Supernatant Treatment Technology
Development: Report for the Second
Quarter FY 1994

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**SUPERNATANT TREATMENT TECHNOLOGY DEVELOPMENT:
REPORT FOR THE SECOND QUARTER FY 1994**

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SUMMARY

This report describes the experimental work conducted at the Pacific Northwest Laboratory during the Second Quarter FY 1994 under the Supernatant Treatment Technology Development Task of the Tank Waste Remediation System (TWRS) Pretreatment Technology Development Project. Experiments were performed in the areas of batch equilibrium studies of ion exchangers, ion exchanger loading, ion exchanger elution, and radiation and chemical stability of selected ion exchangers. Technical highlights were:

- ✖ Two 200 mL column loading experiments were performed using a high sodium and high potassium DSSF simulant for two batches of the Resorcinol-Formaldehyde (R-F)¹ resin, BSC-187 and BSC-210. The results showed that cesium removal efficiency was lower than predicted based upon batch equilibrium testing. This is believed to be due to both the higher potassium content and the fluid properties of the solution. The BSC-210 material showed loading behavior similar to that observed in the BSC-187 material.
- ✖ Elution experiments were also carried out on both batches of the R-F resin columns loaded with DSSF simulant. The elution curves (i.e. the amount of eluent required to remove cesium from the columns) were similar to those observed in earlier experiments, given the same conditions of temperature, eluent and flow rate and regardless of the feed solution composition. The elution behavior of the BSC-210 material was superior to that observed in the BSC-187 material. The BSC-210 material did not show the agglomeration problems noted with the BSC-187 material, allowing for better settling of the resin during elution and effectively eliminating channeling.
- ✖ Radiation and chemical stability studies were continued on the R-F resin. Irradiation of a control NCAW solution, no resin added, showed

¹ R-F resin is an experimental resorcinol-formaldehyde condensate ion exchange resin manufactured by Boulder Scientific company.

generation of stoichiometric quantities of hydrogen and oxygen gases with trace quantities of nitrogen and nitrous oxide gases. The gases generated in the resin containing experiments contained excess hydrogen as compared to oxygen, with relatively high quantities of nitrogen and nitrous oxide.

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1.0 INTRODUCTION

The contents of Hanford's 177 underground storage tanks include a mixture of sludge, salt cake and alkaline supernatant liquids. The insoluble sludge fraction of the waste consists of metal oxides, hydroxides and phosphates and contains the bulk of most radionuclides. The salt cake materials, generated by extensive evaporation of aqueous solutions, consist primarily of dried sodium salts. The supernates consist primarily of concentrated aqueous solutions of sodium and potassium nitrate salts. The water soluble salt cake and supernatant solutions contain the bulk of the important radionuclide ^{137}Cs . Although the pretreatment and disposal requirements are still being defined, one of the first processes in most pretreatment scenarios will be a supernatant and sludge separation and sludge washing step followed by a solids/liquid separation. Since a majority of the cesium is expected to be in the aqueous liquids, it is these solutions that are the focus of the cesium ion exchange removal process. This process is being designed with the goal of removing enough cesium so that the resulting immobilized low-level waste (LLW) form will meet the NRC 10CFR61 Class A limits for ^{137}Cs (1 Ci/m³). The separated cesium will be concentrated and vitrified with the washed sludge.

The technology for cesium (Cs) recovery from Hanford high-level alkaline wastes and sludge wash waters is being developed at the Hanford Site (Bray et al., 1993); the Westinghouse Savannah River Company (WSRC), Aiken, South Carolina (Bibler et al., 1991); and at the West Valley Nuclear Services Company, Inc. (WVNS) in West Valley, New York (Kurath et al., 1989). Using this known technology as a starting point, experimental studies are being conducted by the Pacific Northwest Laboratory (PNL)² as part of the TWRS Program, to continue the evaluation of ion exchange process performance using simulated and actual Hanford wastes.

