PILOT-SCALE HYDRAULIC TESTING OF RESORCINOL FORMALDEHYDE ION EXCHANGE RESIN

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ABSTRACT

Pilot-scale hydraulic/chemical testing of spherical resorcinol formaldehyde (RF) ion exchange (IX) resin was conducted by the Savannah River National Laboratory (SRNL). This testing was in support of 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 scales. A total of twenty-three hydraulic/chemical cycles were successfully completed on the spherical RF resin. Sixteen of these cycles were completed in the 24” IX Column (½ scale).

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 3 times better than the design requirements of the WTP full-scale IX system. The RF resin bed 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. Cesium (Cs) loading tests were conducted on the RF resin in pilot-scale IX columns. Laboratory analyses concluded the Cs in the effluent essentially never exceeded the detection limit.

The hydraulic and chemical performance of the spherical RF resin during cycle testing was found to be superior to all other tested IX resins, The pilot–scale 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

The Savannah River National Laboratory (SRNL) under contracts DE-AC27-01RV14136 and DEAC09-96-SR18500 from the United States Department of Energy, conducted pilot-scale hydraulic testing of spherical resorcinol formaldehyde (RF) ion exchange resin in support of the River Protection Project in Richland, Washington. The purpose of this project is to design, construct, and commission a plant to treat and immobilize high-level waste (HLW) and low-activity waste (LAW) stored in underground storage tanks at the Hanford Site. Unit operations of the LAW treatment process include the separation of cesium-137 by ion exchange from the liquid portion of the waste stream.

Per the Test specification, 24590-WTP-TSP-RT-04-0003, a total of twenty-three hydraulic/chemical cycles where completed on the spherical RF resin in the pilot-scale IX column testing.[1] Seven of the cycles were completed in the ¼ scale IX Column (12”) and sixteen cycles were completed in the ½ scale IX Column (24”). 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.[2]

DISCUSSION

Test facility

The ½ scale IX column was constructed from 316L, 24” stainless steel (SST) 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 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 due to the swelling of the resin in sodium form.

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 2,270 liters (600-gallon) equivalent bed in the WTP IX column. The interior finish of the stainless steel wall where the resin bed resided was polished to 63 micro-inches, mimicking the full-scale design.

Non-radioactive cesium was injected into the simulant supply during some simulant loading steps of the 24” IX column tests. 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 1 is a P&ID drawing, showing the complexity of the 24” IX Test System.

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

Air was injected into the simulant flow downstream of the column to oxygenate the simulant supply. The RF resin may become oxidized by oxygen exposure which is expected in the WTP. The air was injected into the simulant stream to determine what affects the oxygen may have on the performance of the resin. The compressed house air passed through two pre-stage filters to remove liquid water and oil, then through a CO_2 absorber and then through an after-filter. An isolation valve was used to start and stop the air flow into the simulant and a rotameter was used to monitor the flow rate. The air entered the simulant stream through a 7-micron sintered metal injector to provide a well-dispersed bubble stream. The CO_2 was filtered out to prevent undesirable CO_2 precipitate when contacting the simulant.

The supply/storage tanks used in the test system were open-top tanks made of Polyethylene ranging from 225 liters (60 gallons) to 5,680 liters (1,500 gallons) capacity. Each tank was covered with a polyethylene lid to reduce evaporation, fume emissions, and prevent foreign objects from entering the tanks.

