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Hydraulic Permeability of Resorcinol-Formaldehyde Resin

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Nuclear Science and Technology Division

HYDRAULIC PERMEABILITY OF RESORCINOL-FORMALDEHYDE RESIN

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ACRONYMS

DO	dissolved oxygen
FCV	flow control valve
ICP-MS	inductively coupled plasma–mass spectroscopy
K_d	distribution coefficient
PVC	polyvinyl chloride
RF	resorcinol-formaldehyde
SCIX	small column ion exchange
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
VFD	variable frequency drive
WTP	waste treatment plant

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EXECUTIVE SUMMARY

An ion exchange process using spherical resorcinol-formaldehyde (RF) resin is the baseline process for removing cesium from the dissolved salt solution in the high-level waste tanks at the Hanford Site, using large scale columns as part of the Waste Treatment Plant (WTP). The RF resin is also being evaluated for use in the proposed small column ion exchange (SCIX) system, which is an alternative treatment option at Hanford and at the Savannah River Site (SRS). A recirculating test loop with a small ion exchange column was used to measure the effect of oxygen uptake and radiation exposure on the permeability of a packed bed of the RF resin. The lab-scale column was designed to be prototypic of the proposed Hanford columns at the WTP. Although the test equipment was designed to model the Hanford ion exchange columns, the data on changes in the hydraulic permeability of the resin will also be valuable for determining potential pressure drops through the proposed SCIX system. The superficial fluid velocity in the lab-scale test (3.4−5.7 cm/s) was much higher than is planned for the full-scale Hanford columns to generate the maximum pressure drop expected in those columns (9.7 psig). The frictional drag from this high velocity produced forces on the resin in the lab-scale tests that matched the design basis of the full-scale Hanford column. Any changes in the resin caused by the radiation exposure and oxygen uptake were monitored by measuring the pressure drop through the lab-scale column and the physical properties of the resin.

Three hydraulic test runs were completed, the first using fresh RF resin at 25°C, the second using irradiated resin at 25°C, and the third using irradiated resin at 45°C. A Hanford AP-101 simulant solution was recirculated through a test column containing 500 mL of Na-form RF resin. Known amounts of oxygen were introduced into the primary recirculation loop by saturating measured volumes of the simulant solution with oxygen and reintroducing the oxygenated simulant into the feed tank. The dissolved oxygen (DO) concentration of the recirculating simulant was monitored, and the amount of oxygen that reacted with the resin was determined from the change in the DO concentration of the recirculating simulant solution. Prior to hydraulic testing the resin for runs 2 and 3 was covered with the simulant solution and irradiated in a spent fuel element at the Oak Ridge National Laboratory High Flux Isotope Reactor (HFIR). Both batches of resin were irradiated to a total gamma dose of 177 Mrad, but the resin for run 2 reached a maximum temperature during irradiation of 51°C, while the resin for run 3 reached a temperature of 38°C. The different temperatures were the result of the operating status of HFIR at the time of the irradiation and were not part of the test plan; however, the results clearly show the impact of the higher-temperature exposure during irradiation.

The flow rate and pressure drop data from the test loop runs show that irradiating the RF resin reduces both the void fraction and the permeability of the resin bed. The mechanism for the reduction in permeability is not clear because irradiation increases the particle size of the resin beads and makes them deform less under pressure. Microscopic examination of the resin beads shows that they are all smooth regular spheres and that irradiation or oxygen uptake did not change the shape of the beads. The resin reacts rapidly with DO in the simulant solution, and the reaction with oxygen reduces the permeability of a bed of new resin by about 10% but has less impact on the permeability of irradiated resin. Irradiation increases the toughness of the resin beads, probably by initiating cross-linking reactions in them. Oxygen uptake reduces the crush strength of both new and irradiated resin; however, the pressures that caused the beads to crush are much higher than would be expected during the operation of an ion exchange column. There was no visible evidence of broken beads in any of the resin samples taken from the test loop. Reaction with oxygen reduces the cesium distribution coefficient of the resin beads, as does irradiation. Higher temperatures during irradiation or during contact with the simulant solution further reduce the cesium distribution coefficient.

1. INTRODUCTION

An ion exchange process using spherical resorcinol-formaldehyde (RF) resin is the baseline process for removing cesium from the dissolved salt solution in the high-level waste tanks at the Hanford Site using large-scale columns as part of the waste treatment plant (WTP). The RF resin is also being evaluated for use in the proposed small column ion exchange (SCIX) system, which is an alternative treatment option at Hanford and at the Savannah River Site (SRS). Previous testing at Pacific Northwest National Laboratory[1] has measured the hydraulic permeability of fresh RF resin. The testing described in this report has determined the impact of radiation exposure and oxygen uptake by the RF resin on the hydraulic permeability of the resin. Small samples of the resin were periodically removed from the hydraulic test columns to measure physical properties (bead size and compressibility) and cesium uptake.

The full-scale treatment system planned for the WTP at Hanford will use ion exchange columns containing 600 gal of resin, which will treat 30 gpm of waste solution. The full-scale ion exchange columns are designed for a typical resin bed pressure drop of 2 psig, with a maximum of 9.7 psig.

The lab-scale column was designed to be prototypic of the proposed Hanford columns, with the bed-length-to-diameter ratio (1.5) scaled to match the Hanford column with a 680 gal bed (to conservatively bound the potential resin bed volume). Although the test equipment was designed to model the Hanford ion exchange columns, the data on changes in the hydraulic permeability of the resin will also be valuable for determining potential pressure drops through the proposed SCIX. The fluid velocity in the lab-scale test was much higher than planned for the full-scale Hanford columns to generate the maximum pressure drop expected in those columns (9.7 psig). The frictional drag from this high velocity produced forces on the resin in the lab-scale tests that matched the design basis of the full-scale Hanford column. Any changes in the resin caused by the radiation exposure and oxygen uptake were monitored by measuring the pressure drop through the lab-scale column and the physical properties of the resin.

2. MATERIALS AND METHODS

2.1 TEST DESCRIPTION

Three hydraulic test runs were completed, the first using a column of fresh RF resin at 25°C, the second using a column of irradiated resin at 25°C, and the third using a column of irradiated resin at 45°C. A Hanford AP-101 simulant solution (see Sect. 2.3) was recirculated through a test column containing 500 mL of Na-form RF resin. The flow rate was adjusted over a range of 2.6−4.3 gpm as necessary to maintain the desired pressure drop of 9.7 psig. Measured amounts of oxygen were introduced into the primary recirculation loop by saturating measured volumes of the simulant solution with oxygen and reintroducing the oxygenated simulant into the feed tank. The dissolved oxygen (DO) concentration of the recirculating simulant was monitored, and the amount of oxygen that reacted with the resin was determined from the change in the DO concentration of the recirculating simulant solution. About 15 batches of oxygenated simulant were required to reach the final oxygen dose for each run. Before the first oxygen dose and after oxygen doses of about 1.5, 3.0, 4.5, 6.0, and 7.0 mmol/g, the column was backwashed with the simulant solution, expanding the bed about 50%, and any change in pressure drop after backwashing was monitored. After each backwash a small sample of resin was removed from the column to measure the physical properties and cesium sorption of the resin.

2.2 EQUIPMENT

A test loop was designed and fabricated for recirculating a simulant solution through a column containing the RF resin while controlling the flow rate and temperature of the simulant and monitoring the pressure drop through the resin bed (Figs. 1 and 2). The feed tank was a 55 L polyethylene conical-bottom tank. A separate 50 L polyethylene carboy (on the right side in Fig. 1) was used to oxygenate batches of the simulant solution using four aeration stones connected to a common header, which was connected to an oxygen gas cylinder, to supply fine bubbles of oxygen gas into the simulant solution. A rotameter and valve were used to control the oxygen gas flow rate at 5 L/min. The oxygenated simulant (40 L per batch) was pumped back into the feed tank and recirculated through the column of resin, where the DO reacted with the resin.

