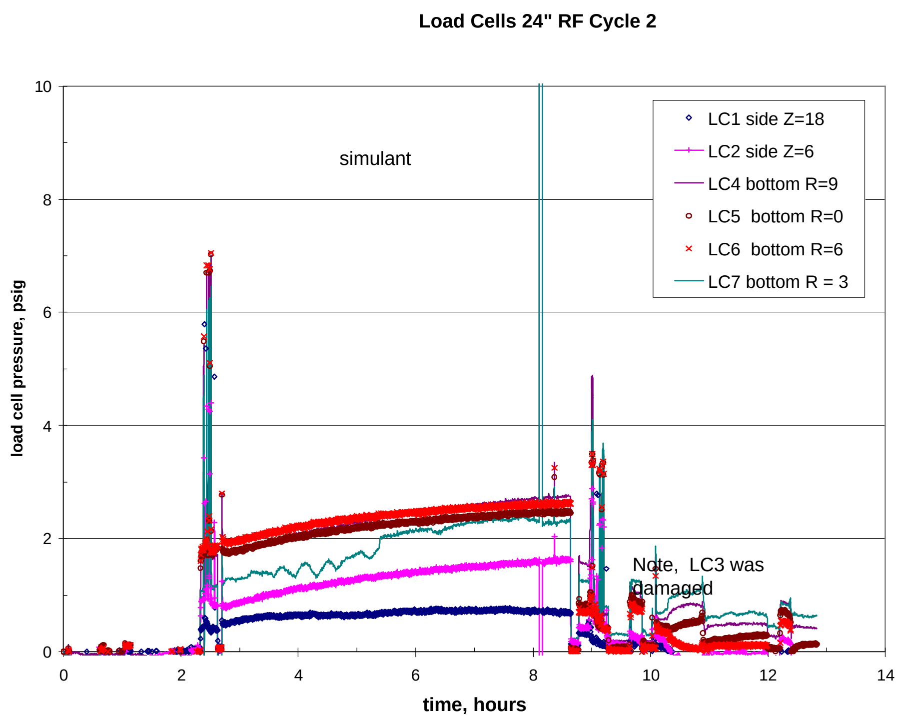

Figure 3. Typical Solid Pressures, 24" IX Column

MEASUREMENT OF CESIUM IN LAW SIMULANT

Measurement of concentration of cesium in actual low active waste (LAW) simulant is relatively easy because of the hard gamma emitted by cesium 137. Measurement of non-radioactive cesium in simulated LAW using ICP-MS is more difficult because of the five molar salt loading. Testing samples were analyzed or re-analyzed by SRNL, General Engineering Laboratory in Charleston, SC, and by Pacific Northwest National Laboratory (PNL). Detection limits were found to be to 1 µg/L to 2.5 µg/L. Figure 10 shows some ICP-MS measurements of cesium concentrations inlet simulant to the column. The simulant was formulated to be 6700 µg/L, so measurement accuracy is good. Figure 11 plots the measured vs. formulated concentrations for simulant samples. Accuracy is also good.

