**MID-YEAR STATUS REPORT FOR TTP #SR-1320-02 UST: Cs
EXTRACTION TESTING (U)**

by

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UST: Cs EXTRACTION TESTING

1.0 SUMMARY

The resorcinol/formaldehyde resin developed at WSRC (Westinghouse Savannah River Company) has been studied with simulated Hanford 242-101-AW (HW) liquid waste. In the course of these studies new properties of the resin have been identified. Pertinent findings from these studies include:

- Studies in which HW was processed at increasingly greater flow rates on a two-milliliter column of resin that had been pretreated in 2 M NaOH showed that Cs^+ ion was not efficiently sorbed by the resin. Increasing the flow rate decreased the number of column volumes that could be processed before breakthrough occurred. Data from these experiments indicated that this feed would be difficult to decontaminate using this resin. The sorption of Cs^+ from the simulant appeared to be limited by diffusion of the ion to the resin.
- Pretreating the resin with 6 M NaOH increased swelling of the resin in a manner similar to the swelling observed in HW. A 2-mL column pretreated with the more concentrated caustic was used to decontaminate 450 mL of HW at a flow rate of five column volumes per hour. Apparently, proper pretreatment of the resin allows efficient cesium decontamination from this waste simulant at reasonable flow rates.
- The breakthrough curve for the column pretreated with 6 M NaOH showed a distinct, sharp breakthrough at 225 column volumes throughput and a second less well defined breakthrough at 450 column volumes. This indicates that the second hydroxide functional group was participating in ion exchange, effectively doubling the capacity of the resin. Activation of the second hydroxide had never before been observed. Elution of the spent resin was accomplished in 47.5 column volumes of 0.1 M HNO_3 .
- Radiolysis studies in the $1 \text{ E}+8$ rad dose region show no significant change in the resin cesium distribution constants (K_d) with increasing dose when the resin is irradiated in deionized water.
- Researchers working with the resorcinol/formaldehyde resin at WSRC, Oak Ridge (ORNL), and PNL (Pacific Northwest Laboratories) have all experienced a degradation of the resin with time. It was determined at a

meeting of the researchers that the resin has a shelf life, probably less than its process life, that is determined by oxidation of the resin. A program was outlined to determine the shelf life, storage requirements, and mechanism of degradation of the resin. Oxidation is suspected as the chemical process of degradation.

- Because all of the resin being used at this time in the DOE (Department of Energy) complex is from one production batch and, because it is displaying decreasing ion exchange performance with time, a recommendation to purchase a new batch of resin from a vendor has been made. This will generate a uniform supply of resin for all researchers and will demonstrate once again that quality resin can be commercially made in acceptable quantity.

2.0 INTRODUCTION

This project was designed to perform several tasks to provide transfer of technology to PNL concerning optimization of a cesium-specific ion exchange resin, developed at WSRC. The tasks support the development of a Compact Processing Unit (CPU) for Cs-removal from a variety of waste streams at Westinghouse Hanford (WH).

In a series of experiments, WSRC has studied the behavior of a small column of the resin at various, increasingly greater flow rates with the HW simulant solution to determine an optimum column loading rate. Elution studies of the resin after saturation with Cs^+ will generate an elution profile from which an optimum elution medium, flow rate, and volume can be determined. Small column tests at temperatures ranging from 40°C - 80°C are planned but have not yet begun.

Further, WSRC has begun a study in which the resin is subjected to ionizing radiation in a Co-60 source. This study will determine if any flammable or hazardous compounds, that might require special process controls, are formed as a result of irradiation. It will also define the ability of the resin to maintain its selectivity and capacity in a radiation field. During this period, a literature survey of the effects of radiation on this type of resin and similar compounds was initiated. For this survey, the extensive database established by the Radiation Chemistry Data Center at the University of Notre Dame is being used.

3.0 EXPERIMENTAL

This report summarizes work accomplished to date on the project as a whole. Studies for which data is not yet available are not reported.

3.1 *Small Column Studies with Simulated Hanford 241-101-AW Waste*

A sample of resin, freshly prepared in the laboratory, was treated with excess 2 M NaOH, washed with deionized water, and air-dried at room temperature. A portion of resin treated in that manner was placed in a graduate cylinder under 2 M NaOH and allowed to stand until it had finished swelling. Resin was withdrawn from the cylinder using a dropper until 2 mL of resin remained. That 2 mL of resin was transferred with a dropper to a small ion exchange column. The column was prepared in 2 M NaOH.