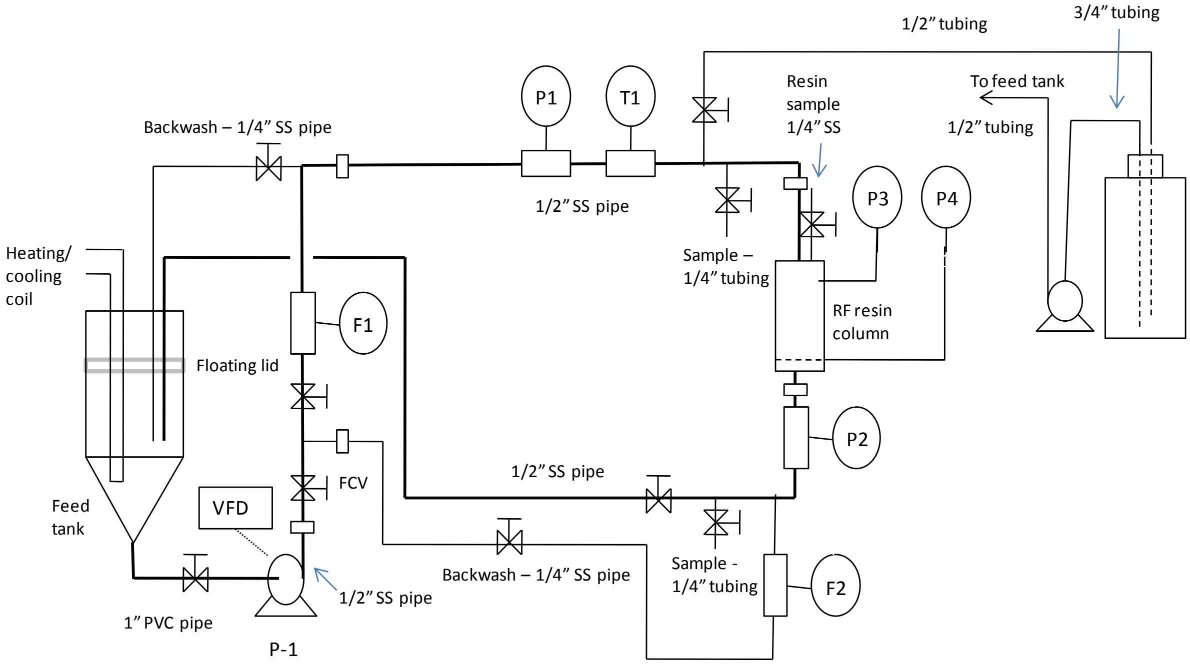

Fig. 1. Diagram of test loop.

A 3.07 in. inside-diameter clear polyvinyl chloride (PVC) pipe with stainless steel end caps was used for the ion exchange column in the test loop. Figure 3 shows a photograph of the column in use and a diagram of the column design. The top screen (inlet) was originally a 7/8 in. diameter by 1 in. long wedge-wire screen (Johnson Screens, Inc., New Brighton, MN); however, during the first run it was noted that there was a large pressure drop through the screen that restricted the flow rate. The pressure on P-1 was >20 psig for flow rates above about 2 gpm. Before the second run, the wedge-wire screen was replaced with a 1.5 in. pipe connector with a 100-mesh screen welded across the opening (Fig. 4). The pressure drop across this new inlet screen during runs 2 and 3 was minimal.

The recirculation pump was a magnetic-drive, 1/2 hp centrifugal pump (Model 75226-15, Cole-Parmer, Vernon Hills, IL) with a variable frequency drive (VFD) (model VFD02-D230AC, Minarik Drives, South Beloit, IL) (gray box in Fig. 2) to control the flow rate. A globe valve (flow control valve [FCV] in Fig. 1) was also installed in the test loop, but it was not needed to control the flow rate. A turbine flow meter (Model 05, Great Plains Industries, Inc., Wichita, KS) was used to measure the flow rate of the recirculating simulant solution. A digital thermometer (mounted on the VFD box) with a K-type thermocouple probe installed in the flow path was used to monitor the temperature of the simulant. Two pressure gauges (0–15 psig, USG, Inc. Sellersville, PA), connected near the top and just above the bottom screen of the column (P-3 and P-4 in Fig. 1), were used to monitor the pressure drop through the resin bed. A heated/refrigerated water bath circulator (Model 11505, VWR International, Inc., West Chester, PA) was used to control the temperature of the simulant by recirculating water through a 1/2 in. tubing coil inside the feed tank. A DO meter (Symphony Model SP70D, VWR International, Inc.) was used to monitor the DO concentration of the simulant solution. The DO probe was not stable during long-term exposure to the simulant, so samples of the recirculating solution were periodically removed, and the DO was measured using minimal agitation.

Fig. 2. Photograph of the test loop.

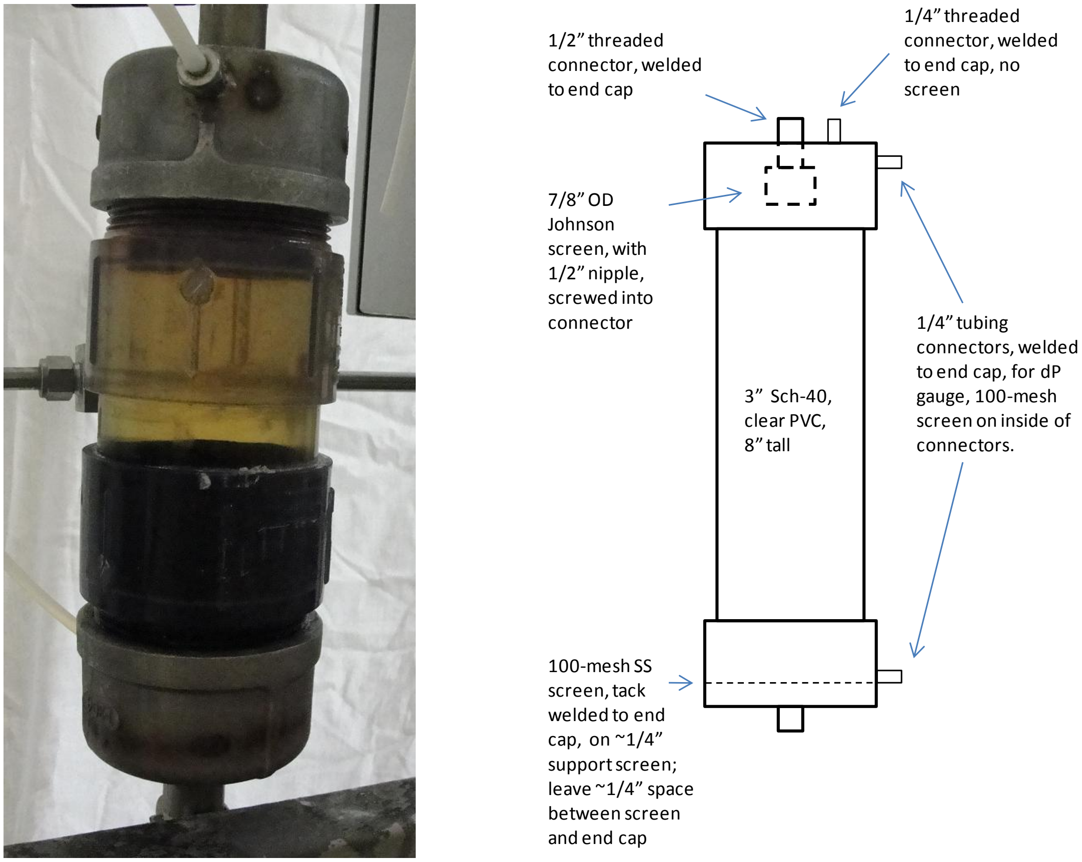

Fig. 3. Photograph and diagram of the test loop column.

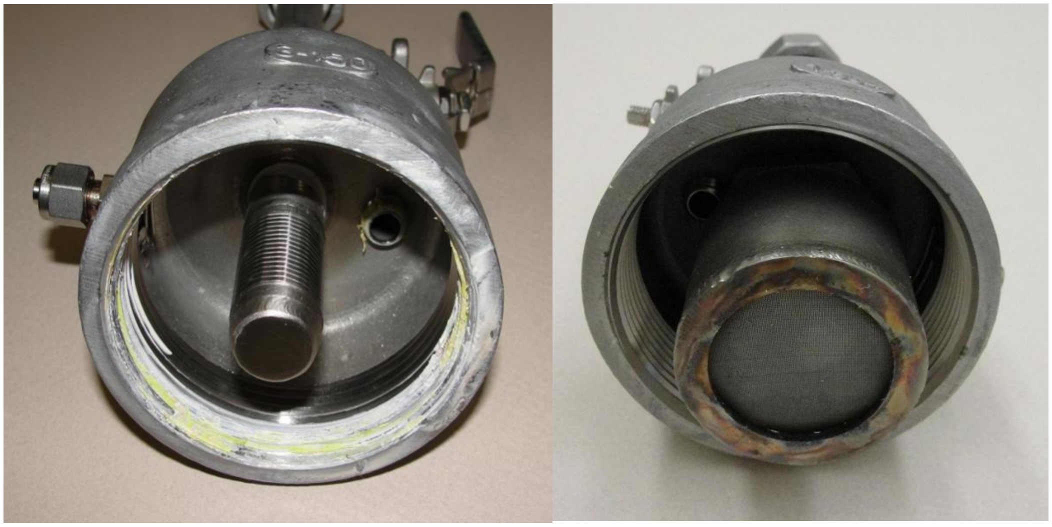

Fig. 4. Original top end cap of column, with Johnson screen on left and modified end cap with 1.5 in. screened fitting on right.