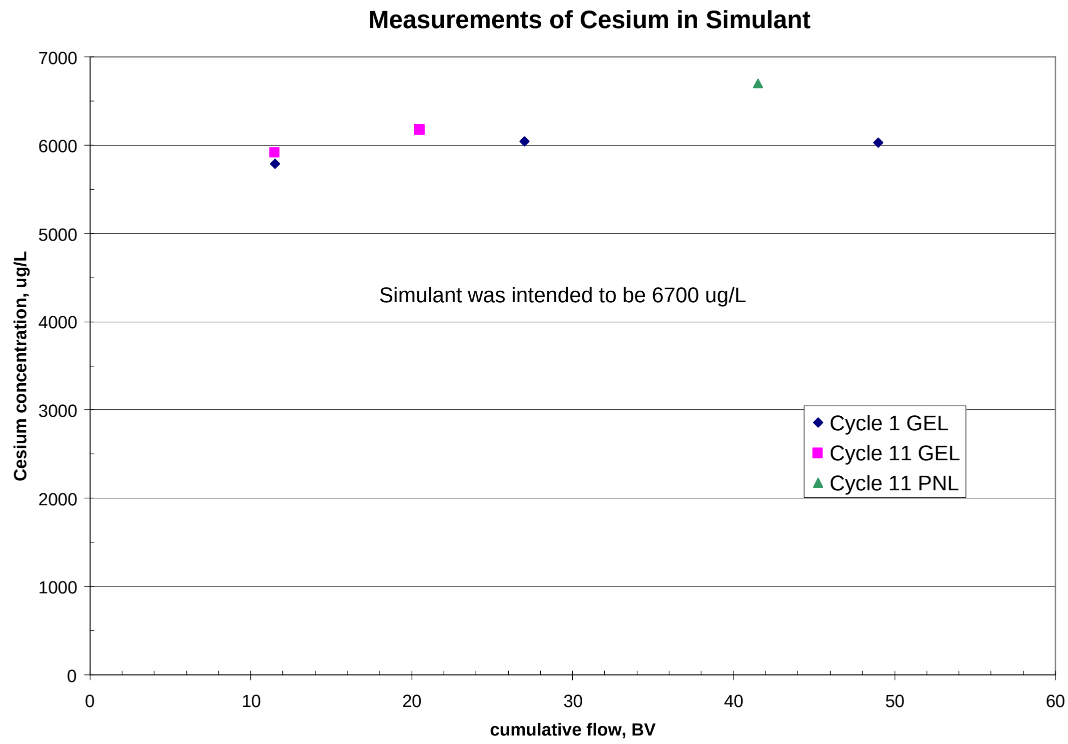

Figure 10. 24" IX Column Cesium Concentration in Inlet Simulant

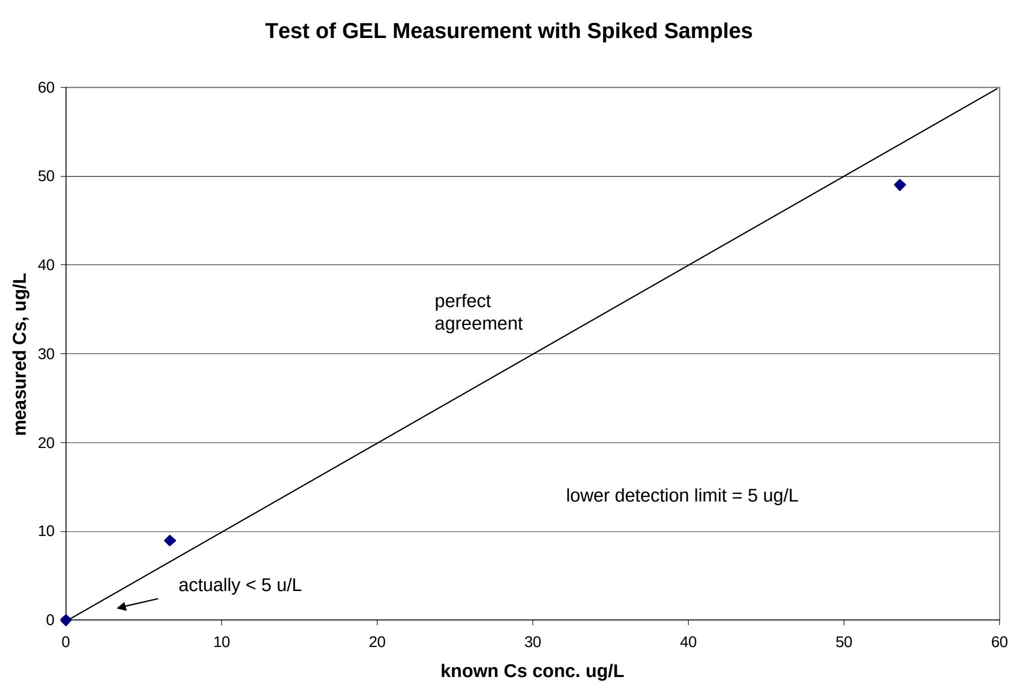

Figure11. Measurement of Cesium in Spiked Samples

FigureFigure and Figure plot cesium concentrations in the simulant exiting the column for Cycle 1 and Cycle 11, the two cycles for which cesium nitrate was added to the simulant. With the exception of concentration measured at 7 μg/L, all of the measured concentrations are at the detection limit, which was 1 μg/L for some samples and 2.5 μg/L for other samples. Therefore, the RF resin had excellent performance for removing cesium from a five molar salt solution.

