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Radiation Testing of Organic Ion Exchange Resins

C. D. Carlson
L. A. Bray
S. A. Bryan
J. A. Franz
D. E. Kurath
S. R. Adami

G. N. Brown
J. R. DesChane
R. J. Elovich
J. C. Linehan
W. S. Shaw
M. R. Telander

September 1995

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Pacific Northwest Laboratory
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Summary

A number of ion exchange materials are being evaluated as part of the Tank Waste Remediation System (TWRS) Pacific Northwest Laboratory (PNL) Pretreatment Project for the removal of ^{137}Cs from aqueous tank wastes. Two of these materials are organic resins; a phenol-formaldehyde resin (Duolite CS-100) produced by Rohm and Haas Co. (Philadelphia, Pennsylvania) and a resorcinol-formaldehyde (RF) resin produced by Boulder Scientific Co. (Mead, Colorado). One of the key parameters in the assessment of the organic based ion exchange materials is its useful lifetime in the radioactive and chemical environment that will be encountered during waste processing. The focus of the work presented in this report is the radiation stability of the CS-100 and the RF resins. The scope of the testing included one test with a sample of the CS-100 resin and testing of two batches of the RF resin (BSC-187 and BSC-210).

Samples of the exchangers were irradiated with a ^{60}Co source to a total absorbed dose of 10^9 R over a period of 5 months in a static (no flow) and a flowing configuration with neutralized current acid waste (NCAW) simulant as a feed. Based on a maximum concentration of ^{137}Cs on the resin that would result from processing NCAW, this dose represents an operational period of at least 150 days for the RF resin and at least 1260 days for the CS-100 resin. Gas generation in the static experiment was continuously monitored and G values (molecules of gas per 100 eV) were determined for each species. Resin samples were obtained periodically and the equilibrium behavior of the resins was assessed by determining the distribution coefficients (K_d s). Structural information was also obtained by ^{13}C cross polarization magic angle (CPMAS) nuclear magnetic resonance (NMR) spectrometry and Fourier Transform Infrared (FTIR) spectroscopy so that changes to the chemical structure could be correlated with changes in K_d .

During the flowing tests, a significant drop in the K_d s was not noticeable until after 10^8 R total dose, so the usable lifetime of the resins appears to be quite good. Based on the maximum estimated dose rates, the time required to reach 10^8 R is roughly 15 days for the RF resin and 126 days for the CS-100 resin. These times both exceed the resin lifetime of 2.1 days for CS-100 and 14.5 days for RF that are implied in flowsheets developed for both of these resins (Penwell 1994; Eager 1994). These lifetimes are based on 5 load/elute cycles, a total operating efficiency of 100%, and the processing rates given in the flowsheets. Since most of the aqueous wastes contain less cesium, dose rates will be lower and the time required to cause significant radiation damage will be correspondingly longer. It is also noted that the RF resin degrades to a greater extent than the CS-100 resin, although the K_d s, even after 10^9 R, are higher for the RF resin than the nonirradiated K_d s for the CS-100. These results suggest that radiation damage will not be a limiting factor during normal operation. Much of the damage to the RF resin may have been due to oxidation of the organic structure by oxygen or oxygen precursors, such as $\text{OH}\cdot$ that are generated by the radiolysis of water. Very little oxygen was detected in the gases generated in the static experiment even though radiolysis of water normally produces O_2 and O_2 was detected in the CS-100 static experiment.

NMR analyses also indicate the formation of oxidation products such as quinones and carboxylates. The FTIR data corroborate the NMR data by showing the reduction in aromaticity of the resin and an increase in the oxidation products. The FTIR data also show that the degradation is a surface phenomenon, which would indicate that oxidation is more of a concern than the radiolytic degradation of the resin.

The utility of using NMR spectrometry and FTIR spectroscopy as methods for characterizing the structure of the resins was demonstrated. These analytical tools indicate that it is oxidation of the resin structures by oxygen or oxygen precursors that are probably responsible for the decrease in resin performance. Characterization of the resin structures could also be useful as a method for acceptance of the organic resins if these resins are implemented in a process.