2.3 MATERIALS

The spherical RF resin used in these tests was from lot #5E-370/641, manufactured by Microbeads AS (Skedsmokorset, Norway), and was obtained from Savannah River National Laboratory. The resin was pretreated by converting the as-received H-form resin to the Na-form using 1 *M* NaOH, then back to the H-form using 0.5 *M* HNO_3, and finally back to the Na-form using a procedure developed at SRS.[2] The Na-form resin was dewatered, the 500 mL of resin for each test loop column was weighed to determine the damp weight, and then additional samples of the damp resin were dried and weighed to determine the percent moisture and calculate the dry weight of resin added to the column. Additional samples of damp resin were weighed, converted to the H-form, and dried and weighed to calculate the dry H-form resin weight that was added to the column. The resin samples were dried in a vacuum oven at 50°C to a stable weight, which took several days. For the resin batches that were irradiated, the resin was pretreated as described above, then placed in several bottles with Hanford AP-101 simulant and delivered to the Oak Ridge National Laboratory High Flux Isotope Reactor (a user facility supported by the U.S. Department of Energy), where the bottles of resin were gamma irradiated in a spent fuel element. The first bottle of resin was placed in a fuel element with a dose rate of 20 Mrad/h for 6 h. After removing the bottle from the element, it was discovered that most of the simulant solution had been pushed out of the vented lid of the bottle into the secondary containment vessel. The temperature inside the bottle was not measured during the irradiation, but presumably it reached the boiling point of the simulant (~107°C). This bottle of resin was not used in the test loop because it had reached such a high temperature. The subsequent bottles of resin and simulant were irradiated in an older spent fuel element, which had a dose rate of 1.6 Mrad/h, and a thermocouple was placed in the bottles to monitor the temperature. The planned dose was 120 Mrad; however, dosimeters placed on the bottles showed a reading of 177 Mrad. Apparently the bottles were picking up additional radiation from adjacent fuel elements. The temperature measured inside the bottles was 51°C for the first two bottles, which were used in run 2, and 38°C for the last bottle, which was used in run 3. The reactor was shut down during the time that the final bottle was being irradiated, so the water in the pool, which is shared by the reactor and spent fuel elements, was cooler and kept the temperature inside the bottle lower.

The Hanford AP-101 simulant used in the test loop was prepared in a 50 L batch using reagent-grade chemicals and deionized water. The composition of the simulant was analyzed using inductively coupled plasma–mass spectroscopy (ICP-MS) for metals and ion chromatography for anions. Extra water was mistakenly introduced into the simulant in the test loop, so the concentrations were lower than planned (Table 1).

Table 1. Composition of Hanford AP-101 simulant solution

Component	Target (*M*)	Measured (*M*)
NaOH	2.0	NA[a]
$NaNO_3$	1.0	0.78
$NaNO_2$	0.7	0.56
$NaAlO_2$	0.3	0.30
Na_2SO_4	0.04	0.034
Na_2CO_3	0.4	NA
NaCl	0.04	0.036
KNO_3	0.7	0.59

[a] Not analyzed

The density and viscosity of the simulant solution were measured at various temperatures. A volumetric flask and calibrated analytical balance were used to determine the density, and a glass capillary (Cannon-Fenske) viscometer was used to measure the viscosity. The results are shown in Table 2.

Table 2. Density and viscosity of simulant solution

Temperature (°C)	Density (g/mL)	Viscosity (cP)
25.0	1.239	2.728
30.0	1.236	2.450
35.0	1.232	2.150
40.0	1.230	1.918
45.0	1.227	1.754

3. RESULTS AND DISCUSSION

Run 1, using new, pretreated resin, was originally planned to be a short-term scoping test of the equipment and procedures; however, because of delays in obtaining the irradiated resin for runs 2 and 3, the testing continued until the resin had reacted with 7 mmol O_2/g resin. All of the oxygen uptake numbers use the dry weight of H-form resin in the column to calculate the value. Operations for run 1 were periodically conducted over a span of 33 d. The temperature of the recirculating simulant solution was controlled at 25°C, with a measured range of 23−26°C. The settled volume in simulant solution of the Na-form resin placed in the column for run 1 was 500 mL prior to hydraulic testing, and the calculated dry H-form weight of the resin was 150.7 g. Because of the pressure drop caused by the wedge-wire inlet screen (see Sect. 2.2), the pump could not be continuously run at a flow rate that would give the desired pressure drop through the resin bed of 9.7 psi without tripping the overload protection in the VFD. The system was run at a lower flow rate (~2 gpm) most of the time and then increased to a flow rate (3.4–3.9 gpm), which would give a pressure drop of 9.7 psi for short periods of time. The resin used in run 1 was exposed to the maximum compression force, caused by the 9.7 psi pressure drop through the bed, for a much shorter period of time than was the resin in runs 2 and 3. The change in the inlet screen for runs 2 and 3 (see Sect. 2.2) corrected this problem, and the flow rate for these runs could be kept at the desired value full time. The resin was backwashed, and a small sample of resin was removed from the column after oxygen uptake amounts of 3.35, 5.32, and 7.01 mmol O_2/g resin.

Run 2 used resin that had been irradiated to a total dose of 177 Mrad at a maximum temperature of 51°C. The calculated dry H-form weight of the resin added to the column was 133.9 g, which gave a settled volume of 500 mL of Na-form resin in a graduated cylinder containing simulant solution, prior to hydraulic testing. The test loop was continuously run for 7 d, and the temperature of the recirculating simulant was controlled at 25°C, with a measured range of 22−26°C. The resin was backwashed, and a small sample of resin was removed from the column after oxygen uptake amounts of 1.44, 2.94, 4.43, 5.90, and 7.02 mmol O_2/g resin.

The resin used for run 3 had been irradiated to a total dose of 177 Mrad at a maximum temperature of 38°C. The initial settled volume of the Na-form resin that was added to the column was 500 mL, and the calculated dry H-form weight of the resin was 142.6 g. The test loop was continuously run for 6 d, and the temperature of the recirculating simulant was controlled at 45°C. The carboy in which batches of simulant were oxygenated was not temperature controlled, so the temperature of the oxygenated simulant was 41–42°C when it was pumped back into the feed tank of the test loop. The temperature of the recirculating simulant was brought back to 45°C before readings were taken of the flow rate required to give a pressure drop of 9.7 psi. The resin was backwashed, and a small sample of resin was removed from the column after oxygen uptake amounts of 1.47, 2.92, 4.32, 5.77, and 6.7 mmol O_2/g resin. The resin samples that were converted to the H-form and then dried, which were used to calculate the weight of H-form resin that was added to the column, were not completed until after run 3 was complete. The H-form resin weight from run 2 was used to estimate the oxygen uptake amounts during the run, and because the actual H-form resin weight was higher for run 3 than it had been for run 2, the oxygen uptake concentrations were lower than planned when each of the resin samples from the column was taken.

The differences in the weight of the resin that was required to give a settled volume of 500 mL for the three runs were the result of changes in the particle size of the resin beads caused by irradiation and temperature (see Sect. 3.3).

3.1 DISSOLVED OXYGEN REACTION

Figure 5 shows the reduction in DO concentration as one batch of oxygenated simulant from each run was recirculated through the bed of RF resin. Comparison data without any resin in the column are also shown. The results for runs 1 and 2, in which the simulant solution was at a temperature of 25°C, are essentially the same, so irradiating the resin (run 2) had no effect on the reaction rate with oxygen. The results from run 3, which used simulant at 45°C, showed a lower initial DO concentration because the higher temperature reduced the saturation concentration, but the reaction rate was faster. The control tests, with no resin in the column and a high initial DO concentration, showed a very slow loss of DO to the atmosphere. Given the reaction with the resin was very fast, there would be very little time for any oxygen loss from the simulant before the concentration was reduced below the equilibrium concentration with air. For calculating the oxygen uptake by the resin, it was assumed that all of the change in DO concentration of the simulant was caused by the resin. The final control test used simulant with a very low DO concentration, achieved by bubbling nitrogen gas into the simulant. After the nitrogen gas was stopped, the DO concentration in the recirculating simulant was monitored to determine any pickup of oxygen from the atmosphere. There was only a very slow increase in the DO concentration, so any extra pickup of oxygen by the resin between batches of oxygen-saturated simulant should be minimal.

Figure 6 shows the reduction in DO concentration for six batches of oxygenated simulant throughout run 2. The oxygen concentrations listed in the figure legend are the cumulative oxygen uptake by the resin prior to introducing that batch of oxygenated simulant into the test loop. The results show that there was no change in the reaction rate as the total oxygen uptake by the resin increased. The other runs showed the same pattern.

The DO concentrations before and after the resin bed were measured several times during the testing. For DO concentrations of 15–23 mg/L entering the column, the outlet concentration typically dropped by about 4 mg/L. The change in concentration was lower as the inlet oxygen concentration was reduced, with a drop of about 1 mg/L at an inlet concentration of 2–4 mg/L. For a resin bed volume of 500 mL, a flow rate of 11–15 L/min (3–4 gpm), and a void fraction within the resin bed of about 40%, the contact time of the simulant with the resin within the column was about 1–1.5 s. The reaction of the resin with DO was very rapid under these conditions.