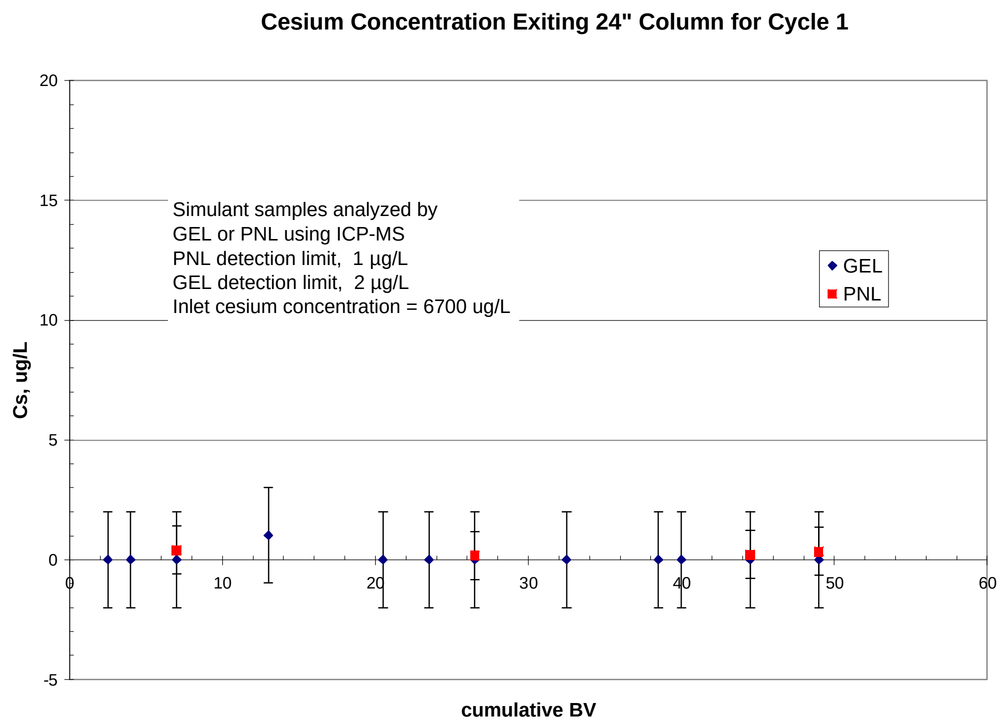

Figure 12. Cesium Concentrations in Effluent Simulant for 24" IX, Cycle 1

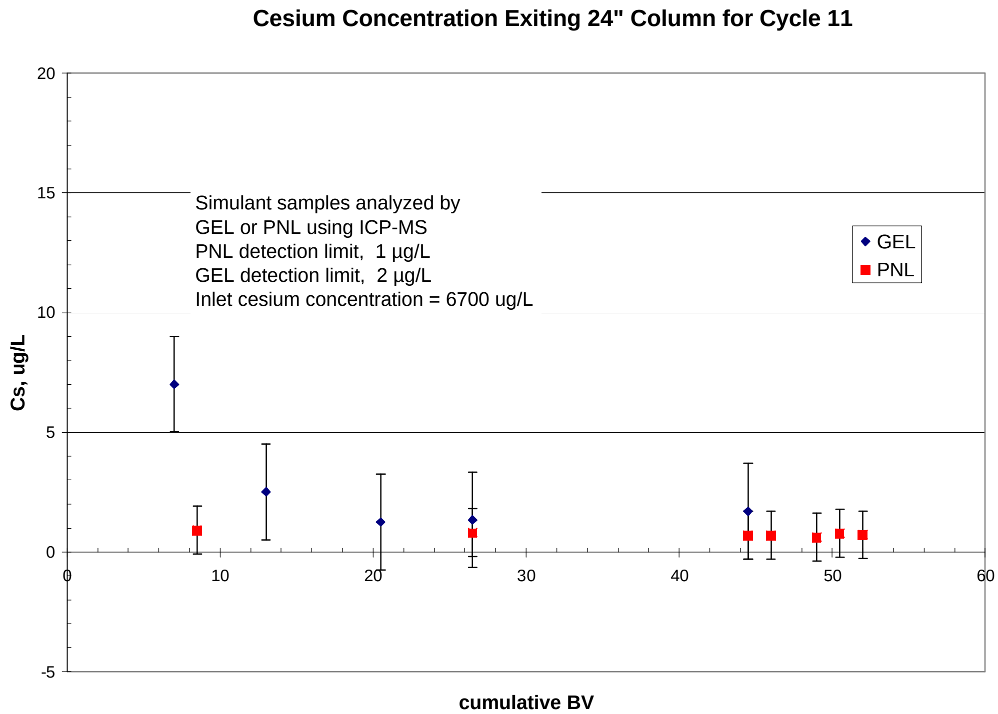

Figure 13. Cesium Concentrations in Effluent Simulant for 24" IX, Cycle 11

In addition to measuring cesium by ICP-MS, rubidium concentration was also measured by ADS for 12" and 24" RF hydraulic testing samples. The rubidium was apparently added as an impurity in one of the several compounds provided by vendors for the simplified simulant mixed by SRNL. The results of the rubidium concentration were consistently in the range of several hundred micrograms/liter throughout both the 12" and 24" hydraulic testing. These results applied to simulant feed into the IX column as well as simulant that had passed through the RF resin bed. Two conclusions can be drawn from these results. First, the rubidium was not absorbed onto the RF resin. Thus, the rubidium will not be a competitor with cesium and other elements for sites on the RF resin. Second, the fact that the concentration was consistent on the large number of RF bed inlet and outlet samples implies that the dilutions were properly characterized in the analysis of results. As a basis of comparison, the PNL results for rubidium during their RF testing were consistent with the SRNL observations. Based on these observations, there does appear to be a selection process by the RF resin for elements that is not all inclusive.

Resorcinol Formaldehyde (RF) Resin

The spherical RF ion exchange resin used in the pilot scale testing was manufactured by Microbeads AS in Skedsmokorset, Norway and was shipped in acid form. The resin was pretreated and converted to a sodium form before adding it to the ion exchange column for testing.