2 PNL is operated for the U.S. Department of Energy by Battelle Memorial Institute.

2.0 CESIUM ION EXCHANGER LOADING AND ELUTION STUDIES

This section summarizes the results from the loading and elution experiments performed on the Boulder Scientific resorcinol formaldehyde (RF) resin. Loading and elution curves from two separate batches of the RF resin are described. First, column loading experiments of the old RF resin (BSC-187) using a high potassium, high sodium DSSF simulant in a three column system will be discussed followed by a description of the loading of the new RF resin (BSC-210) and the elution experiments of these both batches of resins. In addition to the column testing, batch equilibrium measurements using the DSSF feed will also be presented.

The highlight findings of these results are:

- 1) Column tests with the R-F resin and a high potassium, high sodium DSSF simulant exhibited more efficient loading characteristics when slow flow rates were used.
- 2) The new R-F resin (BSC-210) exhibited better elution characteristics than the old BSC-187 material. This difference can be attributed to the physical adherence of the old material, causing channeling, which is not observed in the BSC-210 resin.
- 3) Batch equilibrium data with the high potassium DSSF simulant showed lower K_d values than observed with the CC or NCAW simulant, as observed in the column testing.

2.1 EXPERIMENTAL

The effect on cesium loading and breakthrough was measured during column operation by selecting time-dependent variables (superficial velocity, bed volumes per hour, or flow rate). Other effects such as temperature or feed variables (Na to K mole ratio and OH^-) may be the subject of future column tests. The equipment consists of a constant temperature water bath, an

analytical balance, temperature controlled ion exchange columns, and gamma counting equipment.

2.1.1 Ion Exchange Column System

The ion exchange column system consists primarily of up to six ion exchange columns, feed storage bottles, pumps and effluent weighing bottles. The glass columns each have a capacity of 200 mL of ion exchange material, Figure 2.1. Each column is 2.54 cm in diameter and 41.9 cm tall (including head space for solution above the resin bed). They are equipped with water jackets connected to a water bath so that a constant temperature is maintained. The columns may be run independently or connected in series. The feed solution is normally fed to the columns downflow through pumps from the feed storage bottles. A feed pump is located just upstream of the first column and is used to control the flow rate. A valve is located at the bottom of each column from which the column's effluent is sampled as a function of time. The effluent from the final column is routed to the weighing bottle. The column volumes (cv's) of effluent processed are determined by the effluent weight divided by the specific gravity of the feed. A $24,600 \pm 0.1$ -g balance is used to determine the weight of the effluent.

The operation of the ion exchange system for removing cesium, containing ^{137}Cs tracer, from simulated NCAW or DSSF alkaline salt solution was varied as each test procedure was developed. The influent and effluent ^{137}Cs γ emission counting rates (C_0 and C , respectively) were measured to obtain the breakthrough curves (C/C_0 vs. cv) and determine optimum performance of the ion exchange columns as a function of time and feed flow rate. Samples were obtained at the bottom of each column at 15 to 60 minute intervals, depending on the resin and the flow rate. Four milliliters of each sample was analyzed using gamma counting equipment to determine the extent of column breakthrough. The detection limit for the gamma counter was calculated using the method detection limit procedure described in the Federal Register (Federal Register, 1984). The results of the calculations show that the detection limit is 270 counts, which translates to a C/C_0 of 0.002 for the level of tracer that is being used.

Figure 2.1 Setup of 200 mL columns for loading and elution testing of ion exchange resins.

2.1.2 Column System Configuration

Ion exchange columns were operated as single columns or in a multi-column array. Single column operation consisted of individual ion exchange columns operated independently. Multi-column operations were performed by connecting two to six columns in series. Each column test was operated 24 hours per day until the objective of the test was met. Samples were taken as a function of time at the bottom of each column. Care was taken to limit the amount of solution in the head space on the top of each column so that the liquid mixing area did not perturb the overall results.