3.2 VOID FRACTION AND PERMEABILITY

The flow rates required to give a pressure drop through the RF resin bed of 9.7 psi (66.9 kPa) are shown in Fig. 7. For run 1 there was a slight, but uneven, decrease in the required flow rate as the resin reacted with more oxygen, indicating a decrease in bed permeability. The required flow rate for run 2, using irradiated resin, was significantly lower than for run 1, which used new resin. Irradiating the resin made it more difficult for the simulant solution to flow through it. For run 3, with irradiated resin and simulant at 45°C, the required flow rate was about the same as for run 1. The higher temperature reduced the viscosity of simulant solution (see Table 2), which increased the required flow rate for a given pressure drop.

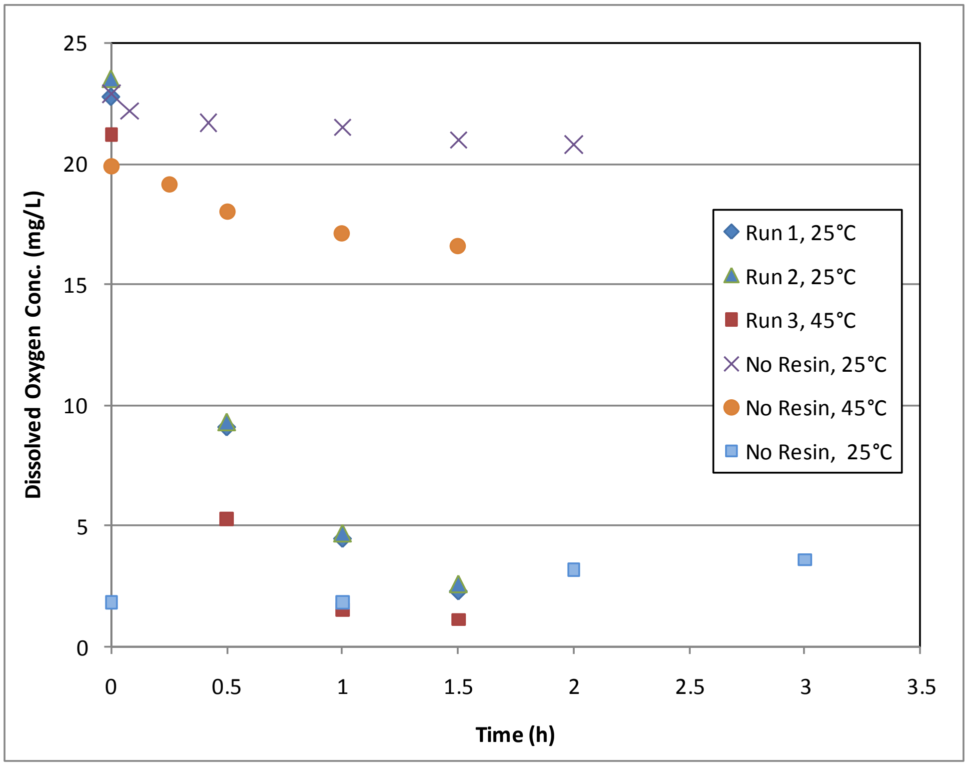

Fig. 5. Change in DO concentration of recirculating simulant solution.

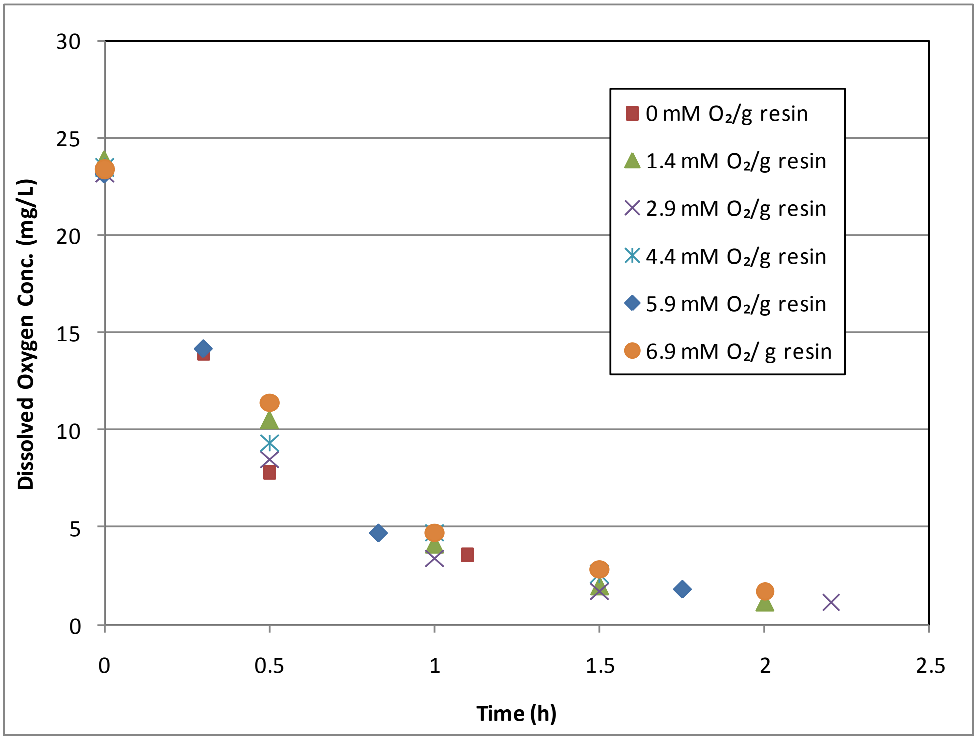

Fig. 6. Reaction of DO with the RF resin during run 2.

For run 1 the resin in the column was backwashed just before the data points at 3.35 and 5.32 mmol O_2/g resin. After the first backwash, the flow rate that gave a pressure drop of 9.7 psi did not change, but the flow rate increased by almost 0.5 gpm (2 L/min) after the second backwash, although it was still 0.2 gpm below what it was at the beginning of the test. The volume of resin in the column under flow conditions, calculated by the measured resin heights, averaged 467 mL, with a range of 462–472 mL. The pressure drop through the resin compressed the bed by almost 7% compared to the initial volume of 500 mL with no flow.

For run 2 the first two backwashes at 1.44 and 2.94 mmol O_2/g resin increased the flow rate required to give a pressure drop of 9.7 psi; however, the later backwashes did not change the required flow rate, which slowly declined after the second backwash. The third backwash at 4.32 mmol O_2/g resin had no impact on the required flow rate, while the backwash at 5.77 mmol O_2/g resin resulted in a small (0.1 gpm) increase. By the end of the test, the required flow rate was 0.4 gpm higher than it was at the beginning. It is not understood why the required flow rate increased rather than decreased during the testing for this sample. The measured resin bed height during flow conditions did not change during the test, and the calculated resin volume was 510 mL.

For run 3 the flow rate that gave a pressure drop of 9.7 psi slowly increased during the first part of the test before the first backwash at 1.47 mmol O_2/g resin. The first backwash did not change the required flow rate, which continued a gradual decline until the next backwash at 2.92 mmol O_2/g resin. This backwash resulted in a 0.6 gpm increase in the required flow rate. The required flow rate rapidly decreased after the second backwash, and the third backwash had only a minor impact on the required flow rate. There were no obvious differences in the backwashes, so it is unknown why the second one had such a different impact on the required flow rate. The calculated resin volume in the column started at 534 mL and the resin had compacted to 515 mL before the second backwash. The initial resin volume in the column, after heated simulant was flowing, was almost 7% higher than the 500 mL of settled resin that was added to the column. It appears that the 45°C simulant expanded the volume of the resin. After the second backwash the resin volume had increased to 538 mL, which would explain the higher flow rate after the backwash. The resin volume had decreased to 519 mL by the end of the test, and the required flow rate was 0.1 gpm below what it had been before the second backwash.

Ergun's equation[3] (Eq. 1) was used to calculate the void fraction (ε) in the resin beads from the measured pressure drop (ΔP), bed length (L), simulant viscosity (μ) and density (ρ), superficial velocity (u_o), and resin particle diameter (D_p). The results are shown in Fig. 8.

$$\frac{\Delta p}{L} = \frac{150\mu(1-\varepsilon)^2 u_o}{\varepsilon^3 d_p^2} + \frac{1.75(1-\varepsilon)\rho u_0^2}{\varepsilon^3 d_p} \tag{1}$$

Because the superficial velocity, which is calculated from the flow rate required to give a pressure drop of 9.7 psig, is the only variable in the Ergun equation that significantly changes during each run, the trend of the void fraction data in Fig. 8 mirrors the flow rate data in Fig. 7. The decrease in the viscosity and density of the simulant at 45°C shifted the void fraction data for run 3 compared to the flow rate data in Fig. 7 relative to the data for runs 1 and 2. The irradiated resin used in runs 2 and 3 showed a lower void fraction than the new resin that was used in run 1. The changes in the void fraction as the oxygen uptake increased were impacted by the backwashes the same way the required flow rates were. Void fraction results for a packed bed of new resin, calculated by Arm et al.[1], ranged from 0.37−0.38.