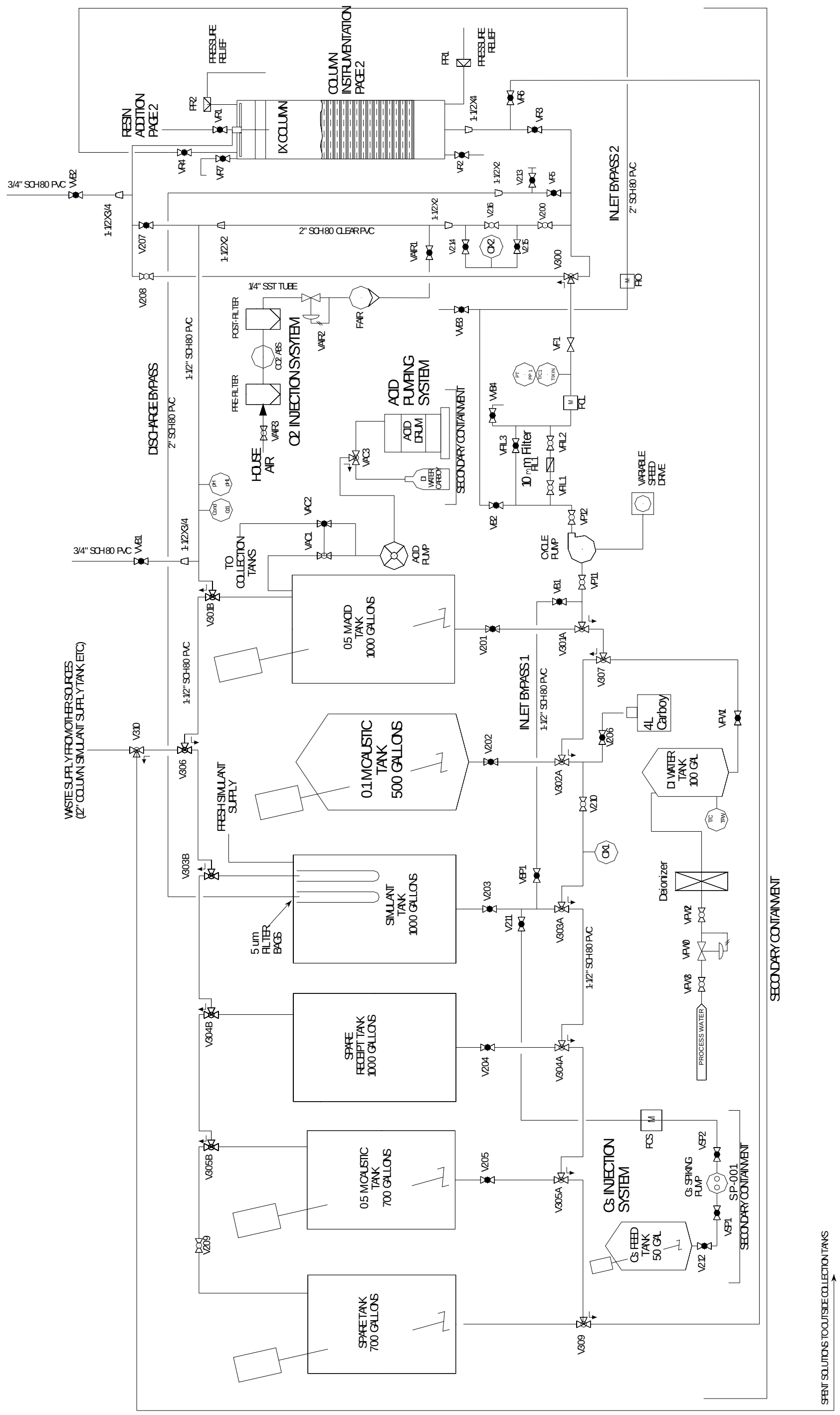

Fig. 1: 24” Ion Exchange Column Test System P&ID

Test Matrix and Conditions

Testing in the 24" IX column included two preliminary chemical cycles, Cycles 0.1 and 0.2 and fourteen formal chemical cycles, Cycles 1 through 14. The flow rates used in the pilot-scale testing were 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 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 I.

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

Cycle #	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)
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
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
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
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
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
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
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
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
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
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 #	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)
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
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
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
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
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
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. As shown in the table, the sixteen cycles consisted of six steps; regeneration in 0.5 NaOH solutions, 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 66.9 kPa (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 II. For example, the table shows that the 1st step of regeneration was at 9.0 gpm, upflow.

Table II. 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,			---	---	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	---	---	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 test data are shown in Table III for simulant. The RF resin was found to have excellent hydraulic properties. The average adjusted permeability in simulant was 3.40 x 10^{-6} cm^2 for the sixteen cycles.