References:

Eager, K. M., D. L. Penwell, B. J. Knutson. 1994. *Preliminary Flowsheet: Ion Exchange Process for the Separation of Cesium from Hanford Tank Waste Using Duolite CS-100 Resin*. WHC-SD-WM-TI-667, Westinghouse Hanford Company, Richland, Washington.

Penwell, D. L., K. M. Eager, and B. J. Knutson. 1994. *Preliminary Flowsheet: Ion Exchange Process for the Separation of Cesium from Hanford Tank Waste Using Resorcinol-Formaldehyde Resin*. WHC-SD-WM-TI-638, Westinghouse Hanford Company, Richland, Washington.

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1.0 Introduction

1.1 Background

The contents of the Hanford Site'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 and hydroxides and contains the bulk of many radionuclides. The salt cake, generated by extensive evaporation of aqueous solutions, consists primarily of dried sodium salts. The supernates consist of concentrated aqueous solutions of sodium and potassium nitrate salts. The bulk of the water-soluble radionuclides, such as ^{137}Cs , are contained in the water-soluble salt cake and supernatant solutions.

Although the pretreatment and disposal strategy for tank waste is still being defined, one of the first steps in most pretreatment scenarios will be the separation of the supernatant and dissolved salt cake from the sludges. Cesium will be removed from the aqueous solutions using an ion exchange process and the decontaminated solutions will be immobilized as a low-activity waste. The specific cesium decontamination requirements will depend on the waste composition and the disposal requirements for the low-activity waste. The separated cesium will be concentrated and vitrified with the high-level waste (HLW) sludge for disposal in the HLW repository.

1.2 Scope

A number of ion exchange materials are being evaluated as part of the Pacific Northwest Laboratory (PNL) ion exchange work for the removal of cesium from the aqueous fraction of the Hanford Site tank wastes. These exchangers include CS-100, a phenol-formaldehyde resin produced by the Rohm and Haas Co. (Philadelphia, Pennsylvania); resorcinol-formaldehyde (RF) resin developed at the Westinghouse Savannah River Laboratory and produced by the Boulder Scientific Co. (BSC) (Mead, Colorado); powdered (IONSIV® IE-910, referred to as IE-910) and engineered (IONSIV® IE-911, referred to as IE-911) forms of crystalline silico-titanate (CST) inorganic exchanger developed by Sandia National Laboratory/Texas A&M and prepared by UOP Inc. (Des Plaines, Illinois); TIE-96, an inorganic exchanger produced by UOP Inc.; and Superlig 644, an organic exchanger developed by IBC Inc. (Provo, Utah). One of the key parameters in the assessment of the organic-based ion exchange materials is its useful lifetime in the radioactive and chemical environment that will be encountered during waste processing. The focus of the work presented in this report is the radiation stability of the CS-100 and the RF resins. The scope of the testing included one test with a sample of the CS-100 resin and testing of two batches of the RF resin (BSC-187-077 [henceforth referred to as BSC-187] and BSC-187-210 [henceforth referred to as BSC-210]).

1.3 Experimental Objectives

The experimental objectives of the work presented in this report are to

- provide information on the loss of cesium uptake capacity in the ion exchange materials as measured by the batch distribution coefficient (K_d) as a function of total absorbed dose up to 10^9 R
- provide a determination of the G values (molecules of gas per 100 eV) for each gas species generated (i.e., O_2 , N_2 , H_2 , N_2O)
- characterize the changes in the chemical structure induced by the radiation
- characterize any gross physical changes in the resins.