For a full-scale Hanford column with a bed height of 5.3 ft, a flow rate of 30 gpm, the waste solution viscosity and density used for runs 1 and 2, and a void fraction of 0.37, the predicted pressure drop would be 3.95 psi. For the same conditions except using a void fraction of 0.41, which is the calculated value for new resin, the predicted pressure drop would be 2.55 psi. The change in void

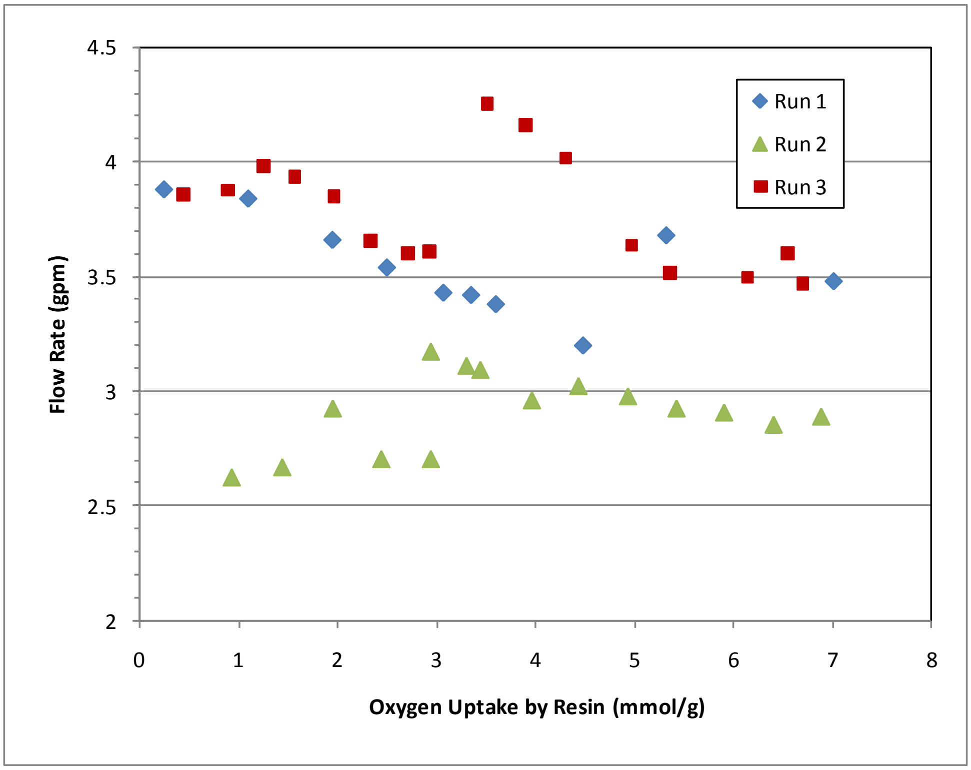

Fig. 7. Flow rate needed to give a pressure drop of 9.7 psi through resin bed as oxygen uptake increases.

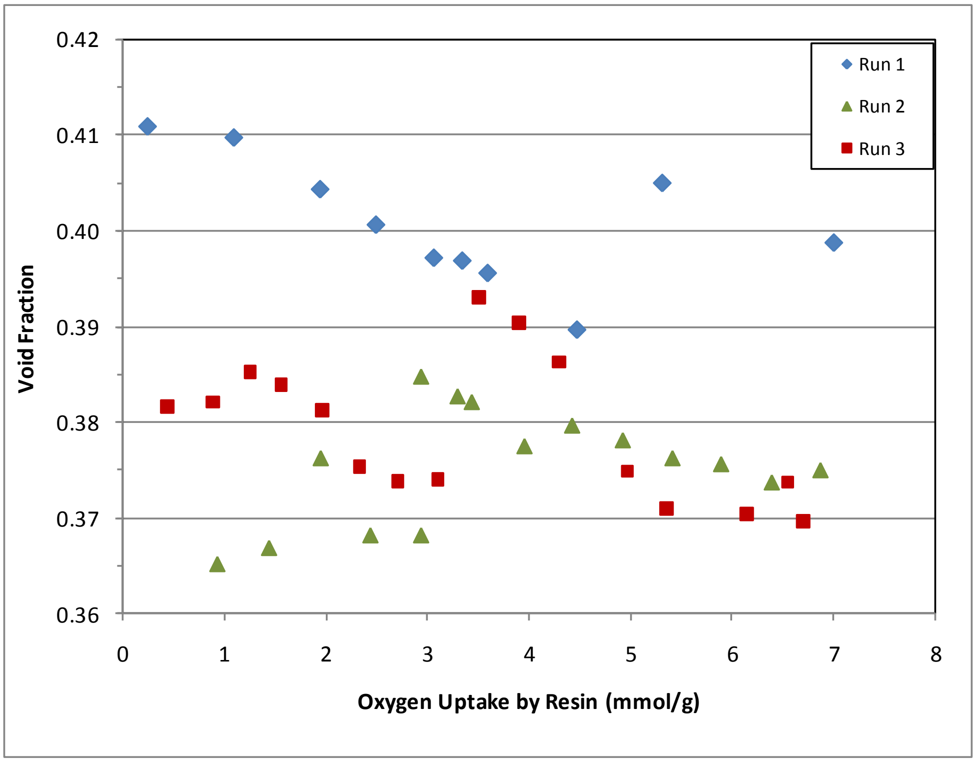

Fig. 8. Calculated void fraction in resin beds.

fraction resulting from irradiation and oxygen uptake by the resin would not cause a large change in pressure drop in the Hanford column.

The first term in the Ergun equation dominates for laminar flow, while the second term dominates for turbulent flow. The flow through the resin beds was in the transitional range for these tests. For run 1 the second term contributed about 16% of the pressure drop prediction. The second term contributed about 13% of the pressure drop prediction for run 2 and 23% for run 3.

Darcy's equation ($K = u_o \mu L / \Delta P$) was used to calculate the permeability (*K*) of the resin beds. This equation is accurate for laminar flow, but the flow through the resin beds in these tests was in the transition range, so the calculated permeabilities are approximate. The results are shown in Fig. 9. The calculated permeabilities follow the same pattern as the void fraction calculations. Irradiation definitely reduces the permeability of the resin bed, which is consistent with the reduction in void fraction. The permeability of a packed bed of new resin, calculated by Arm et al.[1], ranged from 3.1−3.4E-9 ft^2. A tabulation of the void fraction and permeability results is given in Appendix A.