Simulated Hanford 241-101-AW waste, prepared according to the composition given in Table 1 was processed downflow through the 2 mL column at flow rates of 30 mL/hr, 20 mL/hr, 15 mL/hr, and 6 mL/hr (15, 10, 7.5 and 3 column volume/hr). The treated effluent was collected and analyzed for Cs-137 by γ -counting. Samples of the simulant batches were sent for analysis by γ -counting for Cs-137, ICPES (inductively coupled plasma emission spectroscopy) for several metals, and AA (atomic absorption) for K. A titration was made with standard acid to determine the free $[\text{OH}^-]$.

A 1-gram sample of resin was placed in a graduate cylinder and allowed to swell in 6 M NaOH. When the swelling had stopped, the final volume occupied by the resin was recorded. This value constitutes the bulk density of the resin in 6 M NaOH. A 0.72 gram sample of resin pretreated in 6 M NaOH (2.2 mL) was transferred to a small column (1.1 cm x 0.9 cm) and used to treat HW simulant in a downflow mode at 10 mL/hr. Samples of treated effluent

from the column were analyzed for Cs-137 by γ -counting to determine breakthrough curves. This column was stopped after 300 column volumes had been processed and was allowed to stand in simulant feed for one week before restarting. Similarly, the column stood inactive in simulant feed for two days after 325, 360, 400, and 450 column volumes, and for two weeks after 500 column volumes before restarting feed operations.

Table 1. Hanford 101-AW Simulant Composition

<u>Chemical Formula</u>	<u>g/Liter</u>	<u>Molarity</u>
NaOH	203	5.1
$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	188	0.5
NaNO_3	204	2.4
$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	26.5	0.21
Na_2SO_4	2.6	0.01
KOH	57	1.1
CsNO_3	0.009	4.4 E-5
NaNO_2	152	2.2
Cs-137	25 λ *	1.3 E-11

* Taken from a stock $^{137}\text{CsNO}_3$ solution (1.43 E-5 Ci/mL)

The Cs-saturated resin from the column prepared in 6 M NaOH was washed with 100 mL of deionized water and eluted in an upflow mode using 0.1 M HNO_3 . The eluted material was analyzed for Cs-137 by γ -counting, for Na by ICPES, and for K by AA.

3.2 Batch Tests on Resorcinol/Formaldehyde Resins

Grab samples of resorcinol/formaldehyde resin, purchased from Boulder Scientific Co. in 1989 were taken from storage drums, converted to the Na-form with 2 M NaOH, and tested for their cesium distribution constants, K_d 's, using four WSRC waste simulants (see Table 2). The procedure for determining K_d 's is to shake a weighed amount of resin

with a measured volume of solution until the system has reached equilibrium. The untreated solution and the equilibrated solution are then analyzed for cesium content. The distribution constant is calculated from the relationship in Eq. (1):

$$K_d = [\text{Cs on resin}]/[\text{Cs in solution at equilibrium}] = [(C_o/C)-1]*V/g \quad (1)$$

where C_o = initial Cs^+ concentration in solution
 C = equilibrium Cs^+ concentration in solution
 V = volume, in mL, of solution used
 g = grams of dry resin used

This same procedure was used in the radiolysis studies associated with this work, when testing resin that had been frozen and oxidized, and in testing resin that had been newly-prepared in the laboratory. K_d values obtained were compared with each other and with those already in a data base from previous work done using the resorcinol/formaldehyde resin.