Table III. Hydraulic Summary with Simulant for 24" Column

Cycle #	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
0.1	13.39	61.8	73.0	3.10	1.26	3.28	3.31	downflow
0.2	10.39	64.4	71.2	3.01	1.25	2.31	2.33	upflow
1	1.81	7.9	72.5	3.05	1.26	3.39	3.40	upflow
2	13.41	61.0	73.0	3.00	1.26	3.22	3.25	upflow
3	26.95	123.0	72.3	3.04	1.26	3.22	3.28	upflow
4	13.42	58.0	73.5	3.01	1.25	3.43	3.45	upflow
5	13.39	55.0	73.2	3.05	1.26	3.64	3.67	upflow
6	13.39	74.0	73.5	3.00	1.25	2.67	2.69	downflow
7	13.41	58.0	73.7	2.98	1.25	3.40	3.43	upflow
8	13.42	58.0	73.9	2.81	1.25	3.22	3.24	upflow
9	26.95	118.0	73.4	2.96	1.25	3.32	3.38	upflow
10	59.05	263.5	73.5	2.86	1.24	3.15	3.27	upflow
11	1.80	7.9	73.9	2.85	1.24	3.22	3.22	upflow
12	13.42	52.5	74.1	2.85	1.24	3.61	3.64	upflow
13	26.95	104.2	74.3	2.85	1.24	3.67	3.73	upflow
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.

$$K = \frac{V\mu L}{\Delta P} \qquad \text{Eq. 1}$$

Where:
K – Permeability
V – Velocity of liquid flowing through the resin bed
μ - Viscosity of the liquid
L – Resin bed height or thickness
ΔP – 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 in Table III) by removing the turbulent contribution to pressure drop.

Figure 2 is a 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. During the sixteen 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) was the worst case scenario for permeability where the flow rate was 163 L/min (43 gpm) and the dP across the RF resin bed was 66.9 kPa (9.7 psi). For this cycle, the permeability was essentially the average of the sixteen cycles at 3.27 x 10^{-6} cm^2. The plot also depicts that the RF resin bed permeability is approximately 3 times better than the design bases requirement of 1.17 x 10^{-6} cm^2.

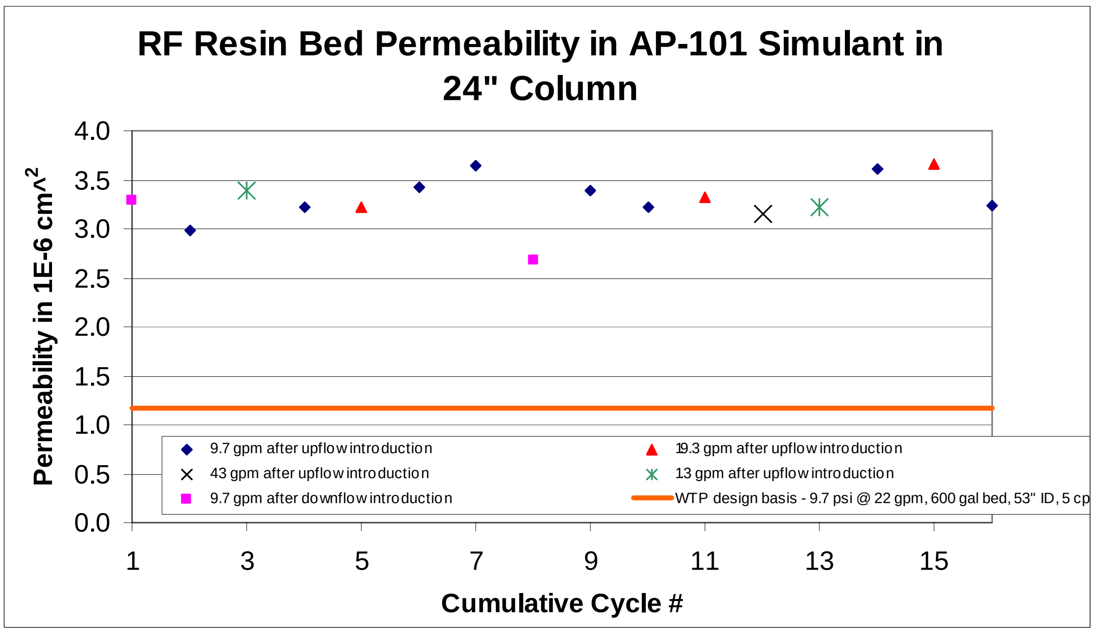

Fig. 2. RF Resin Bed Permeability in AP-101 Simulant in 24" Column

Solid pressures are created in the IX column due to resin swelling in sodium form. Load cells were used to determine solid pressure at various locations in the column. The highest solid pressures were measured in the high flow rate cycle. Cycle 10 of the 24" IX testing had a simulant superficial velocity of 59 cm/min resulting in a flow rate of 163 L/min (43 gpm). The highest pressures, up to 62 kPa (9 psig), were axial pressures measured at the support screen because hydraulic drag was pressing the plug of resin down. Regeneration of the resin bed in upflow is the main reason that low solid pressures were realized. As the resin swells in Upflow Regeneration, the resin beads are allowed to expand without causing pressure to the wall. Whereas in downflow Regeneration and Simulant downflow, the resin bed particles pack tightly together and produce higher solid pressures against the IX walls as the resin beads swell.

