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PILOT-SCALE HYDRAULIC TESTING OF RESORCINOL FORMALDEHYDE ION EXCHANGE RESIN

AUTHOR

Duane J. Adamson,
Savannah River National Laboratory
Savannah River Nuclear Solutions, LLC
786-5A
Aiken, SC 29808
duane.adamson@srnl.doe.gov

ABSTRACT

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 hydraulic 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. Sixteen of these cycles were completed in the 24” IX Column (1/2 scale 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 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.

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.

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 RF resin is durable and should hold up to many hydraulic cycles in actual radioactive Cesium (Cs) separation.

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 were 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 hydraulic results from the sixteen cycles completed on the 24” IX Column.

TEST FACILITY

The ion exchange (IX) column was constructed from a section of 316-L, 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 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 visual observations below the bed. The resin was mostly contained within the stainless steel section of the column due to anticipated bed stresses as a result of 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 bed volume (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, mimicking the full-scale design.

Figure 1 is a process and instrumentation drawing (P&ID), showing the complexity of the 24” IX Test System.

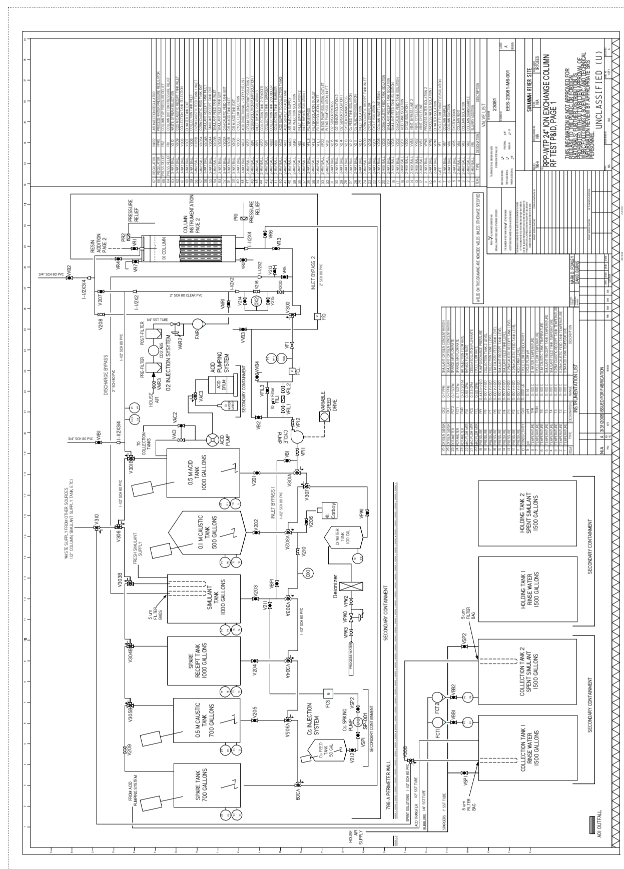

Fig. 1: 24” Ion Exchange Column Test System P&ID

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 measurement and test equipment (M&TE) was logged by a PC based Data Acquisition System (DAS) with National Instruments LabView® software. The data from the testing was logged by the DAS. 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.

Polyethylene, open-top storage tanks ranging from 60 gallons to 1,500 gallons capacity 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

TEST MATRIX AND CONDITIONS

Testing in the 24" IX column included two preliminary hydraulic cycles, Cycles 0.1 and 0.2 and fourteen formal 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 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 simulant used had a density of 1.25 g/ml and the viscosity was approximately 2.9 cP for the hydraulic test campaign.

Testing was conducted on the 24" IX column using an approved procedure, covering sixteen full cycles. The sixteen cycles consisted of six steps; regeneration in 0.5 M 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. Below gives additional detail of each step in a cycle.

Regeneration - is the step where the resin is regenerated and the resin will swell. This was conducted by flowing 0.5 M NaOH up through the bed (up-flow) on all sixteen cycles. The velocity of the fluid flowing through the resin bed was 12.4 cm/min for 30 min. the flow was stopped for approximately 3 minutes, and then the flow was restarted at 2.0 cm/min for an additional 20 minutes.