Table 2. WSRC Simulated Solutions Used for K_d Tests

<u>Solution</u>	<u>Composition</u>
1	4.5 M NaNO_3 ; 1.5 M NaOH ; trace Cs-137
2	4.5 M NaNO_3 ; 1.5 M NaOH ; trace Cs-137; $2.5\text{E-}4\text{M Cs}^+$
3	4.5 M NaNO_3 ; 1.5 M NaOH ; trace Cs-137; $2.5\text{E-}3\text{M Cs}^+$
SS	Simulated WSRC supernate solution- $2.5\text{E-}4\text{M Cs}^+$, 2.9M NaOH , 0.76M $\text{Al}(\text{NO}_3)_3$, 1.2M NaNO_3 , 0.7M NaNO_2 , 0.01M KNO_3 , 0.01M Na_2SO_4 , 0.40M Na_2CrO_4

3.2 Freezing of Resorcinol/formaldehyde Resin

Samples taken from drums containing resorcinol/formaldehyde resin manufactured by Boulder Scientific Co. in 1989 were converted to the Na-form in 2 M NaOH . Air-dried samples of the resin were placed in a freezer at 0°C for three-day intervals, after which they were removed and allowed to return to room temperature, 23°C . Batch distribution constants were determined for resins, treated in this manner. This process was repeated three times for a total freeze time of 9 days.

3.3 Exposure of Resorcinol/Formaldehyde Resin to Air

A portion of resorcinol/formaldehyde resin from Drum 1995 was converted to the Na-form using 2 M NaOH . It was placed in a Büchner funnel and compressed air was delivered upflow through the resin for 1 week. At the end of that time, the Cs K_d 's for the resin were determined.

3.4 Radiolysis Studies

3.4.1 Irradiation Facility

The samples were irradiated with Co-60 gamma rays at a dose rate of 2.6E06 rads/hour. The Co-60 slugs were submerged in 20 feet of water for shielding. The dose rate was determined using thin-filmed nylon dosimeters containing a radiochromic dye. ¹ These dosimeters were calibrated using the Fricke dosimeter ² which is a chemical dosimeter that measures the absolute amount of radiation sorbed by a system when exposed to gamma rays.

3.4.2 Irradiation of Samples

The resin was irradiated as received in the Na-form. For the initial tests samples were irradiated in graduated, conical-bottomed, glass centrifuge tubes (15 mL capacity). Two mL of the resin were added to each tube followed by the addition of 10 mL of either simulated Hanford supernate or deionized water. Resin was irradiated in deionized water to aid in determining the mechanism of the radiolytic degradation. (Hanford supernate is highly caustic and contains high concentration of ions which would interfere with many of the solution analyses.) Twelve samples were prepared - six resin-supernate and six resin-water. Eight of the samples (four of each kind) were irradiated. Four (two of a kind) were retained as blanks. To decrease evaporation of water during the irradiation, the open ends of the tubes were covered with Al foil secured by a wire. Radiation times were 67.5, 162.6, and 235.2 hours giving doses of 1.6E08, 3.7E08, and 5.4E08 rads, respectively. During the irradiation, the temperature of the samples increased to 45-50°C due to heating by sorption of the gamma rays. Two samples (a resin-supernate and a resin-water) were removed at each of the first two doses. The remaining four samples were removed at the final dose.

3.4.3 Analyses After Irradiation

After irradiation, the properties of the irradiated solutions were compared to those of the unirradiated solutions. The volumes of the resins were noted along with any other visible changes. The pH values of the resin-water solutions were measured. The resin was collected, rinsed, and air dried. The Kd values of the unirradiated and irradiated resins were then determined and compared. The solutions from the resin/water samples were analyzed by ion chromatography for soluble anions. Samples of the solutions were submitted for analyses of the soluble organic compounds by HPLC (High Performance Liquid Chromatography).

4.0 Results and Discussion

The results of analyses on HW simulants are found in Table 3. These analyses were performed to establish the concentration of key ions in the simulant. Aluminum was lower than expected in each batch.

The bulk density, ρ_B , was determined to be 0.36 g/mL in 2 M NaOH and 0.33 g/mL in 6 M NaOH.

Table 3. Analytical Results for Three Batches of Hanford 241-101-AW Simulant

<u>Species</u>	<u>mg/L</u>			
	<u>Estimated</u>	<u>Batch 1</u>	<u>Batch 2</u>	<u>Batch 3</u>
Na	2.53E+5	2.24E+5	2.14E+5	2.28E+5
K	4.29E+4	3.23E+4	3.03E+4	3.16E+4
Al	1.35E+4	6.40E+3	6.67E+3	6.58E+3
total OH ⁻	1.05E+5	-	-	9.18E+4
free OH ⁻	8.84E+4	-	-	8.36E+4
Al(OH) ₄ ⁻				2.09E+4

4.1 Small Column Tests

Resin pretreated with 2 M NaOH did not perform well in column mode with the HW simulant. Table 4 lists the ratio of concentration of Cs-137 found in column effluents relative to the influent concentration at various flow rates. The breakthrough curves are represented graphically in Figure 1.