2.1.3 Column Loading Conditions

The conditions selected for the initial ion exchange column loading tests were set to determine the effect on the cesium loading of the time-dependent variables (superficial velocity or column volumes per hour); to keep the temperature (25°C), and feed variables (Na^+ concentration, Na/Cs mole ratio) constant during each test series; to use an ion exchange column consisting of one to three 200 mL segments; to obtain samples between each segment; and to continue operation until the final column had a Cs C/C_0 value greater than 0.90.

The R-F resin was tested using variable column configurations. The amount of material placed in each column (200 mL) was added by weight as determined by the following method. First, the specific gravity of the material was determined (grams of the dry exchanger in a known volume). This was accomplished by weighing the "as received" R-F resin into a 200 mL volumetric cylinder containing 2M NaOH to a final tap resin volume of 200 mL, allowing the resin to equilibrate in the solution for 16 h. This specific gravity was then used to determine the mass of 200 mL of "as received" resin to be used in the columns. At the same time, a separate small sample (2g) of the "as received" resin was dried at 85°C for 16 h to determine an F-factor (fraction of wet resin representing the dried resin).

To load the resin into a column, the column was filled with 2M NaOH and the ion exchange resin added based on weight. Each column was then back

flushed with 2M NaOH to remove resin fines before being connected in series. The temperature of the water jacketed columns was controlled at $25 \pm 2^\circ\text{C}$. The ion exchange system (including the pump and either one or three columns) was flushed and tested using at least 3-cv of 2M NaOH solution at a flow rate required for the specific test.

To initiate an ion exchange column test, the solution head on the top of each column was reduced to the minimum volume (excess 2M NaOH above each exchange bed was removed through the bottom sampling valve). DSSF feed was then started through the first column and the liquid heads above each column reestablished and held as close to 1-inch as possible.

After the last column has been loaded to >90% Cs breakthrough [^{137}Cs effluent count rate (C) $\div$ ^{137}Cs feed count rate ($C/C_0 \geq 0.9$)], the test was terminated.

The system was then flushed downflow with 3 cv of 2M NaOH solution followed with 6 cv of water at (2 cv/h), prior to elution. The sodium hydroxide wash is used to remove residual feed from the column. The feed contains aluminum hydroxide compounds, which have low solubilities at pHs ranging from 2 to 13. If water or acid is introduced to the column while feed remains, aluminum hydroxide precipitates fouling the column. If the columns were not eluted immediately, they were stored in either the feed solution or caustic wash. The Cs-loaded columns were then decoupled and individually eluted using either formic or nitric acid (Section 2.1.4).

2.1.4 Column Elution Conditions

Cesium elution experiments were performed using the cesium loaded R-F resins. The experiments were designed to determine the effect of flow rate, temperature, and type of acid eluate on the cesium elution characteristics of each resin. The acid types were limited to nitric and formic with the concentration of the nitric acid limited to <0.5M due to the concern for autocatalytic reactions with the resin at higher acidities. Prior to initiation of the ion exchange column elution tests, the columns were pretreated as

described in the previous section by washing with 3 cv of 2M NaOH and 6 cv of water. The excess water above each exchange bed was then removed through the bottom sampling valve. Nitric or formic acid was then started downflow (unless otherwise noted) through the column and the liquid head above each column reestablished and held at >1-inch.

2.1.5 Batch Equilibrium Testing

The procedure to measure a batch distribution ratio or coefficient for ion exchange materials is found in a separate document (Bray, 1989). This procedure describes a method to determine the batch distribution coefficient for specific radionuclides. For ion exchange research and testing, the batch distribution measurement methodology provides a rapid and cost-effective method of comparing a wide variety of ion exchange conditions for their selectivity of specific radionuclides.