Simulant Introduction - is the step where simulant is introduced to the IX column. The volume added is one column volume (CV). This up-flow step prevents the resin bed from being disturbed or un-leveled by any previous down flow regimes. The velocity of the fluid was 2.5 cm/min for 52 minutes then reduced to 4.0 cm/min to finish one column volume.

Simulant Loading – was always in down-flow and for most cycles the velocity of the fluid was 26.9 cm/min for 72 bed volumes of fluid flow.

Displacement – is the step where 0.1 M NaOH flowed through the bed to displace the simulant from the column. The velocity of the fluid was 8.8 cm/min for 3 bed volumes.

Pre-elution – This step displaces the 0.1 M NaOH from the column by down-flowing DI water through. This procedure prevents precipitation of solids during elution. The velocity of the fluid was 13.3 cm/min for 2.5 bed volumes.

Elution – This step removed the cesium from the resin bed by down-flowing 0.5 M HNO_3 through the bed. This is the step where the resin will fully shrink. The fluid was down-flowed through the bed at 6.1 cm/min for 15 bed volumes.

Post- elution - this step removes the 0.5 M HNO_3 from the column by down-flowing DI water. This procedure prevents precipitation of solids during simulant introduction. The velocity of the fluid was 13.3 cm/min for 1.2 column volumes.

The sixteen cycles had the following 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.

The differences that existed between the cycles were as follows.

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. Downflow was conducted on these cycles to show affect on pressure drop across the resin

bed and to demonstrate disturbance of the resin bed if simulant was introduced in this manner.

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 pressure drop across the resin bed of 9.7 psig, which would simulate the maximum bed ΔP 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 subsequent cesium injection cycles.

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

Table 1. 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 is shown in Table 2 for simulant. Excluding the two cycles with downflow introduction (cycles 0.1 and 6) of simulant and Cycle 0.2 of which flow rate measurements deviated substantially. This was attributed to flow meter failure. The average permeability was 3.40 x 10^{-6} cm^2.

Table 2. Hydraulic Summary 24" IX Column

	Velocity cm/min	ΔP, inch H_2O	Resin height, cm	Perme-ability, $cm^2 * 10^{-6}$
Cycle 0.1	13.39	61.8	73.0	3.28
Cycle 0.2	10.39	64.4	71.2	2.31
Cycle 1	1.81	7.9	72.5	3.39
Cycle 2	13.41	61.0	73.0	3.22
Cycle 3	26.95	123.0	72.3	3.22
Cycle 4	13.42	58.0	73.5	3.43
Cycle 5	13.39	55.0	73.2	3.64
Cycle 6	13.39	74.0	73.5	2.67
Cycle 7	13.41	58.0	73.7	3.40
Cycle 8	13.42	58.0	73.9	3.22
Cycle 9	26.95	118.0	73.4	3.32
Cycle 10	59.05	263.5	73.5	3.15
Cycle 11	1.80	7.9	73.9	3.22
Cycle 12	13.42	52.5	74.1	3.61
Cycle 13	26.95	104.2	74.3	3.67
Cycle 14	13.41	58.5	74.4	3.24

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
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.

Figure 2 is a plot of the permeability for each of the 16 cycles run 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 completed cycles) where the Simulant Introduction step occurred in downflow. Cycle 10 (twelve completed cycles) was the worst case scenario for permeability where the flow rate was 43 gpm (turbulent flow) and the ΔP 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 x 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 x 10^{-6} cm^2.