The RF resin bed showed no tendency to form fissures or pack more densely as the number of cycles increased. Particle size measurements for the RF resin showed no indication of particle size change (for a given chemical) with cycles and essentially no fines formation.

The particle size distribution (PSD) for the RF resin that under went testing in the 24" IX Column are listed in Table 1. The PSD results were determined using MicroTrac. The term mv refers to mean by volume diameter, the term mn refers to mean by number diameter and ma is the mean by area diameter. As shown in the table, there was no significant difference in the particle size before and after the sixteen cycles. From the MicroTrac data there was no evidence of particle breakage or fines being created. Assuming that bulk resin volume is proportional to diameter cubed, these diameters predict that the bulk volume of resin in simulant will be approximately 32% greater than in acid solution.

Table 1. RF Resin (641) Size from 24" Column Testing

Sample	mv (μm)	mn (μm)	ma (μm)
As Received, H form	387.8	364.8	382.1
Pre-treated, Na form (in 0.5 M NaOH)	459.5	430.2	451.5
Pre-treated, Na form (in simulant)	460.7	432.7	453.1
Pre-treated, H form	427.4	399.5	417.6
Before Resin Addition, Na form (in 0.5 M NaOH)	454.1	426.0	446.4
Cycle 8, H form (in DI water) - A	423.7	397.4	413.9
Cycle 8, H form (in DI water) - B	423.4	395.9	413.3
Cycle 8, Na form (in 0.5 M NaOH)	452.8	425.0	445.0
Cycle 8, Na form (in simulant)	456.1	426.7	447.9
Cycle 14, H form (in DI water) - A	422.5	397.8	413.7
Cycle 14, H form (in DI water) - B	423.6	396.3	413.7
Cycle 14, Na form (in 0.5 M NaOH)	440.2	414.8	433.1
Cycle 14, Na form (in simulant)	458.7	432.1	451.5