Table 4. Breakthrough Curve Data - 2M NaOH Pretreatment

<u>Column Volumes</u>	<u>15 CV/hr</u>	<u>10 CV/hr</u>	<u>7.5 CV/hr</u>	<u>3 CV/hr</u>
0	0	0	0	0
2.5	0	0	0	0
5	0.40	0	0	0
7.5	0.56	0.28	0.32	0
10	0.71	0.37	0.26	0
12.5	0.80	0.46	0.29	0
15	0.74	0.36	0.55	0
17.5	0.90	0.53	0.52	0
20	0.85	0.61	0.53	0.29
25	0.80	0.64	0.51	0.35
27.5				0.45
30				0.43

Figure 1. Breakthrough Curves for Four Flow Rates After 2M NaOH Pretreatment

Data for the breakthrough curve(s) generated by treating HW at 23°C at 5 column volumes per hour in a downflow mode on 0.72 g (2.18 mL of fully swollen resin) of the sodium form of the resorcinol/formaldehyde resin are found in Table 5. A graph of selected data is shown in Figure 2. As noted earlier, the column was allowed to idle in contact with the feed for several, long intervals during the run. The net effect of this was to establish a new equilibrium for the column, resulting in a lowering of the breakthrough curve after each shutdown. A saw-tooth pattern was generated in the breakthrough curve and those irregularities were smoothed in Figure 2 by using selected data points.

Figure 2 Breakthrough Curve at 5 CV/hr After 6M NaOH Pretreatment

Table 5. Breakthrough Curve Data - 6M NaOH Pretreatment

<u>CV</u>	<u>CsC/C₀</u>	<u>CV</u>	<u>CsC/C₀</u>	<u>CV</u>	<u>CsC/C₀</u>	<u>CV</u>	<u>CsC/C₀</u>	<u>CV</u>	<u>CsC/C₀</u>
2.5	0.00	72.5	0.00	145.0	0.00	250.0	0.19	322.5	0.23
5.0	0.00	75.0	0.00	147.5	0.00	252.5	0.13	325.0	0.25
7.0	0.00	77.5	0.00	150.0	0.00	255.0	0.21	327.5	0.25
5.0	0.00	80.0	0.00	185.0	0.00	257.5	0.18	330.0	0.26
10.0	0.00	82.5	0.00	187.5	0.00	260.0	0.18	332.5	0.25
12.5	0.00	85.0	0.00	190.0	0.00	262.5	0.19	335.0	0.35
15.0	0.00	87.5	0.00	192.5	0.00	265.0	0.24	337.5	0.35
17.5	0.00	90.0	0.00	195.0	0.00	267.5	0.22	340.0	0.35
20.0	0.00	92.5	0.00	197.5	0.00	270.0	0.23	342.5	0.47
22.5	0.00	95.0	0.00	200.0	0.00	272.5	0.25	345.0	0.32
25.0	0.00	97.5	0.00	202.5	0.00	275.0	0.24	347.5	0.32
27.5	0.00	100.0	0.00	205.0	0.00	277.5	0.26	350.0	0.34
30.0	0.00	102.5	0.00	207.5	0.00	280.0	0.28	352.5	0.39
32.5	0.00	105.0	0.00	210.0	0.00	282.5	0.31	355.0	0.37
35.0	0.00	107.5	0.00	212.5	0.00	285.0	0.29	357.5	0.35
37.5	0.00	110.0	0.00	215.0	0.00	287.5	0.21	360.0	0.34
40.0	0.00	112.5	0.00	217.5	0.00	290.0	0.32	362.5	0.39
42.5	0.00	115.0	0.00	220.0	0.16	292.5	0.27	380.0	0.42
45.0	0.00	117.5	0.00	222.5	0.19	295.0	0.27	382.5	0.51
47.5	0.00	120.0	0.00	225.0	0.17	297.5	0.32	385.0	0.43
50.0	0.00	122.5	0.00	227.5	0.23	300.0	0.29	387.5	0.41
52.5	0.00	125.0	0.00	230.0	0.19	302.5	0.21	390.0	0.42
55.0	0.00	127.5	0.00	232.5	0.15	305.0	0.16	392.5	0.44
57.5	0.00	130.0	0.00	235.0	0.16	307.5	0.18	395.0	0.56
60.0	0.00	132.5	0.00	237.5	0.22	310.0	0.12	397.5	0.47
62.5	0.00	135.0	0.00	240.0	0.23	312.5	0.19	400.0	0.40
65.0	0.00	137.5	0.00	242.5	0.21	315.0	0.22	402.5	0.45
67.5	0.00	140.0	0.00	245.0	0.23	317.5	0.24	405.0	0.51
70.0	0.00	142.5	0.00	247.5	0.23	320.0	0.26	407.5	0.46