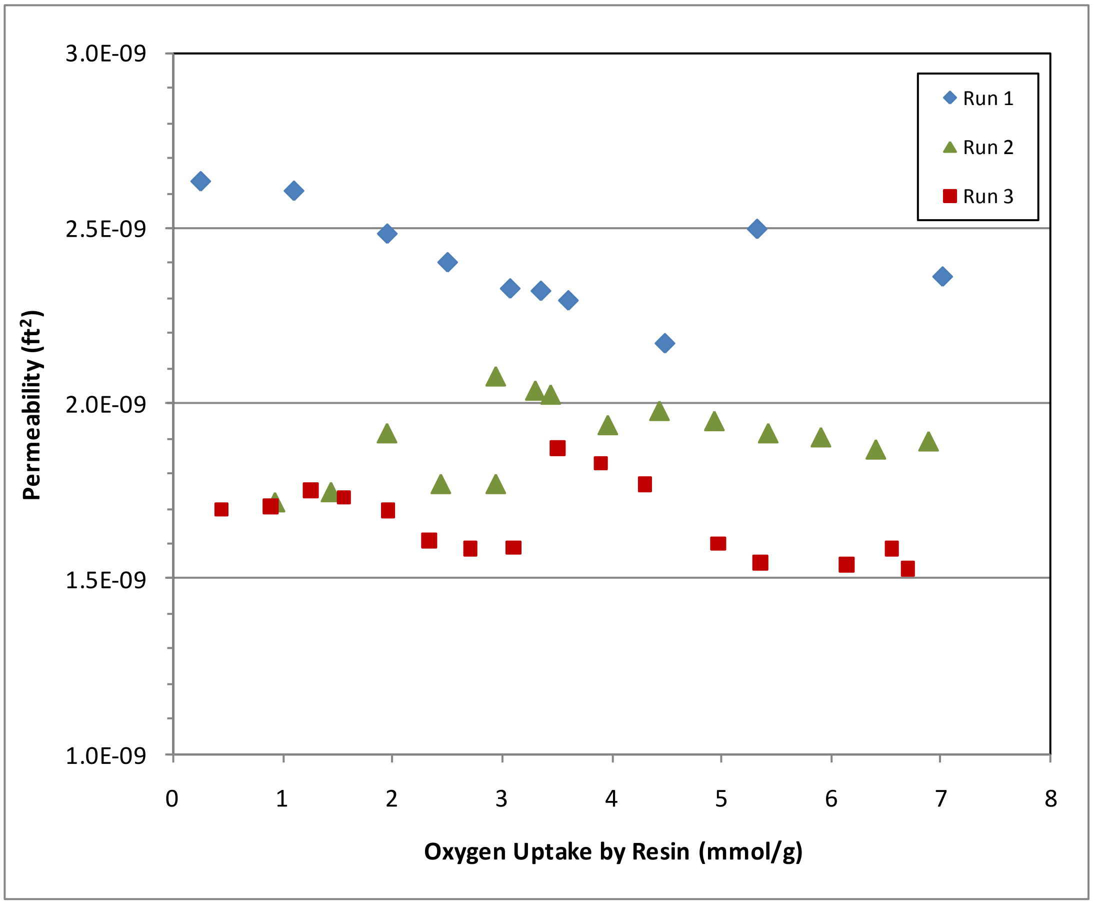

Fig. 9. Calculated permeability of resin beds.

3.3 RESIN PARTICLE SIZE AND STRESS-STRAIN MEASUREMENTS

A Model LS130 Coulter Counter (Coulter Scientific Instruments, Hialeah, FL) was used to measure the particle size of the resin samples from the test loop. The results are shown in Fig. 10. Small but measurable changes in the average particle size were observed in each run. A small amount of resin and simulant solution was added to deionized water in the measurement cell when analyzing the particle size, so the resin beads were in a solution of about 99.5% water when analyzed.

The new pretreated resin used in run 1 had the smallest particle size at the start of the run, but the largest particle size after reacting with 7 mmol O_2/g resin. The resin used in run 3, which was irradiated at a maximum temperature of 39°C initially had a slightly larger particle size than the new resin, but the size did not increase as much as with the new resin as it reacted with oxygen. The resin samples from run 2, which reached a maximum temperature of 51°C during irradiation, initially had the largest particle size, and the size increased at about the same rate as for the run 3 resin samples from reaction with oxygen. The particle size range for each of the samples was very tight, with a coefficient of variation of 4–6%.

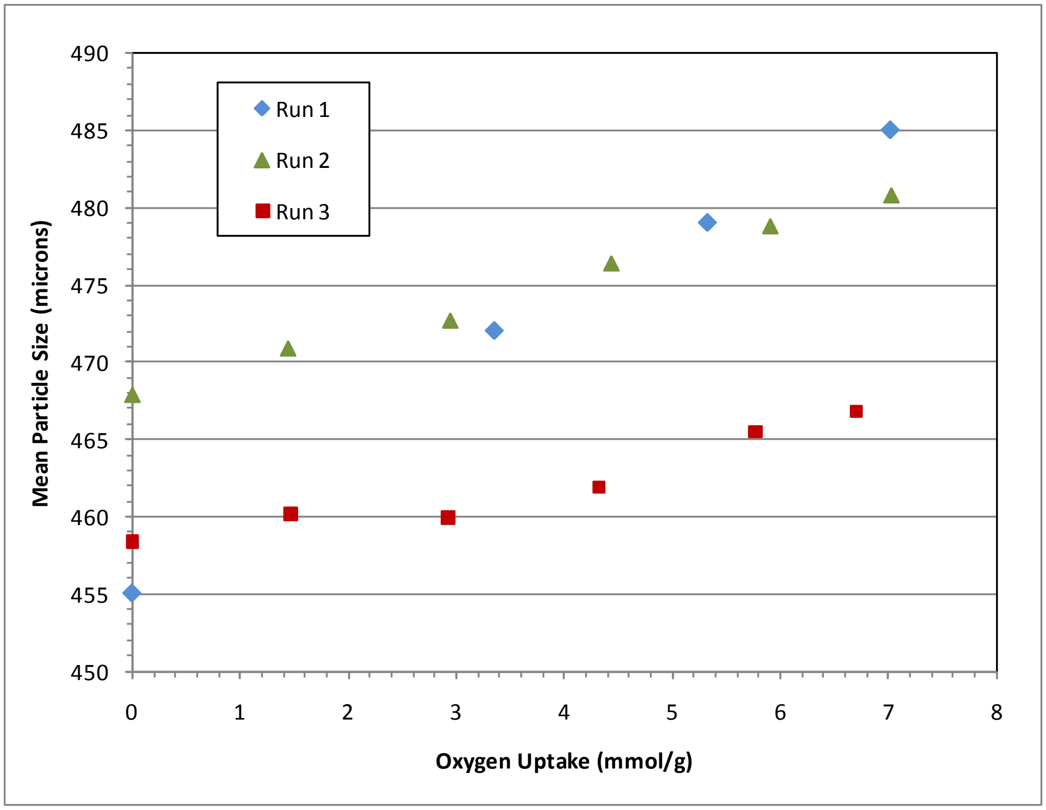

Fig. 10. Particle size results for resin samples.

The stress-versus-strain relationship for individual resin beads was measured using the modified balance shown in Fig 11. The micrometer at the top pushed on a spring-loaded piston above the balance pan. The micrometer measured the distance that the piston moved (strain), and the balance measured the force from the piston (stress). Resin beads were placed between two layers of cellophane tape to keep the beads damp with simulant and control the movement of the beads under the piston. The movement of the balance pan without any resin beads was measured at various weights, then this value was subtracted from the reading with the beads to calculate the net movement (strain) for just the beads.

The results for the measurements for the resin beads from run 2 are shown in Fig. 12. The oxygen uptake by the resin had no consistent effect on the stress-versus-strain results. The resin samples from runs 1 and 3 showed the same pattern, with no impact of oxygen uptake on the results. The results for the initial resin samples from all three runs are shown in Fig. 13. The new resin from run 1 compressed more at each stress level than the irradiated resin from runs 2 and 3. Irradiating the resin made it tougher, possibly by initiating cross-linking reactions in the resin.

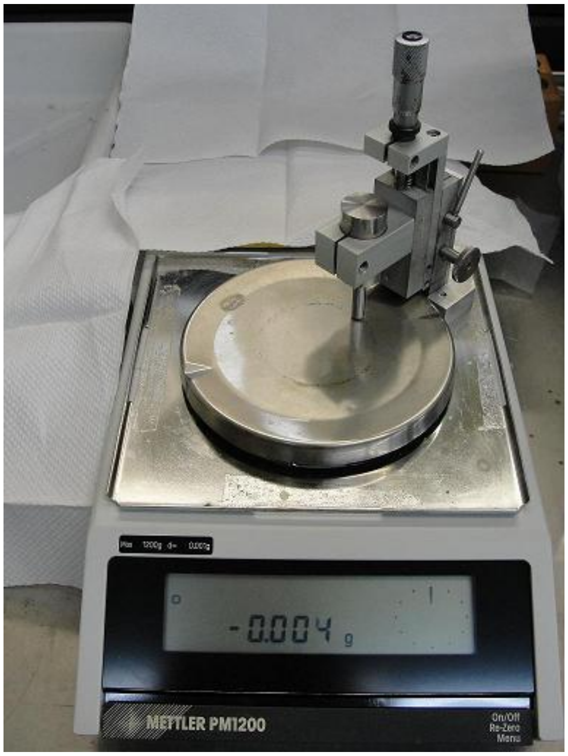

Fig. 11. Modified balance for stress-strain measurements.