Figure through Figure are photomicrographs of virgin RF resin in hydrogen form and resin in hydrogen form after Cycle 8 and Cycle 14. The picture also shows that a negligible quantity of fines was removed from the column over the 24" IX Column test campaign. Two of the pictures show a ruler with 1 mm graduations, so the resin diameter in hydrogen form is about 400 um, in agreement with the Microtrac measurements. Representative samples shown in the photomicrographs also suggest no damaged beads.

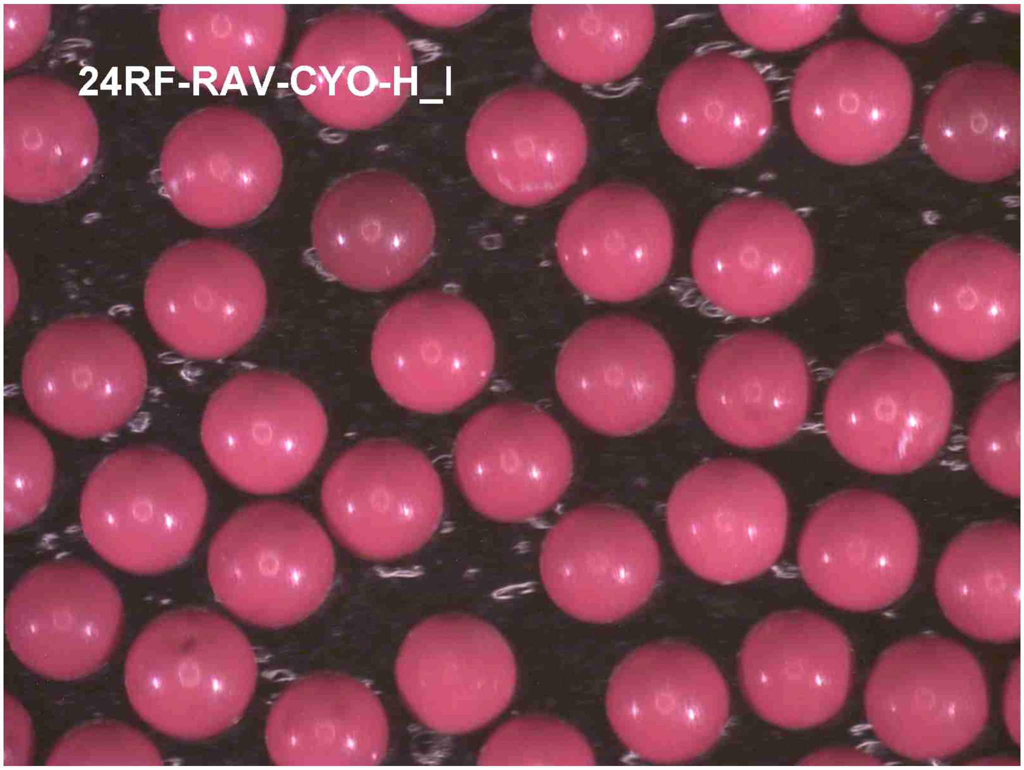

Figure 14. Virgin Resin in Hydrogen Form before 24" IX Testing

Figure 15. Resin in Hydrogen Form after Cycle 8 in 24" IX Column

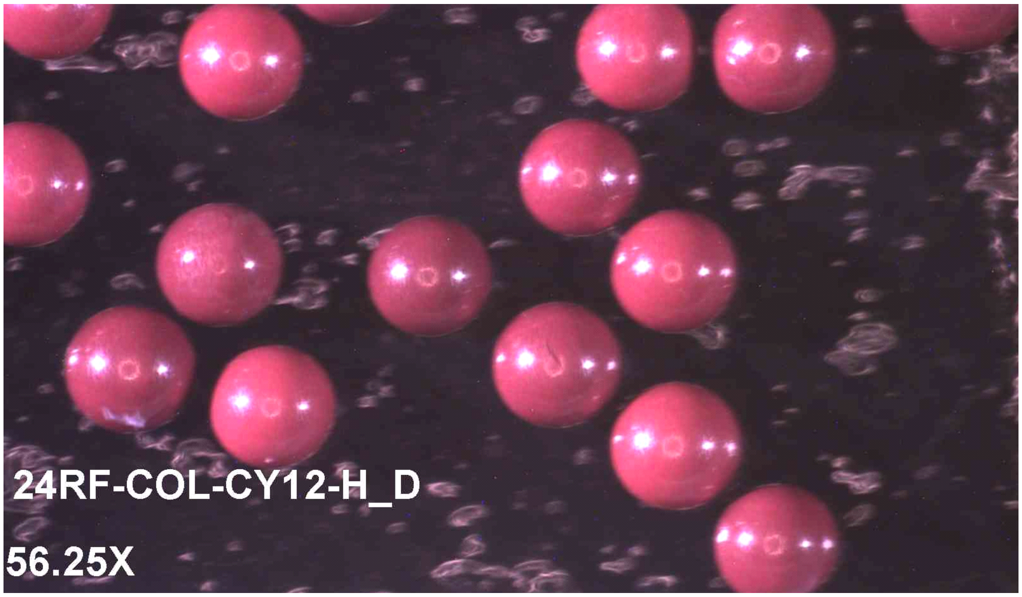

Figure 16. Resin in Hydrogen Form After Cycle 14 in 24" IX Column

Micrographs comparing representative bead samples before and after the sixteen cycles in the 24" IX Column indicated no change in bead morphology. The skeletal density of the RF resin from the 24" IX Column, increased slightly with cycles in both hydrogen and sodium form.

Resin addition to the 24" IX Column gave an initial resin bed height of 72 cm (28.4") or an L/D of 1.22, slightly exceeding the desired L/D of 1.185. Resin heights were measured during each of the cycle test. Figure plots resin bed height vs. cycle for both fully swollen sodium form in simulant and fully shrunken form in acid for the sixteen cycles. The two curves fit lines show a trend of slightly increasing bed heights. In simulant the resin bed height increased about 3% over the 16 cycles. The resin height in simulant is about 30% greater than the height in acid.