As determined from Table 5, the fraction of Cs-137 fed to the column that was actually loaded was 0.761 ($[3.30\text{E-}1 \mu\text{Ci}-7.89\text{E-}2 \mu\text{Ci}]/3.30\text{E-}1 \mu\text{Ci}$). The resin column, then sorbed a total of

$$0.761 * (4.4\text{E-}5 \text{ moles/L}) * (1.1 \text{ L}) * (135 \text{ gCs/mole}) * (1\text{E+}3 \text{ mg/g}) * (1 \text{ CV resin}/0.72\text{g}) = \\ 6.9 \text{ mg Cs/g resin} \quad \text{or} \quad 5.1\text{E-}2 \text{ milliequivalents Cs/g resin.}$$

Pretreating the column with a strong enough caustic solution that will allow the resin to swell as much as it does in the feed allows the column to operate effectively for ion exchange. Earlier premature breakthrough curves may have been the result of channeling while the resin continued to swell in the early stage of column feeding. It might also have resulted from microscopic precipitation of aluminum on the resin, a process that would ultimately blind the column to ion exchange. This is the first test in which the second hydroxide moiety has been active. Previous work with WSRC and Hanford NCAW (Neutralized Current Acid Waste) and CC wastes had only observed one breakthrough for those feeds, all of which are only between 1 and 2 molar in free hydroxide. The net effect of the activation of the second hydroxide is to increase the capacity of the resin. This flow rate, 5 column volumes per hour, gave a very sharp initial breakthrough, indicating that a more rapid flow rate could be accommodated if desired.

Based on these observations, the resin should be pretreated with a solution that closely resembles the expected feed to minimize swelling or shrinking of the resin in the column after the feed cycle begins.

4.2 Elution

The elution of the column that had been pretreated with 6 M NaOH was accomplished in an upflow mode with 0.1 M HNO₃ after washing the resin with 100 mL of deionized water to remove any interstitial supernate. Table 6 shows the eluate concentrations of Cs-137 and potassium ion. Sodium analyses are not complete. Data is presented graphically in Figures 3 and 4. The eluted amount of Cs-137 (0.252 μCi) is equal to the calculated amount of Cs-137 sorbed by the column (0.251 μCi). Potassium ion that was eluted from the resin surprisingly showed two elution peaks. Potassium ion began eluting from the column before cesium ion. Essentially all of the cesium and potassium ions was eluted in 47.5 column volumes of 0.1 M HNO₃.

Figure 3. Elution of Cs^+ With 0.1 M HNO_3

Figure 4. Elution of K^+ With 0.1 M HNO_3

Table 6 Concentrations of Ions in 0.1 M HNO₃ Eluate

<u>CV(1 CV=2 mL)</u>	<u>μCi Cs-137</u>	<u>mg K</u>
2.5	0	0.130
5.0	0	0.205
7.5	0	0.935
10	0	2.03
12.5	0	2.09
15	0	2.08
17.5	0	2.32
20	0.034	3.60
22.5	0.039	3.57
25	0.032	3.20
27.5	0.024	2.95
30	0.024	0.050
32.5	0.023	0.045
35	0.022	0.035
37.5	0.020	1.23
40	0.017	0.720
42.5	0.012	0.175
45	0.004	0.005
47.5	0.001	0.010
50	0	0.005
52.5	0	0.005
55	0	0.005
57.5	0	0.015
60	0	0.015
62.5	0	0.005
65	0	0.005
67.5	0	0.005
70	0	0.005
72.5	0	0.005
65	0	0.005
Total	0.252	25.8

4.3 Shelf-life Related Studies

4.3.1 Kd Tests After Five Years In Storage

Batch distribution coefficients determined on grab samples of resin from drums that were received at WSRC in 1988 are compared with those determined for resin grab samples tested with solutions of the same composition when the resin was newly received. Resin

from four drums was tested. These results appear graphically in Figure 5 and in tabular form in Table 7. They represent Kd's determined using solution number 2 (see Table 2).