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 340,687 liters (90,000 gallons) of chemicals/test solutions were pumped through the RF resin bed in the ½ scale column.

Measurement of Cesium in LAW Simulant

Measurement of concentration of cesium in actual low activity 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. Two cesium loading tests were conducted on the 24" pilot-scale IX column where the simulant being pumped into the column had a concentration of 6,700 μg/L of Cs. Test samples were analyzed or re-analyzed by SRNL, General Engineering Laboratory in Charleston, SC, and by Pacific Northwest National Laboratory (PNNL). Detection limits were found to be to 1 μg/L to 2.5 μg/L.

Figure 3 plot cesium concentrations in the simulant exiting the column for Cycle 11. With the exception of one sample (7 BV) measured at 7 μg/L, all of the measured concentrations are at the detection limit, for both Cycle 1 and Cycle 11.

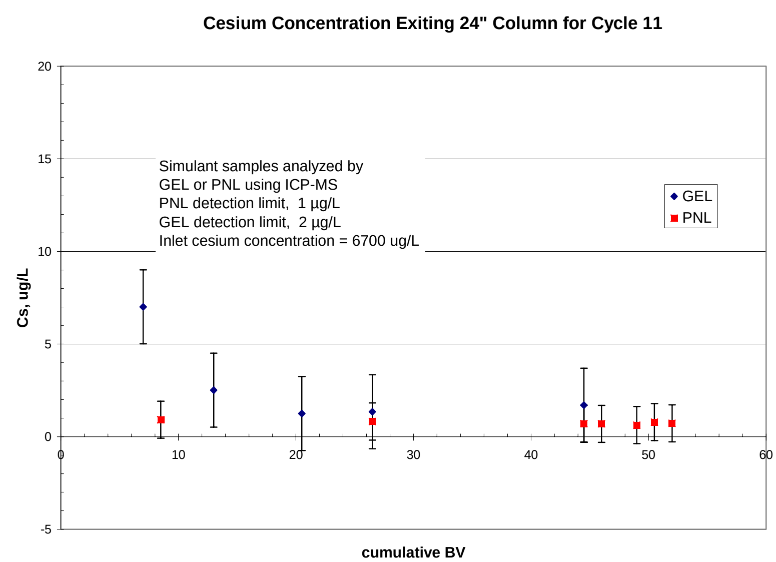

Fig. 3. Cesium Concentrations in Effluent Simulant for 24" IX, Cycle 11

The RF resin was found to be very efficient in removing cesium. Laboratory analyses concluded the Cs in the effluent essentially never exceeded the detection limit of the analysis method employed. After thirteenth cycles (Cycle 11), the RF resin showed no measurable degradation in cesium removal performance from chemical cycling.

In addition to measuring cesium by ICP-MS, rubidium concentration was also measured for the 24" RF hydraulic testing samples. The rubidium was apparently added as an impurity in one of the several compounds provided by vendors for the simulant mixed by SRNL. The results of the rubidium concentration were consistently in the range of several hundred micrograms/liter throughout the RF resin 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 PNNL 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 to SRNL in acid form. The resin was pretreated and converted to a sodium form at SRNL before adding it to the IX column for testing.

The particle size distribution (PSD) for the RF resin that under went testing in the 24" IX Column are listed in Table IV. 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.

Table IV. 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

From this 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. The 32% is in agreement with the actual bed height measurements taking during each cycle.

Figure 4 is photomicrographs of random samples of RF resin in hydrogen form, before and after cycle testing. The picture on the left is new virgin resin and the picture on the right is after completing 16 total cycles. The pictures indicate a negligible quantity of fines in the random samples which also suggest no damaged beads after the sixteen cycles. Also the picture indicates that the spherical geometry of the beads where not changed due the cycling.

From the photomicrographs it was determined that in hydrogen form the beads has a diameter of about 400 um, which is in agreement with the Microtrac measurements. Micrographs comparing representative bead samples before and after the sixteen cycles in the 24" IX Column indicated no change in bead morphology.