A batch distribution ratio is a measure of the overall ability of the solid phase to remove an ion from solution. The data in this report are reported as radionuclide distribution coefficients (K_d) and/or λ . K_d has units of ml/g (volume of solution/mass of dry exchanger) and represents a theoretical volume of solution that can be processed per mass of exchanger. To convert to (λ), the K_d value can be multiplied by the bed density of the exchanger ρ_b to obtain a value which is equivalent to the volume of the solution per volume of exchanger. The formula for the determination of K_d is:

$$K_d = C_s \div C_l, \text{ mL/g}$$

where,

C_s = the concentration of the radionuclide exchanged on the solid phase (Ci or g of radionuclide/g of anhydrous material)

C_l = the concentration of the radionuclide remaining in the liquid phase after batch contact (Ci or g of radionuclide/mL).

The formula for the determination of λ is:

$$\lambda = K_d \times \rho_b$$

where,

λ represents the number of exchanger bed volumes of feed that can be loaded on an exchanger (column volumes).

This is an artificial number because under conditions of solution flow it is difficult to achieve 100% loading of a column. Under certain conditions, λ approximates the bed volumes which are processed when a breakthrough C/C_0 of 0.5 is achieved during column loading.

2.2 LOADING TESTS WITH DSSF SIMULANT

Three column loading tests were performed during the first quarter of FY 1994. All of the tests used a high potassium, high sodium DSSF (Double Shell Slurry Feed) simulant which was prepared in the laboratory. The feed was prepared at the direction of the Westinghouse Hanford Company (WHC) assuming that the worst case would be a high Na/Cs ratio (10^5) and the highest concentration of potassium (lowest Na/K ratio) present in DSSF tanks. After the preparation of the simulant at 50°C, it was diluted with water to the extent that all of the compounds present would remain in solution at slightly lower than room temperature. Since the analyses of the DSSF tank samples were performed on samples as received from the tank (i.e. at greater than 40°C), most of the salts would have greater solubility than in the solutions at plant operating temperatures, causing the precipitation/crystallization of salts as the solution cools. In order for these solutions to be processed, they will either have to be kept above 40°C during processing or they will have to be diluted to assure that nothing will crystallize during processing. This set of experiments was performed to determine how the ion exchange resins would behave when exposed to the most concentrated solution possible (for all constituent to remain in solution) at room temperature. This feed (Table 2.1) was formulated by comparing the analytical results from all of the DSSF tanks, but it most closely simulates tank 241-AW-101.

The column loading runs were performed using the R-F resin, see Table 2.2. In the first test, three 200 mL columns were set up in series and in the second test, only one column was used. The DSSF simulant was spiked with tracer amounts of ^{137}Cs so that cesium behavior could be conveniently followed.

TABLE 2.1. Synthetic Hanford Alkaline Waste Test Solutions

<u>Species</u>	<u>NCAW, M</u>	<u>DSSF-7, M</u>
Na	5.0	7.0
K	0.12	0.945
Rb	5.0E-5	--
Cs	5.0E-4	7.0E-5
Al	0.43	0.721
SO ₄	0.15	0.008
OH(free)	3.4 (1.68)	4.63 (1.75)
CO ₃	0.23	0.147
F	0.089	--
Cl	--	0.12
PO ₄	0.025	0.014
NO ₂	0.43	1.51
NO ₃	1.69	3.52
<u>Mole Ratio</u>		
Na/Cs,	1.0E+4	1.0E+5
Na/K	42	7
Na/Al	12	10

Table 2.2 Column Loading Experimental Parameters

Run	Column	Resin	Temperature	Feed	Flow rate
15	PP	R-F(BSC-187)	25°C	DSSF-7	600 mL/hr
15	QQ	R-F(BSC-187)	25°C	DSSF-7	600 mL/hr
15	RR	R-F(BSC-187)	25°C	DSSF-7	600 mL/hr
16	SS	R-F(BSC-210)	25°C	DSSF-7	1200 mL/hr