These results, also experienced by researchers dealing with the resin at PNL and Oak Ridge, indicate that the resin degrades with time. It was not tested for several years and, during that time, appeared to retain its high selectivity for cesium ion. Exposing the resin to the atmosphere appears to cause it to degrade. The mechanism for that reaction is not known. Elucidation of the mechanism would give insight into the proper storage conditions for the resin to prevent its degradation.

Figure 5. Loss in Kd by Resin with Time

Table 7. Cs Kd's for Resin From Four Drums - A Five Year Time Difference

Drum #	Cs Kd. mL/g	
	1989	1993
1171	1.29E+3	8.51E+2
1995	1.25E+3	6.86E+1
1931	1.31E+3	1.36E+1
1932	1.82E+3	1.30E+3

4.3.2 Effect of Freezing on Cs Kd

The Kd values that were determined for resin grab samples from the same four drums as noted in 4.3.1 after three, three-day freezing and thawing cycles, are reported in Table 8. These Kd's were determined by allowing the resin to equilibrate with solution number 2, Table 2. All four solutions described in Table 2 were used to determine Cs Kd values, but data from those tests is not reported because it was derived from γ -counting shortly

after the counter had been struck by lightning and results are suspect. Data in Table 8 was determined after the instrument had been repaired.

Repetitive freezing and thawing cycles do not have any significant effect on the performance of the resin.

Table 8. Cs⁺ Kd's Determined After Three Freezing/Thawing Cycles

# Freeze/Thaw Cycles	Cs Kd's			
	Drum 1771	Drum 1995	Drum 1931	Drum 1932
0, untreated	8.51E+2	6.86E+2	1.36E+1	1.30E+3
1	7.89E+2	6.45E+1	1.61E+1	1.22E+3
2	9.18E+2	2.97E+1	6.52E+1	1.61E+3
3	9.67E+2	5.55E+1	2.36E+1	1.45E+3

The data is shown in graphic form in Figure 6.

Figure 6 . The Effect of Repeated Freezing and Thawing on Cs⁺ Kd

4.3.3 Exposure of Resin to Air

Cesium Kd's were performed on samples of Drum 1995 resin that had been exposed to 90 psig compressed air for one week. These are contrasted with the Cs⁺ Kd's for the same resin that had not been treated with air. The data is presented graphically in Figure 7.

Figure 7. The Effect on Cs⁺ K after Exposure of the Resin to Air

Air, either oxygen or ozone or both, appears to cause the resin to degrade and lose its specificity and capacity for cesium. Studies on the mechanism of degradation have not been made at this time.

4.4 Radiolysis Results and Discussion (Contributed by N.E. Bibler and C.L. Crawford)

4.4.1 Visual Observations

The resin swelled upon the addition of simulated supernate or water. The unirradiated resin in presence of both supernate and water swelled by 15% (2.0 mL to 2.3 mL). Radiolysis slightly enhanced the swelling. With the irradiation, the resin swelled by values ranging from 20% to 30% (2.0 to 2.6 mL). There was no consistent trend of swelling with radiation dose, and the resin swelled similarly in water or supernate. Radiation-induced volume changes have been observed with this and other resins.^{3,4,5}

When either the supernate, which was originally light yellow, or deionized water was added to the resin, the solutions became brownish. It has been suggested that this brownish color resulted from leaching of the resin in caustic solutions.³ When the resin-supernate samples were irradiated the brownish color was enhanced. When resin-water samples were irradiated, radiolysis caused the supernate to become colorless. In this case

it appears that radiolysis destroyed the species that were causing the color. HPLC will be used in an attempt to identify the species causing the color.