1.4 Approach

The exchanger samples were placed into 200-mL stainless steel columns and exposed to static (no flow) and flowing (0.5 bed volumes/h) supernatant simulant (neutralized current acid waste [NCAW]) in a radiation field generated by a ^{60}Co source. Each of the exchangers was irradiated at a rate of 2.1×10^5 to 2.7×10^5 R/h to a total absorbed dose of approximately 10^9 R over a period of 5 months. This dose represents an actual operational period of about 150 days for the RF resin and about 1260 days for CS-100, assuming a maximum ^{137}Cs concentration from processing NCAW. Since the average aqueous tank wastes to be processed have lower ^{137}Cs concentrations, the expected dose rate will be a factor of 10 lower, giving a longer operational life before the total dose of 10^9 R is absorbed. Gas generation was continuously monitored with samples taken at 2-wk intervals to determine G values for each of the gas species generated. Resin and supernatant samples were collected at 10^5 , 10^6 , 10^7 , 10^8 , and 10^9 R total dose. The equilibrium behavior of the resins was assessed by determining cesium's K_d and a structural characterization was obtained by ^{13}C cross polarization magic angle spectroscopy (CPMAS). The purpose of this characterization is to assess the structural changes as a function of radiation exposure. In addition to the irradiated test columns, control columns were exposed to only the simulated supernatant solution, with samples being collected at the same times as the irradiated samples. Completion of the experiments for two batches of the RF resin provides information on the batch to batch variability.

2.0 Experimental

Experimental work completed from FY 1992 through FY 1993 for cesium recovery included the determination of cesium batch distribution coefficients for three exchangers and two waste types (Bray et al. 1992), the initiation of ion exchange column studies (Bray et al. 1993), and radiation stability studies of the phenol formaldehyde resin CS-100 using ^{60}Co gamma irradiation (Bryan et al. 1993). In FY 1994, column studies were continued (Kurath et al. 1994) and the radiation stability testing of the BSC RF ion exchange resin was initiated.

The resin ability to absorb cesium from simulated alkaline wastes was determined as a function of exposure to radiation. The K_d s for cesium uptake on the resins were used as indicators of radiation damage to the resin structure. Gases released during the irradiation experiment and organic materials found in the aqueous solution were measured and identified.

2.1 Ion Exchange Selection

The ion exchangers studied in these tests were a granular phenol-formaldehyde condensate polymer ion exchange resin (CS-100) prepared by the Rohm and Haas Co., and RF ion exchange resin. The RF resin was first prepared by Dr. Jane Bibler and Dr. Dick Wallace at the Westinghouse Savannah River Laboratory. The RF resin is currently manufactured by BSC. The resins were used as received during the irradiation testing.

Two batches of the RF resin were tested, batch BSC-187 and batch BSC-210. The BSC-210 resin was prepared later using an optimized synthesis. The BSC-187 showed a tendency to agglomerate during acid elutions (not observed in the elution testing of BSC-210) and was observed to clump during irradiation testing at Westinghouse Hanford Company (WHC).^(a) During the initial phase of radiation testing with the BSC-187 material, a clump was observed during the flowing test. For this reason, the radiation testing of BSC-210 was performed to determine if the new material showed the same behavior.

2.1.1 Preparation of Ion Exchange Materials

The samples received from the manufacturer were initially treated with a 2M NaOH solution to obtain the sodium form of the resins. The CS-100 is received in the hydrogen form and the RF resins are received as the potassium form. Since potassium will compete with cesium for exchange sites, pretreatment was necessary to assure both types of resin were tested on an equal basis.

To produce an accurate and reproducible determination of the cesium K_d for the RF resin organic exchanger, a uniform basis for mass and accurate determinations of mass are essential. The most reproducible basis for the mass is that of a dry material (i.e., 85°C for 24 h). A dry material is also much easier to weigh because damp material tends to clump together. However, the exchange capacity of some ion exchange materials may be destroyed during drying. Therefore, the material is usually used as received from the column, and a correction factor is applied using a separately dried sample.

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 cesium K_d . The treatment consisted of a 2M NaOH soak, two water washes, two formic acid washes, and two water

(a) Westinghouse Hanford Company Internal Memo 28110-PCL91-011 Rev. 1. 1991. *Results from Batch Tests of Savannah River Laboratory and Duolite CS-100 Ion Exchange Resins*. From J. S. Buckingham to B. C. Landeene.

washes. The resulting resin was air dried for 30 min in a vacuum filter. A 0.1 g sample of the air dried resin was then weighed out for the determination of the cesium distribution. A stock solution of NCAW (see below), containing cesium tracer was added to the smaller sample and contacted for 72 h at 25°C. The resulting solutions were then compared with the cesium activity in the starting feed.