The breakthrough curve for the multiple column test is described in two ways. The first is a non-normalized depiction where the ordinate is the number of column volumes of feed processed through the columns, and one column volume is taken as being the volume of only the first column (200 mL). The

second way the curves are represented is a normalized depiction in which the column volume values are more properly adjusted to reflect the volume of resin through which the solution has passed, that is, the first sampling point represents a column containing 200 mL of resin, the second sampling point represents a column with 400 mL of resin, and the third sampling point represents a column with 600 mL of resin. This effectively allows one experiment to give the results for three different flow rates (column volumes per hour) and one superficial velocity. The term breakthrough is defined as the point at which a measurable quantity of the tracer is detected in the effluent. For the level of tracer used in these experiments, the breakthrough was determined to be C/C_0 of 0.002.

The first loading test was performed on the old batch of R-F resin, BSC-187, at 25°C with a flow rate of ~600 mL/hr (3 cv/hr). Figures 2.2 and 2.3 show the non-normalized and normalized breakthrough curves for this loading test, respectively. During the measurement of the samples for column QQ and RR, high background readings were observed. These readings were due to temporary conditions in the laboratory which effectively raised the detection limit of the counter to a C/C_0 value of 0.04. At these flow rates (3, 1.5, and 1 cv/hr, respectively, for the three columns), the first column exhibited cesium breakthrough after 8,000 mL (40 cv) of feed processed. The second column showed cesium breakthrough through by 34,000 mL (170 cv) and the third column showed breakthrough by 72,000 mL (360 cv). The 0.5 C/C_0 for the curves (see Figure 2.2) is 34,000 mL (170 cv) for the first curve, 34,000 mL (170 cv) later for the second column, and 34,000 mL (170 cv) later for the third column, for an average of 34,000 mL (170 cv) per column. This result is much lower than the 70,000 mL (350 cv) that was predicted using earlier NCAW batch equilibrium data.

Since the 0.5 C/C_0 is an estimate of the capacity of the column and should be the same for a given resin and feed solution, regardless of the volume of the column. The normalized curves should, therefore, cross at a C/C_0 of 0.5. Figure 2.3 shows that the three columns do cross at a C/C_0 of 0.5, as expected. In an earlier experiment run with DSSF-7 simulant at 1800

Figure 2.2

Cesium loading curves for three 200 mL columns of BSC-187 in series with a high potassium, high sodium DSSF Simulant. Flow rate = 600 mL/hr, Temperature = 25°C

Figure 2.3

Normalized cesium loading curves for three 200 mL columns of BSC-187 in series with a high potassium, high sodium DSSF Simulant. Flow rate = 600 mL/hr, Temperature = 25°C

mL/hr (9 cv/hr), the three curves crossed at a C/C_0 of 0.7, which indicates that mass transfer through the solution is the rate limiting step. At the lower flow rate, the solution is in contact with the particle long enough such that the cesium can diffuse completely into the particles.

The second loading test was performed using the newer BSC-210 R-F resin at 25°C with a flow rate of ~1200 mL/hr (6 cv/hr). Figure 2.4 shows the breakthrough curve for this loading test and a curve from a previous DSSF-7 loading of the older BSC-187 resin. The 0.5 C/C_0 for the BSC-210 material is lower than for the BSC-187 material giving the new material a lower cesium capacity than the older material. The curve for the BSC-210 is straighter and has a steeper slope, showing that it is more efficient at the removal of cesium. The lower capacity and the better efficiency of the new material is probably due to the particle size of the two resins, the BSC-210 resin having a smaller average particle size.