One other visual observation was noted. After the resin-supernate samples were irradiated, a small amount of white solids was visible on the resin. These solids did not form when the resin-water samples were irradiated. Also, they did not appear in any of the unirradiated samples. Since the resin-supernate samples were highly caustic, it was speculated that radiolysis may initiate dissolution of the glass tube. The tubes were emptied, dried and reweighed. Those tubes in which the resin-supernate were irradiated actually lost weight, albeit a very small amount. Perhaps this result is due to the radiation-enhanced caustic dissolution of glass. The solids will be analyzed for Si to determine if this is indeed the case. The possibility of performing the resin-supernate irradiations in stainless steel vessels is being investigated.

4.4.2 pH Measurements

The pH values for the resin-water samples are shown as a function of dose in Table 9. The supernate was already highly caustic, thus its pH could not be measured accurately. The initial pH of the water was in the range of 6 to 7. (Exact pH measurements of completely deionized water are difficult because the water is not poised and rapidly sorbs CO₂ from the air.) After the deionized water was added to the resin, the pH increased to 10.4. The initial pH increase may be due to washing residual KOH from the resin. KOH is used in the synthesis of the resin. As seen in Table 9, radiolysis caused the pH to decrease in a consistent manner with dose, suggesting the formation of soluble organic acids. Acids resulting from the radiolysis of a resorcinol-type structure could be substituted phenols. This will be investigated by submitting samples for HPLC for soluble organic species.

TABLE 9. pH Changes Caused by Radiolysis of Resin-Water Mixtures

<u>DOSE (rad)</u>	<u>pH</u>
0	10.48
1.6E08	9.82
3.7E08	9.73
5.4E08	9.63

4.4.3 Effect of Radiation on the Kd Values

Kd values were measured on the irradiated and unirradiated samples. When duplicate values were measured, the precision was poor especially with the resin-supernate samples. For example, for two different unirradiated resin-supernate samples and for two different resin-supernate samples irradiated to the highest dose, the results varied by a factor of 2X. Consequently, the Kd results for the resin-supernate samples were too imprecise to evaluate the effect of radiation on Kd. There are two possible sources of the imprecision. One was the drying of the resin after it was irradiated. The resin-supernate samples were dried using two different techniques. As a result, varying amounts of water remained in the resin samples. Since the Kd values are based on resin weight, this caused

the results to be imprecise. Second, the white solids, if they were formed by dissolution of a portion of the glass irradiation vessel, would add varying amounts to the weight of the resin samples and would also increase the imprecision of the results. The resins from the resin-water irradiation were all dried by the same method (air dried for one hour at room temperature). As mentioned before, these samples contained no white solids. Consequently, the Kd values for these samples were more precise (relative precisions of 4 and 22% were obtained for the two sets of duplicate samples). The Kd values shown in Table 10 were measured in four different solutions. The compositions of these solutions were given earlier in Table 2.

TABLE 10. Effect of Gamma Radiation on Kd (mL/g)^a

DOSE, rads	SOLUTION NUMBER			
	1	2	3	SS
0.00	(1.6±0.3)E+3	(1.6±0.3)E+2	26±3	(1.8±0.4)E+2
1.6E+8	1.7E+3	1.6E+2	25	1.2E+2
3.7E+8	2.2E+3	0.68E+2	21	2.0E+2
5.4E+8	(2.3±0.1)E+3	(2.4±0.4)E+2	27±0.2	(2.7±0.1)E+2

^a Resin samples dried for one hour.

The Kd values in Table 10 are nominally an order of magnitude less than those previously reported.^{6,7} Again, this is due to different drying techniques. The samples used in the previous reports were air dried overnight and those used to generate the data in Table 10 were air dried for only one hour. The presence of larger amounts of water in the resin samples would lower the Kd value. Subsequent drying at 100°C of the samples used for the data in Table 10 indicated that they contained nominally 70% water. Those air-dried overnight contained less than 30% water.³

Even though the Kd values in Table 10 are lower than those reported previously, the values do show the same trend with Cs concentration as that reported previously.⁶ The data in Table 10 indicate that, with an increasing Cs concentration (solutions 1, 2, and 3), the Kd values decrease. This decrease is consistent with results from a previous study.⁶ The results in that study also indicate that when the solutions have similar Cs concentrations, the Kd values should be similar. Solutions 2 and 4 have the same Cs concentration (2.5E-4 M) and indeed their Kd's are similar. Thus the values in Table 10 are valid even though the resins were dried only one hour.