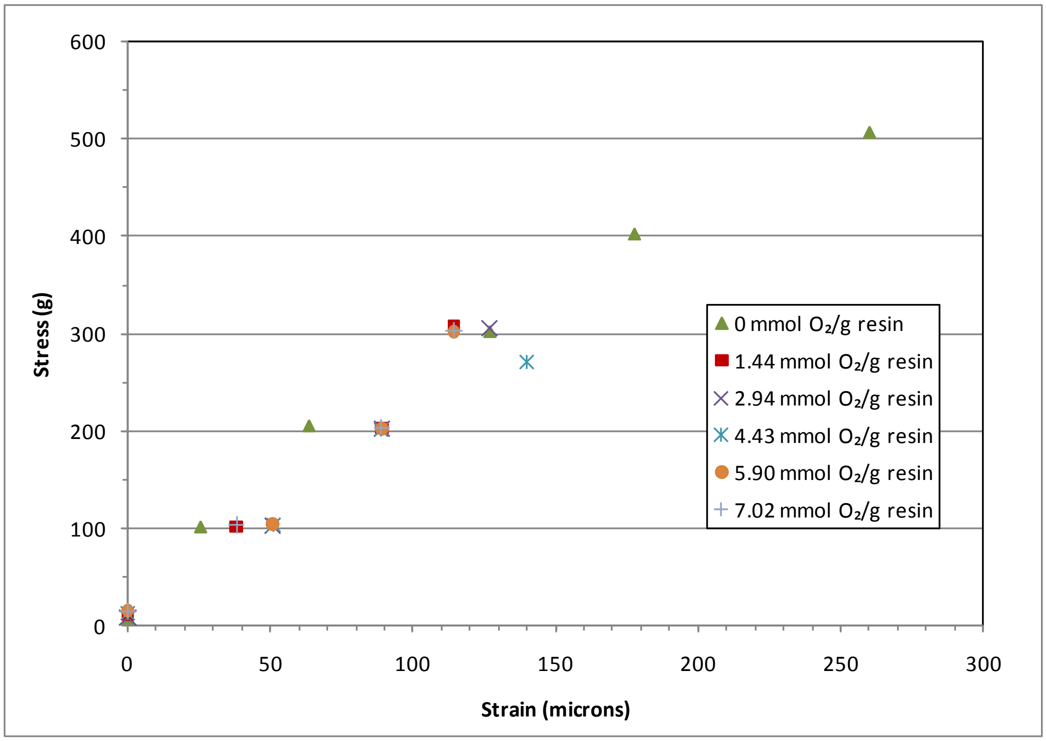

Fig. 12. Stress-versus-strain results for resin samples from run 2.

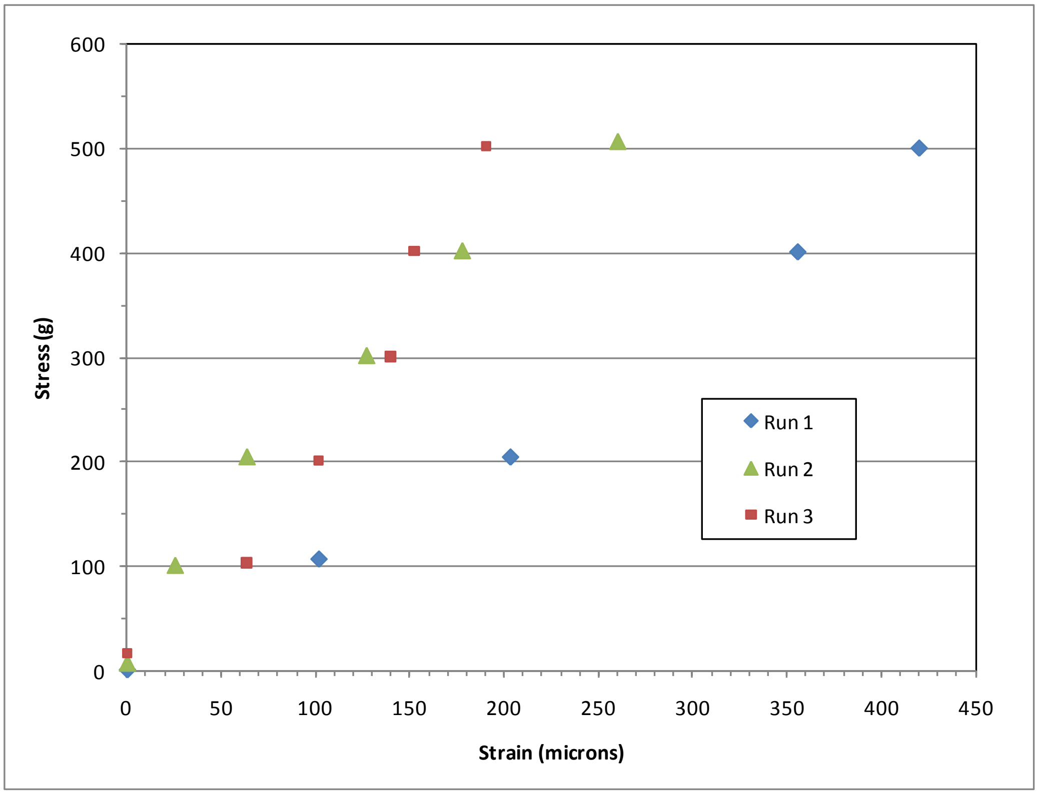

Fig. 13. Stress-versus-strain results for initial resin samples from runs 1–3.

Although oxygen uptake had no effect on the stress-versus-strain relationship of the resin, it did impact the crush strength of the resin beads. While the beads were being compressed, they would reach a stress level (weight reading on the balance) at which the bead would shatter and the weight reading would drop significantly. The beads that had reacted with oxygen broke at lower stress levels than did the initial resin samples with no oxygen exposure. For the new resin used in run 1, the oxygen uptake was inversely proportional to the crush strength. For the irradiated resin used in runs 2 and 3, oxygen uptake lowered the crush strength, but there was no correlation with the amount of oxygen exposure. The crush strength results, which are an average of three to five beads from each sample, are shown in Table 3.

Table 3. Crush strength of resin beads from runs 1–3

Run 1 resin samples		**Run 2 resin samples**		**Run 3 resin samples**	
O_2 uptake (mmol/g)	Crush stress (g)	O_2 uptake (mmol/g)	Crush stress (g)	O_2 uptake (mmol/g)	Crush stress (g)
0	800	0	>1000	0	>1000
3.35	350	1.44	350	1.47	680
5.32	290	2.94	405	2.92	742
7.01	260	4.43	408	4.32	574
		5.9	410	5.77	608
		7.02	365	6.7	690

The irradiated resin samples from runs 2 and 3 were generally stronger than the new resin samples from run 1. The samples from run 3, which were irradiated at a lower temperature, were stronger than the irradiated samples from run 2. If we assume that the area on which the piston of the modified balance pressed was equivalent to the area of a cylinder of the same diameter as the resin bead, the pressure applied to the beads before they were crushed ranged from 2000 to 9000 psi. The crush strength for all of the beads was so high that it would be unlikely that the normal forces encountered in an ion exchange column would cause any of the beads to break. Microscopic examination of beads from new and irradiated resin samples showed that all of the beads were smooth spheres. There was no visible evidence of broken resin beads in any of the samples from the test loop.

3.4 CESIUM UPTAKE RESULTS

A portion of each of the resin samples from the test loop was converted to the hydrogen form using the standard procedure for pretreating the RF resin.[2] The resin was then dewatered by vacuum filtration, with argon gas added to the headspace above the filter to minimize contact with oxygen from the atmosphere. A portion of the damp resin was weighed into a flask containing Hanford simulant solution with a cesium concentration of 1 m*M* . The composition of the simulant solution is shown in Table 4. Another portion of the damp resin was dried at 50°C under vacuum to determine the moisture content of the damp resin. This result was used to calculate the dry weight of the resin added to the simulant solution. The ratio was about 1 g dry H-form resin in 100 mL of simulant solution. The flasks of resin and simulant were placed in a shaker at 125 rpm and 25°C. After shaking for 4 days, a sample of the simulant from each flask was analyzed for cesium concentration using ICP-MS. A control flask with the same simulant and no resin was used to determine any uptake of cesium by the flask. The difference in cesium concentration between the control flask simulant and the simulant solution in contact with the resin was used to calculate the cesium concentration on the resin. The distribution coefficient (K_d) was calculated from the ratio of the cesium concentration on the resin and the equilibrium concentration left in the simulant. The results are shown in Fig. 14, and tables with all of the detailed results are shown in Appendix B.

Table 4. Composition of Hanford AP-101 simulant solution used for K_d tests

Component	Target (*M*)	Measured (*M*)
NaOH	2.0	NA[a]
$NaNO_3$	1.0	1.07
$NaNO_2$	0.7	0.70
$NaAlO_2$	0.3	0.30
Na_2SO_4	0.04	0.041
Na_2CO_3	0.4	NA
NaCl	0.04	0.042
KNO_3	0.7	0.59
Total Na	4.92	4.70

[a] Not analyzed

The new resin used in run 1 had the highest K_d, while the resin irradiated at a maximum temperature of 51°C, used in run 2, had the lowest. Oxygen uptake by the resin had more of an effect on the K_d of the new resin than it did on the irradiated resin at a simulant temperature of 25°C. The initial resin sample from run 3 showed a higher K_d than the resin from run 2 due to the lower temperature (38°C) during irradiation; however, the 45°C temperature of the simulant during run 3 initially caused a faster reduction in the K_d as the resin reacted with oxygen. At the higher oxygen uptake amounts, the effect on K_d was minimal for run 3. It is not known if contact with the higher-temperature simulant would cause a reduction in the K_d without the oxygen uptake or without being irradiated. The new resin from run 1 showed a fairly steady decline in K_d of 3.7% per mmol O_2/g resin, while the resin from run 3 showed a 8.4% reduction up through 2.9 mmol O_2/g resin. A sample of the resin that was irradiated to 120 Mrad at a temperature of about 107°C but not used in the test loop gave a cesium K_d of 200.1 mL/g.