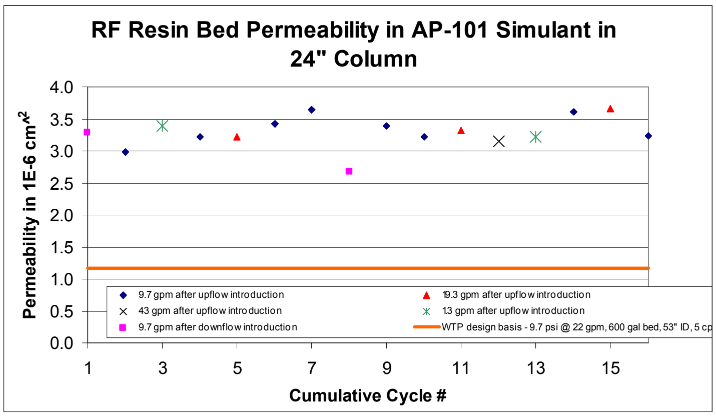

Fig. 2. RF Resin Bed Permeability, 24" IX

Solid pressures were measured using load cells during testing of the 24" column, where the highest solid pressures were measured in the highest flow rate cycle. Cycle 10 had a simulant superficial velocity of 59 cm/min resulting in a flow rate of 43 gpm. 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. Regeneration of the resin bed in upflow is the main reason that low solid pressures were seen. As the resin swells in upflow, the resin beads can reposition without causing radial pressure to the IX wall.

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.

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 hydraulic testing. Below is a picture showing the top of the resin bed after being added to the 24" IX column.

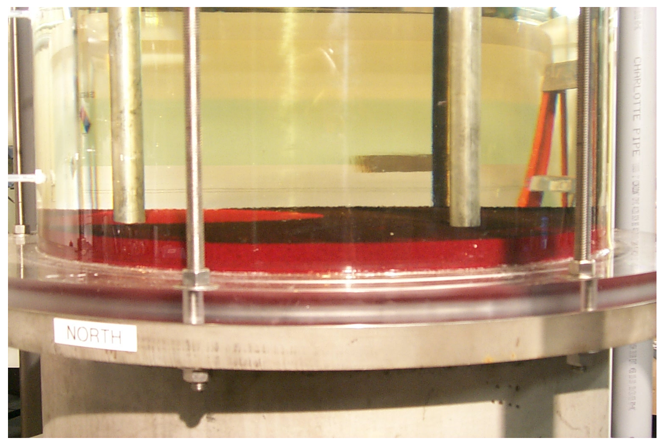

Fig. 3. RF Resin Bed in 24" IX Column

Due to concerns of high radial stresses when the resin was fully swollen, the majority of the resin bed was contained inside a sturdy stainless steel housing to prevent damage to the IX column if high stresses were to occur.

The particle size distribution (PSD) for the RF resin that under went testing in the 24" IX Column is listed in Table 4. 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 Table 4, there was no significant difference in the particle size before and after the sixteen cycles.

Table 4. 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 (0.5 M)	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 (0.5 M)	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. This ratio is in agreement with the actual bed height measurements taking during each cycle.

Figure 4 is a photomicrograph of a random sample of RF resin in hydrogen form after Cycle 14. The pictures indicate a negligible quantity of fines in the random samples which also suggest no damaged beads after a total of sixteen cycles. Also, the picture indicates that the spherical geometry of the beads were not changed due the cycling.

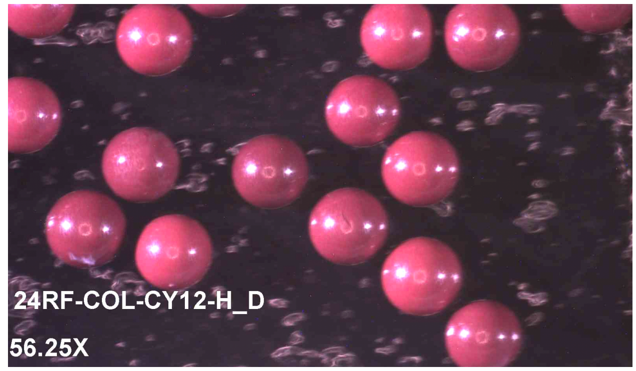

Fig. 4. Resin in Hydrogen Form after Cycle 14

From the photomicrographs it was determined that in hydrogen form the beads have 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.

Resin addition to the 24" IX column gave an initial resin bed height of 72 cm (28.4") or an L/D ratio of 1.22. 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. This change in bed height did not impact the hydraulic performance of the resin bed.

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 indicating excellent hydraulic performance. The permeability did not decrease, which would have been indicative of resin particle fracture or fines creation over the test campaign. The permeability demonstrated during these tests surpassed the WTP full-scale requirement of 1.17 x 10^{-6} cm^2 by a factor of 3.

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. This finding is in agreement with the near constant permeability demonstrated over the hydraulic testing campaign.

Up-flow 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. Conversely, 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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