The number of column volumes of DSSF simulant required to reach a C/C_0 of 0.5 on the R-F resin was much lower than predicted from the batch and column testing performed with the NCAW simulant. The value predicted for a NCAW feed with a Na/Cs ratio of 10^5 and a sodium concentration of 7 M was about 350 column volumes. It is believed that this lower than predicted capacity is due to the high potassium to cesium ratio. The cesium capacity for the previously mentioned tests using the DSSF simulant is about 50% of the predicted capacity. This value is slightly greater than that observed in the faster flow rate tests (1800 mL/hr). At some value below 1800 mL/hr, the flow rate becomes slow enough so that diffusion in the resin is the rate limiting step, instead of diffusion through the solution.

2.3 ELUTION TESTING WITH DSSF LOADED COLUMNS

Elution tests were performed on three columns during the second quarter of FY 1994. All of the elutions were performed on the R-F resin, two on the BSC-187 material and one on the BSC-210 material, see Table 2.3.

Figure 2.4

Cesium loading curves for two parallel 200 mL columns, BSC-187 and BSC-210, with a high potassium, high sodium DSSF Simulant. Flow rate = 1200 mL/hr, Temperature = 25°C

Table 2.3 Column Elution Experimental Parameters

Run	Column	Resin	Eluent	Temp.	Flow Rate	Loading Feed
15	QQ	R-F(BSC-187)	1.0N Formic	40°C	2cv/hr	DSSF-7
15	RR	R-F(BSC-187)	0.4M Nitric	40°C	1cv/hr	DSSF-7
16	SS	R-F(BSC-210)	1.0N Formic	40°C	1cv/hr	DSSF-7

Figure 2.5 shows two elution curves for the BSC-187 RF resin, one with 1.0N formic acid and one with 0.4M nitric acid. The two main differences between these two elutions is the acid used and that column RR was stirred only after 31 column volumes of eluent had passed through whereas column QQ was stirred continuously. The BSC-187 resin has shown a tendency to agglomerate during the shrinkage associated with elution, causing channeling. Other elutions with 0.4M nitric acid have also shown the agglomeration problem, which indicates that only the change of eluent does not solve the problem, only the mechanical stirring. Figure 2.6 shows the elution curve of the BSC-210 material eluted at 40°C with 1.0N formic acid without stirring. For comparison, an elution curve of BSC-187 resin eluted under the same conditions is also shown. The difference between the two materials appears to be a physical phenomenon. The BSC-210 resin does not agglomerate and channeling is not observed but instead settles uniformly during the elution process. If the unstirred elution curve for the BSC-210 resin is compared with that of the stirred BSC-187 material, it can be seen that the majority of the cesium is removed from both of the columns before 10 column volumes of the eluent have passed through. If the cause of the agglomeration problem can be determined and corrected, it appears that the elution characteristics will be similar for the batches of RF resin. Both resins are being analyzed by Dr. James Franz of PNL by various spectroscopic techniques under the Tank Waste Science Task of the TWRS Program. This work is an attempt to physically determine and quantify the differences in the two resins.

Figure 2.5 Cesium elution curves for two BSC-187 RF resin columns loaded with DSSF-7 waste.

Figure 2.6

Cesium elution curves for a BSC-187 and a BSC-210 RF resin column loaded with DSSF-7 waste.

2.4 BATCH EQUILIBRIUM TESTING WITH DSSF SIMULANT

Since the earlier batch equilibrium results with NCAW(0.2 to 5M Na) and CC (3 to 7M Na) simulants failed to provide adequate estimation of the performance of the CS-100 and RF resins, the batch equilibrium constants were determined for the DSSF simulant. The DSSF-7 simulant used is essentially a more concentrated solution of NCAW (7M Na as compared to 5M Na) with a higher concentration of potassium. Figures 2.7 and 2.8 show the batch equilibrium results for the CS-100 and R-F resins, respectively. The CC waste data was obtained in 1992 (Kurath et al, 1994). As observed in the column testing, the higher potassium DSSF-7 simulant gave much lower K_d values than the lower concentration CC simulant in all cases. The differences in K_d between the two batches of R-F resin was negligible.

Figure 2.7

Batch equilibrium constant for CS-100 as a function of the sodium to cesium ratio for two waste simulants, DSSF and CC.