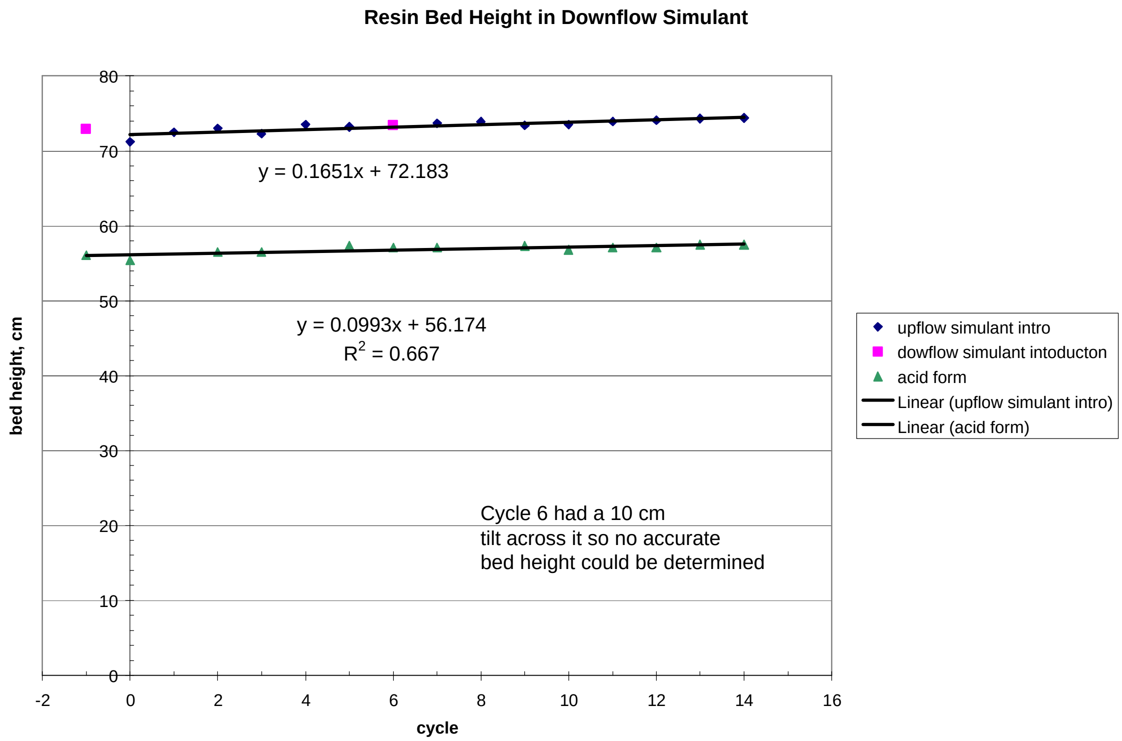

Figure17. Bed Heights in 24" IX Column

CONCLUSION

The resorcinol formaldehyde (RF) resin functioned well, both hydraulically and chemically for the sixteen cycles in the 24" IX column. The permeability of the RF resin bed remained constant (except for downflow Simulant Introduction) from cycle to cycle. The permeability did not decrease which would have been indicative of resin particle fracture. The permeability demonstrated during these tests surpassed the WTP full-scale requirement of 1.17×10^{-6} cm^2 by a factor of approximately 2.5.

The RF resin was found to be very efficient in removing cesium. Two cesium loading tests were conducted on the pilot-scale IX column where the simulant being pumped into the column had a concentration of 6700 µg/L of Cs. Laboratory analyses concluded the Cs in the effluent never exceeded the detection limit of the analysis method employed. On the thirteenth cycle in the 24" column, the Cs in the effluent was less than the detection limit, indicating there was no measurable degradation in cesium removal performance from cycling. The RF resin was also found not to have an affinity for Rubidium, which is a desirable quality for the resin.

A few of the RF resin beads were darkened as the result of oxidation over the sixteen demanding cycles in the 24" IX Column, resulting from the oxygen saturated feeds. Data suggest that the oxidation did not degrade the resin's hydraulic or chemical performance, during which over 90,000 gallons of chemicals/test solutions were pumped through the RF resin bed.

Laboratory analysis of particle size distribution for the RF resin showed no measurable particle size change with cycle testing. After sixteen cycles in the 24" IX column, the Microtrac results showed no increase in fines or the resin breaking down from start of testing to the end of sixteen total cycles. Additionally, solutions such as the simulant remained clear, another indication of lack of resin fracture.
Upflow Regeneration produced negligible solid pressures from the swelling of resin bead. The lift force on the RF particles allowed them to expand more readily. Conversely, Downflow Regeneration produced greater solid pressures.

Out of the fourteen cycles in the 24" IX where Upflow Simulant Introduction was conducted, a level bed with uniform permeability was produced each time. Divergently, where the two cycles involving Downflow Simulant Introduction were conducted, an uneven bed was produced, with the greatest bed surface erosion occurring at the location of the thermowells.

During the upflow Simulant Introduction step, the resin bed is lifted off the resin bed support screen. The RF resin particles fall out to the support screen as simulant comes in contact with the bed. This process produced a perfectly level on all cycles.

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Adamson, D. J., SRNL "Task Technical and Quality Assurance Plan for Hydraulic Testing of Resorcinol-Formaldehyde (RF) Resin In 12" and 24" Ion Exchange Columns (U)," WSRC-TR-2004-00553, SRNL-RPP-2004-00088, Nov. 2004.