2.2 Preparation of Synthetic Wastes

Complexant concentrate (CC) and NCAW were selected for the initial investigation (Bray et al. 1992). Organic CC waste represents a high sodium waste containing organic complexants. NCAW represents a high sodium waste with a low organic content. The results of that investigation show that the organic content of the waste had no effect on the cesium ion exchange equilibrium behavior and that these results can be applied to a broad range of tank waste types. For this study, simulated solutions were prepared to represent NCAW. The NCAW solution used during the irradiation of the samples contained no cesium. The simulant used during the batch distributions is as listed below. The concentrations of the ionic species in NCAW are listed in Table 2.1.

2.3 Equipment Description

This section contains a list of initial test conditions used in this study.

The resin types tested were CS-100 and RF resins. The columns used had a 250-mL total capacity and were constructed of stainless steel. The same vessel type was used in both the flow and static tests. The sample size of resin used was based on the radiotracer column testing performed in FY 1993 and FY 1994. A total of approximately 66 g of resin and 150 g of NCAW simulant (~120 mL) was placed in each column. The flow direction in the flow test was upflow at approximately 0.5 column volume/h. The aqueous feed in the flow and static testing was NCAW simulant. At three intervals and at the end of the test, the columns were removed from the gamma pit and samples removed to test the cesium uptake. Each sample was approximately 0.5 g, the samples were taken from the top of the bed to minimize disturbing the system. Gas production was monitored periodically throughout the irradiation period on the static systems only.

The irradiation testing was performed in the Gamma Irradiation Facility operated by PNL. The facility contains 37 stainless steel irradiation tubes positioned in a 7-ft diameter by 13-ft, 8-in. deep stainless steel tank, Figure 2.1. 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-ft high, surrounds the top of the tank. The irradiation tubes, which

Table 2.1. NCAW - Synthetic Test Solution

Species	NCAW, M
Na	5.0
K	0.12
Rb	5.0×10^{-5}
Cs	5.0×10^{-4}
Al	0.43
SO ₄	0.15
OH(free)	3.4 (1.3)
CO ₃	0.23
F	0.089
NO ₂	0.43
NO ₃	1.69

Figure 2.1. Installation of Test Vessel in Gamma Pit

are sealed on the bottom, vary in length and diameter from 16 to 18 ft and 1.8 to 6 in., respectively. The irradiation flux of the tubes range from 2×10^6 to 2×10^2 R/h. The uniform flux region varies from ~6 in. for the tubes closest to the sources to greater than 12 in. for the tubes farthest away from the sources. All flux measurements of the tubes are traceable to the National Institute of Standards and Testing (formerly the National Bureau of Standards). The total dose to the system was calculated by multiplying the flux by the time the column was in the gamma pit.

Materials, capsules, and test systems are lowered into the irradiation tubes to the desired flux manually or by using the 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 tests ranged from approximately 25°C to 35°C based on the ambient temperatures in the gamma facility.

Radiation testing of the ion exchange materials were performed under static and flow conditions. Static tests involved exposing resin materials to high dose gamma radiation within a sealed reaction vessel containing the resin and the NCAW simulant solution, Figures 2.2 and 2.3. The sealed system allowed convenient measurement of gaseous decomposition products generated from resin materials, Figure 2.4. This configuration also provided a worst-case scenario with respect to oxidizing components which were kept in contact with the resin.

Flow tests were used to mimic actual column performance by allowing the simulated NCAW supernatant solution to flow through the resin in the reaction vessel during radiolysis, Figures 2.5 and 2.6. Comparison of the flow systems versus static systems were made to determine differences in resin performance.

2.4 Batch Distribution Coefficient

A batch distribution coefficient is a measure of the overall ability of the solid phase to remove an ion from solution. Batch distribution data are reported as radionuclide K_d . K_d , in units of mL/g, represents a theoretical volume of solution with a specific radionuclide concentration that can be processed per mass of exchanger, with complete removal of the radionuclide of interest. 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 dry material), and

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

2.5 NMR Spectrometric Characterization

NMR spectrometric characterization was used in this test to determine the structural affects of the radiation on the organic resins. NMR spectrometry provides for the identification of structural elements of an organic compound, such as the aromatic nature of the compound and the types and locations of functional groups, such as carboxylic acids and bridging methylene groups.