The Kd values in Table 10 are not very precise, but they do indicate that there is not a significant effect of radiation on the Kd of the resin when it is irradiated in water to a dose of 5.4E+8 rads. Other studies have shown that when the resin is irradiated in caustic nitrate solutions simulating high-level waste solutions, radiation causes the Kd to decrease. For example, a dose of 1.4E+8 rads lowered the Kd by 98%.⁷ In another study⁶, a dose of 1E+9 rads lowered the Kd by 82% while a dose 9E+7 did not lower it. It may be that in water the resin is stable to attack by intermediates formed by the

radiation, but this is highly unlikely since the resin does radiolytically decompose in caustic solution. However, it is evident that K_d values are not a sensitive measure of the radiation stability of a resin. Future tests will be performed to determine if indeed the resin is stable when irradiated in water.

5.0 Future Work

Column studies continue in order to optimize the flow rate. Viscosity studies are underway to study the effect of temperature on the viscosity of HW. Sodium data for the elution will be soon complete. Elution at different flow rates will be performed to optimize that process. Operation of a small column at temperatures between 40°C and 80°C will be completed. Further analyses of irradiated solutions will continue. In particular, simulated supernate and water solutions above irradiated samples will be analyzed by HPLC for soluble organic compounds, especially compounds such as nitrated organics which might represent an explosion hazard. The solutions from the resin-water samples will be analyzed by ion chromatography for soluble organic anions that may have been formed. These resin-water supernates will also be analyzed to determine concentrations of sodium and potassium ion that would become solubilized as the resin degrades. A major effort of the immediate radiolysis studies will be to determine the effect of radiation on the resin when it is irradiated in the presence of HW. This will require a refining of the determination of the K_d values, a refining of the measurement of weight loss induced by radiation, and determining the best analyses of solutions irradiated with resin.

6.0 BUDGET AND SCHEDULE

Funding for this work was received from the Office of Technology Development in January. Early estimates for a spendout rate of \$30,000 per month for January, February, and March somewhat exceed the \$69,000 that has been actually been spent to date. It should be noted that \$25,520 of analytical costs for those months was incorrectly charged against a Waste Management activity code. That error was corrected and the analytical costs have been assigned to this project. Although the scope of this work has broadened due to the issue of the resin's shelf life, the originally planned tasks are proceeding as proposed in the original schedule.

7.0 QUALITY ASSURANCE

Data for this work can be found in notebooks WSRC-NB-90-188 and DPSTN-4268. Reagent grade chemicals were used for all solutions. Standards used in analyses are traceable to the National Institute of Standards and Testing. These were performed by the WSRC Analytical Development Section following that section's procedures for customer assisted analysis, using blanks and standards.

7.0 REFERENCES

1. N. E. Bibler, "Calibration of Intense Co-60 Sources at the Savannah River Plant", US ERDA Report DP-1414, May, 1976.
2. H. Fricke and E. J. Hart, "Radiation Dosimetry, Vol. 2 (2nd ed.) F. H. Attix and W. C. Roesch, editors, Academic Press, p. 85 (1966).

3. J. P. Bibler, Savannah River Technology Center, Westinghouse Savannah River Co., Aiken, SC; private communication.

4. S. F. Marsh, "The Effects of Ionizing Radiation on Reillex HPQ, A New Macroporous Polyvinylpyridine Resin and on Four Conventional Polystyrene Anion Exchange Resins," Los Alamos National Laboratory report LA-11912 (November 1990).

5. E. W. Baumann, "Gamma Irradiation of Individual and Mixed Ion Exchange Resins", J. Chem. Eng. Data., Vol 11, 256 (1966).

6. J. P. Bibler,, "A Comparison of Duolite CS-100 and Resorcinol/Formaldehyde Ion Exchange Resins with Three High-Level Waste Simulants Before and After Gamma Radiation", WSRC-RP-91-1221, December 11, 1991.

7. J. P. Bibler, R. M. Wallace, and L. A. Bray, "Testing a New Cesium-Specific Ion Exchange Resin for Decontamination of Alkaline High-Activity Waste", Proceedings of Waste Management '90, Vol. 2, pp. 747-757.

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