Figure 2.8

Batch equilibrium constant for RF resin as a function of the sodium to cesium ratio for two waste simulants, DSSF and CC.

3.0 ION EXCHANGER STABILITY STUDIES

Stability testing of the ion exchanger resins is separated into two major parts, the radiation stability of organic and inorganic ion exchangers in NCAW simulant and the chemical stability of inorganic ion exchangers. In this quarter, only the radiation stability studies of the R-F resin are being performed, the other work will be performed later in the fiscal year.

3.1 EXPERIMENTAL

Tests were continued from the first quarter of FY 1994 to determine the radiation stability of the R-F resin. Testing of the resin materials was performed under static and flow conditions. All of the tests were performed under an atmosphere of argon. The static tests involved exposing resin materials to high dose gamma radiation within a sealed reaction vessel. The sealed system allowed convenient measurement of gaseous decomposition products generated from the resin materials. During radiolysis the resin was contacted with an aqueous solution simulating NCAW.

Flow tests were used to mimic actual column performance by allowing the simulated Cs feed supernate to flow through the resin in the reaction vessel during radiolysis. Comparison of the flow system versus the non-flow (static) system was made to determine differences in resin performance under these conditions.

The resin performance was determined as a function of exposure to radiation in a ^{60}Co source gamma pit. The distribution coefficient (K_d) for cesium uptake was used as an indicator of radiation damage to the resin material. The deterioration of the resin performance typically follows an exponential decay curve. Gases released during the experiment and organic materials found in the aqueous solution were measured and identified. Stainless steel coupons were placed in the reaction vessels to assess corrosion during testing.

3.1.1 Preparation of Ion Exchange Materials After Exposure

Because the resin was subjected to static or flowing aqueous waste, each sample of resin (including the starting resin) was treated prior to the determination of a batch $Cs K_d$ to remove any cations that had been exchanged onto the resin. The treatment consisted of a 16 h soak in 2M NaOH, two water washes, two 1N formic acid washes, and two 2M NaOH washes, each carried out for 30 minutes. The resulting resin was air dried for 30 minutes in a vacuum filter. Samples of the air dried resin were then weighed out; 0.1 g for the determination of the Cs distribution and 0.5 g for the determination of the F-factor. The final hydroxide wash was carefully removed from the weighed sample and a stock solution of NCAW, containing cesium tracer was added and contacted for 72 h at 25°C on a shaker table. The resulting solutions were then compared with the cesium activity in the starting feed stock solution.

3.1.2 Equipment Description

The following is a list of initial test conditions used in this study. The sample size of resin used was based on the size of existing equipment to be used within the test. A total of approximately 150 g of resin was placed in each column. For the flow tests, the feed direction was upflow at approximately 0.5 cv/hr. The aqueous feed in the flow and static tests was NCAW simulant. Samples of the resin and the test solution were collected four times throughout during the test. The resin sample size at each sampling was approximately 0.5 g to minimize disruption of the system. Solution samples were 10 mL. The sampled resins were tested for cesium uptake and the solutions were analyzed for organic content. Gas sampling was monitored periodically throughout the irradiation period on the static systems only.

The gamma irradiation facility operated by PNL is located in the 3730 Building in the 300 Area. The facility contains thirty-seven stainless steel irradiation tubes positioned in a 7-foot diameter by 13.7-foot deep stainless steel tank. Two arrays of ^{60}Co with a combined inventory of 32 KCi are located near the bottom of the tank. For radiation shielding purposes, the tank is completely filled with water and a concrete wall, 3.5-feet in height,

surrounds the top of the tank. The irradiation tubes, which are sealed on the bottom, vary in length and diameter from 16-feet to 18-feet and 1.8-inches to 6-inches, respectively. The irradiation flux of the tubes range from 2×10^6 R/hr to 2×10^2 R/hr. The uniform flux region varies from ~6-inches for the tubes closest to the sources to greater than 12-inches for the tubes farthest away from the sources. All flux measurements of the tubes are traceable to the National Bureau of Standards.