4. CONCLUSIONS

The flow rate and pressure drop data from the test loop runs showed that irradiating the RF resin reduced both the void fraction and the permeability of the resin bed. The mechanism for the reduction in permeability was not clear because irradiation increased the particle size of the resin beads and made the beads deform less under pressure. Microscopic examination of the resin beads showed that they were all smooth, regular spheres and that irradiation or oxygen uptake did not change the shape of the beads. The resin rapidly reacted with DO in the simulant solution under high flow conditions, and the reaction with oxygen reduced the permeability of a bed of new resin, but it had minimal impact on irradiated resin. Irradiation increased the toughness of the resin beads, probably by initiating cross-linking reactions in them. Oxygen uptake reduced the crush strength of both new and irradiated resin; however, the pressures that caused the beads to crush were much higher than would be expected during the operation of an ion exchange column. There was no visible evidence of broken beads in any of the resin samples taken from the test loop. Reaction with oxygen reduced the cesium distribution coefficient of the resin beads, as did irradiation. Higher temperatures during irradiation or during contact with the simulant solution further reduced the cesium distribution coefficient.

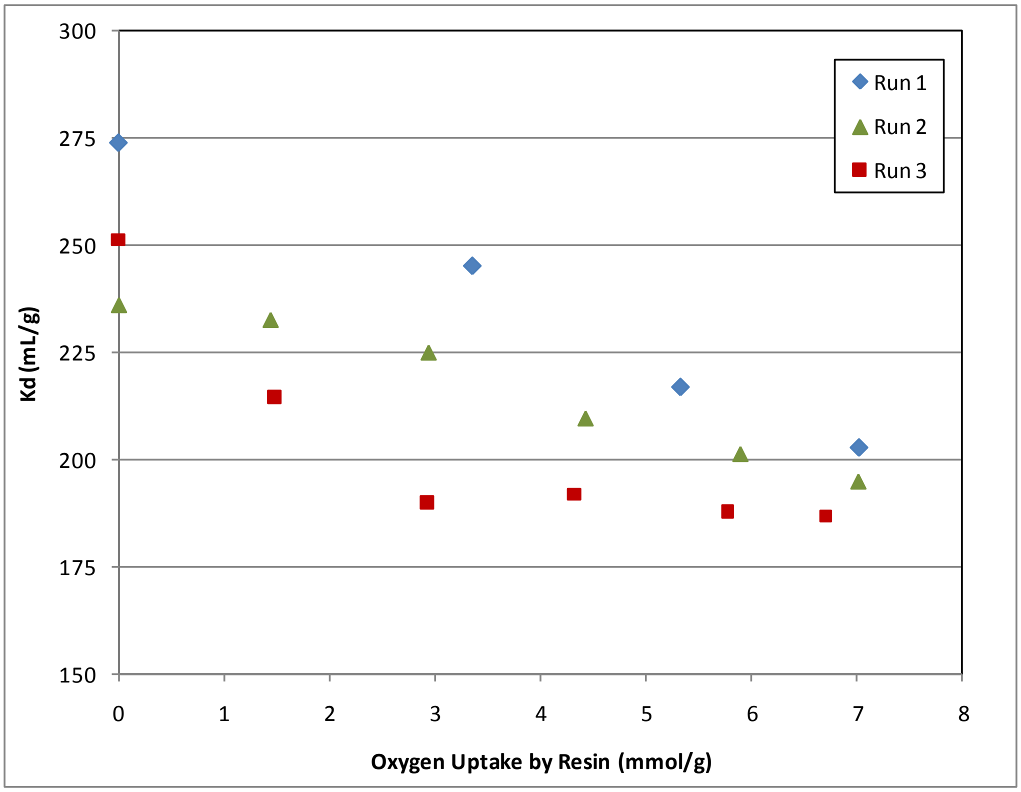

Fig. 14. Cesium uptake results for resin samples.

5. REFERENCES

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2. C. A. Nash, *Hanford RRP-WTP Alternate Resin Program – Protocol P1-RF Spherical Resin Sampling from Containers, Resin Pretreatment, F-Factor, and Resin Loading to Column*, SRNL-RPP-2004-00058, Washington Savannah River Company, Savannah River National Laboratory, Aiken, S.C., 2004.

3. S. Ergun, *Fluid Flow Through Packed Columns*, Chemical Engineering Progress **48**(2), 89–94 (1952).

Appendix A

VOID FRACTION AND PERMEABILITY RESULTS

Appendix A. VOID FRACTION AND PERMEABILITY RESULTS

Run 1		Run 2		Run 3	
O_2 uptake (mmol/g)	Void fraction	O_2 uptake (mmol/g)	Void fraction	O_2 Uptake (mmol/g)	Void fraction
0.25	0.4109	0.93	0.3652	0.44	0.3816
1.1	0.4097	1.44	0.3669	0.89	0.3821
1.95	0.4044	1.95	0.3762	1.25	0.3853
2.5	0.4007	2.44	0.3682	1.56	0.3839
3.07	0.3972	2.94	0.3682	1.96	0.3813
3.35	0.3969	2.94	0.3847	2.33	0.3754
3.6	0.3956	3.30	0.3827	2.71	0.3738
4.48	0.3897	3.44	0.3821	3.10	0.3740
5.32	0.4050	3.96	0.3775	3.51	0.3931
7.01	0.3988	4.43	0.3796	3.90	0.3904
		4.93	0.3781	4.30	0.3863
		5.42	0.3762	4.97	0.3749
		5.90	0.3756	5.35	0.3710
		6.40	0.3737	6.14	0.3704
		6.88	0.3750	6.55	0.3738
				6.70	0.3696

Run 1		Run 2		Run 3	
O_2 uptake (mmol/g)	Permeability (ft^2)	O_2 uptake (mmol/g)	Permeability (ft^2)	O_2 uptake (mmol/g)	Permeability (ft^2)
0.25	2.64E-09	0.93	1.72E-09	0.44	1.70E-09
1.1	2.61E-09	1.44	1.75E-09	0.89	1.71E-09
1.95	2.49E-09	1.95	1.92E-09	1.25	1.75E-09
2.5	2.40E-09	2.44	1.77E-09	1.56	1.73E-09
3.07	2.33E-09	2.94	1.77E-09	1.96	1.69E-09
3.35	2.32E-09	2.94	2.08E-09	2.33	1.61E-09
3.6	2.30E-09	3.30	2.04E-09	2.71	1.59E-09
4.48	2.17E-09	3.44	2.03E-09	3.10	1.59E-09
5.32	2.50E-09	3.96	1.94E-09	3.51	1.87E-09
7.01	2.36E-09	4.43	1.98E-09	3.90	1.83E-09
		4.93	1.95E-09	4.30	1.77E-09
		5.42	1.92E-09	4.97	1.60E-09
		5.90	1.91E-09	5.35	1.55E-09
		6.40	1.87E-09	6.14	1.54E-09
		6.88	1.89E-09	6.55	1.59E-09
				6.70	1.53E-09

Appendix B

CESIUM SORPTION RESULTS

Appendix B. CESIUM SORPTION RESULTS

Run 1

O_2 uptake (mmol/g)	Simulant volume (mL)	Dry resin weight (g)	Cs in liquid (mg/L)	Cs on resin (mg Cs/g)	K_d (mL/g)
NA[a]	100.0	0	131.0	0	NA
0	100.0	0.914	37.4	10.245	274
3.35	100.0	0.983	38.4	9.417	245
5.32	100.0	0.872	45.3	9.830	217
7.01	100.0	1.146	39.4	7.995	203

[a] Not applicable (control sample)

Run 2

O_2 uptake (mmol/g)	Simulant volume (mL)	Dry resin weight (g)	Cs in liquid (mg/L)	Cs on resin (mg Cs/g)	K_d (mL/g)
NA[a]	50.0	0	130.0	0	NA
0	50.0	0.487	39.4	9.301	236
1.44	50.0	0.491	39.6	9.211	233
2.94	50.0	0.534	38.2	8.592	225
4.43	50.0	0.593	37.3	7.812	209
5.9	50.0	0.462	45.5	9.149	201
7.02	50.0	0.527	42.6	8.291	195

[a] Not applicable (control sample)

Run 3

O_2 uptake (mmol/g)	Simulant volume (mL)	Dry resin weight (g)	Cs in liquid (mg/L)	Cs on resin (mg Cs/g)	K_d (mL/g)
NA[a]	50.0	0	128.0	0	NA
0	50.0	0.4839	37.3	9.37	251
1.47	50.0	0.5128	40.0	8.58	215
2.92	50.0	0.5131	43.4	8.24	190
4.32	50.0	0.4976	44.0	8.44	192
5.77	50.0	0.5140	43.7	8.20	188
6.7	50.0	0.5058	44.3	8.27	187

[a] Not applicable (control sample)