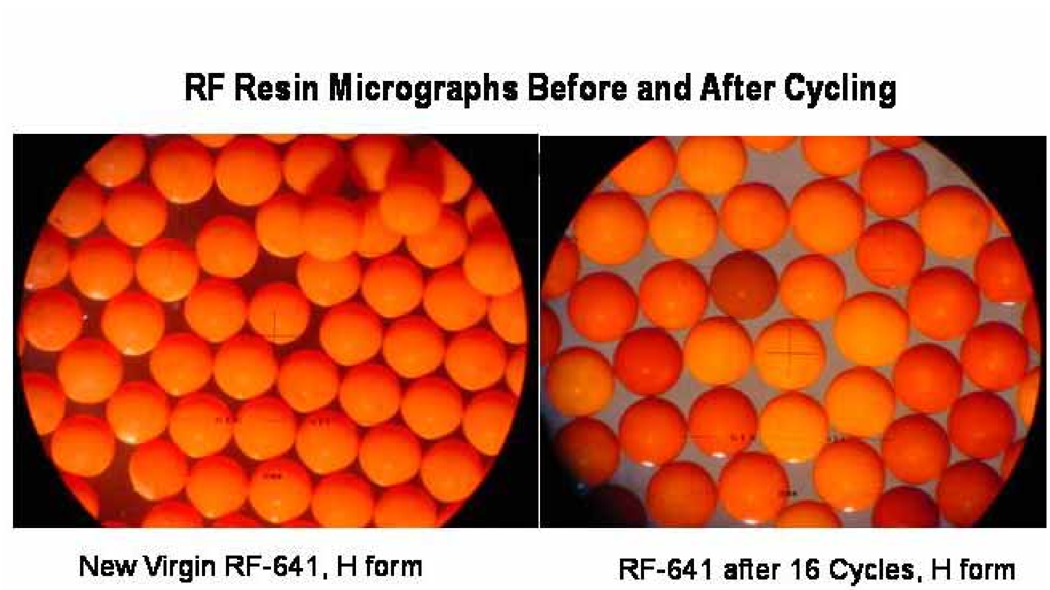

Fig. 4. Resin in Hydrogen Form, Before and After 16 Cycle in 24" IX Column

The skeletal density of the RF resin from the 24" IX Column, increased slightly with cycles in both hydrogen and sodium form. The skeletal density followed the same trend as the density of the resin where it also increased with cycles. The results of the RF resin skeletal density measurements are given in Table V. Over the sixteen cycle campaign, the skeletal density increased a mere 0.028 g/ml.

Table V: Skeletal Density Results, 24" IX Column

RF Resin Sample	Hydrogen Form g/ml	Sodium Form g/ml
New Pretreated Resin from Resin Addition Vessel	1.510	--
Ten total Cycles from the Column Core Sample	1.524	1.589
Sixteen total Cycles the Column Core Sample	1.538	1.602
Sixteen total Cycles top layer dark particles	1.569	1.637
PNWD 3" IX Column new RF, Batch 5E-370/641	1.48	1.63

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 ratio of 1.185. Resin heights were measured during each of the cycle tests. The resin height in sodium form is about 30% greater than the height in acid form. In both fully swollen (sodium) form and fully shrunken (acid) form for the sixteen cycles, the bed height increased. In simulant, the resin bed height increased about 3% over the sixteen cycles as shown in Table VI.

Table VI. Bed Height Change in 24" IX Pilot-scale Column Testing

Cycle #	Bed height acid form cm	Bed height sodium form cm
Cycle 0.1	56.1	72.0
Cycle 0.2	55.4	71.2
Cycle 1	--	72.5
Cycle 2	56.5	73.0
Cycle 3	56.5	72.3
Cycle 4	--	73.5
Cycle 5	57.3	73.2
Cycle 6	57.1	73.5
Cycle 7	57.1	73.7
Cycle 8	--	73.9
Cycle 9	57.3	73.4
Cycle 10	56.8	73.5
Cycle 11	57.1	73.9
Cycle 12	57.1	74.1
Cycle 13	57.5	74.3
Cycle 14	57.5	74.4

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 with an average adjusted permeability of 3.40×10^{-6} cm^2. The permeability did not decrease which would have been indicative of resin breakdown and 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 3.

The RF resin was found to be very efficient in removing cesium (Cs). Cs in the effluent essentially never exceeded the detection limit. After thirteenth total cycles, the RF resin showed no measurable degradation in cesium removal performance from cycle testing.

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. Oxygen saturated feeds caused some oxidation to the resin but did not degrade the resin’s hydraulic or chemical performance.

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.

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