Materials, capsules, and test systems are lowered into the irradiation tubes to the desired flux manually or by using a half-ton crane. They are left in the tubes for a specific amount of time to attain the required exposure. There is no activation associated with the gamma irradiation so the materials can be transported to other facilities for examination after removal from the tubes.

The temperature of the test was approximately 25°C to 35°C based on the ambient temperatures in the gamma facility.

3.2 RESULTS OF GAS ANALYSIS

Gases generated during static testing of CS-100 and R-F resins immersed in NCAW supernate were collected and analyzed for both the irradiated and non-irradiated samples. Gas samples were taken approximately every two weeks, or prior to resin sampling activities. In all cases the thermal generation of gases was negligible. Gas results for the irradiated tests for CS-100 and R-F resins are summarized in Figures 3.1 and 3.2, respectively. For both resin tests, hydrogen was the most abundant gas produced. Nitrogen and nitrous oxide were produced in approximately equal quantities for both the CS-100 and R-F resin. Oxygen was produced at a significant level for the system containing CS-100 resin, however, no oxygen was produced in the system containing R-F resin.

In order to assess the amount of gas generation induced by the presence of added organic resin, NCAW supernate containing no added resin material was

Figure 3.1

Gases produced from the irradiation of CS-100 resin in NCAW supernate simulant.

Figure 3.2

Gases produced from the irradiation of BSC-187 RF resin in NCAW supernate simulant.

Figure 3.3

Gases produced from the irradiation of NCAW supernate simulant.

irradiated. Figure 3.3 contains initial data for the moles of gases generated during radiolysis of the NCAW supernate over a period of approximately 1300 hours. The experiment is continuing in order to cover the same time period as for the resin irradiation tests. As observed from Figure 3.3, the production of hydrogen is lower than the production of this gas when organic resin is present (Figures 3.1 and 3.2). The production of oxygen is higher than either of the experiments containing organic resins at similar exposure times. The hydrogen to oxygen product ratio is approximately the stoichiometric ratio of two expected for the radiolysis of water. Nitrogen and nitrous oxide are observed as minor products and at lower yields than for the parallel experiments containing organic resins. The source of these products is from the reduction of nitrite and nitrate in solution.

Hydrogen and oxygen are expected radiolytic products and result from the initial homolysis of the O-H bond of water initially forming $H^\cdot$ and $OH^\cdot$ radicals. The molecular decomposition products of pure water is a stoichiometric ratio of H_2 and O_2 . In the aqueous system containing organic resins (CS-100 and R-f resin), the radiolytic hydrogen to oxygen ratio is much higher than that for pure water due to the presence of a source of hydrocarbon material which is effective at scavenging $OH^\cdot$ to reform water. This prevents the recombination of $OH^\cdot$ with another hydroxyl radical to form H_2O_2 and the eventual molecular decomposition product, O_2 . The $H^\cdot$ radical can react with a like radical ($H^\cdot$) or directly with the hydrocarbon resin to form H_2 .

Nitrogen and nitrous oxide are products of molecular decomposition observed in all of the irradiated static tests of NCAW simulated waste, whether organic resins are present or not. These species are produced with a higher yield for the systems with organic resins than for the NCAW system only. These nitrogen-containing gases have been produced in similar systems containing nitrite and nitrate with organic carbon present (Bryan et al 1992). Since the resins tested and the NCAW supernate do not contain organic nitrogen, the source of nitrogen in N_2 and N_2O must be from nitrate and nitrite present in the NCAW waste simulant. Under reducing conditions in basic solution, nitrate and nitrite have been shown to be unstable toward reduction forming the gaseous products N_2 , N_2O and NH_3 (Pourbaix 1974).

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