Natural abundance ^{13}C CP MAS solid-state nuclear magnetic resonance spectra were acquired with a Varian VXR-300 spectrometer with carbon observed at 75.4 MHz using a Doty, Scientific Inc. ultra high speed 5-mm CP MAS probe, or with a Chemagnetics CMX-300 spectrometer using a

Chemagnetics high speed 5-mm CPMAS probe. Spectra were acquired with 12 kHz magic angle spinning, a proton 90° pulse width of 4.5 μ s, and proton decoupling at about 70 kHz power. 2 sec. recycle delays and 2 ms contact times were employed. Chemical shifts are reported in ppm from external tetramethylsilane.

The conditions cited above result in semi-quantitative ^{13}C analysis. In typical cases, the cross-polarization conditions lead to slightly decreased intensities (about 20%) of quaternary carbon (carbon not attached directly to hydrogen). However, from sample to sample this attenuation of quaternary signal is consistent and serves for comparison of control and test samples. In certain cases (noted below), the levels of free radical content in resins leads to selective spectral broadening of aromatic carbon.

Figure 2.2. Disassembled Gamma Test Vessel

Figure 2.3. Assembled Gamma Test Vessel for Static Testing and Gas Collection

Figure 2.4. Gas Sampling Activity from Gas Manifold

Figure 2.5. Design Detail of Gamma Test Vessel for Flow Testing

Figure 2.6. Assembled Gamma Test Vessel for Flow Testing

3.0 Results and Discussion

To determine the effect of gamma radiation on the ion exchangers, the resins were tested in two ways, under flowing conditions or in a static solution. Since the resins tested will be used in a column, they will be in contact with flowing solutions for the majority of the treatment, with some static conditions during switching of feeds or down time of the facility. It is believed that static conditions will be a worst-case scenario for the degradations of these resins, therefore both flowing and static experiments were performed to cover all possibilities. In each case, the contacting solution used was synthetic NCAW containing no cesium, Table 2.1. Following the irradiation, the resin samples were analyzed by batch equilibrium tests to determine how the cesium uptake was affected as a function of dose. The loss in cesium uptake was also correlated to the structure (NMR and FTIR), gas generation, and corrosion of the vessel. This section will describe the results of these analyses.

3.1 Batch Equilibrium Studies

To determine how the ion exchange properties were effected, cesium distribution values were determined for the untreated (no gamma dose) RF resins and resins that had been subjected to doses of up to $\sim 10^9$ R. The results are shown in Figures 3.1, 3.2, and 3.3 for CS-100, BSC-187, and BSC-210, respectively. In all cases dealing with RF resin in a flowing system, the K_d s are relatively constant up to 10^8 R accumulated dose but then decrease rapidly at 10^9 R. In contrast, there is a gradual decrease in K_d in the case of CS-100. The results also show that there is a difference between flowing and static conditions. The cesium K_d values for the static tests were generally lower than for the flowing system. This indicates that any static testing results are a worst-case scenario, where the resin is loaded with radioactive cesium and no solution is flowing through the system. The basis for this difference may be due to a higher buildup of chemical species that attack the resin, versus being swept out of the system in the flowing tests. These results compare favorably with results published previously (Bibler 1991).

The K_d results from the BSC-187 show much lower uptake of cesium than the BSC-210 material. This is probably due to the storage of the BSC-187 irradiation samples. There was a delay of several months between the irradiation of the samples and the performance of the batch distribution studies. From this experiment, trends in K_d s and in the structural data can be drawn (see below).

3.2 Physical Consequences of Irradiation

During the testing of the flowing BSC-187 column, the system plugged and blew a pressure relief valve. Upon removing the resin from the column, a large clump was observed about halfway down the vessel. The clump was solid RF resin about 1.5-cm thick and the same diameter as the column, see Figure 3.4. Upon grinding, the clump appeared to fall apart into particles roughly the same size as the non-irradiated resin. The clumped material had a K_d similar to a non-clumped portion of the resin within the column. This led to the testing of the BSC-210 material to determine if the manufacturing process affected the behavior of the resin during the irradiation test. A similar result was observed by scientists at the WHC Process Chemistry Laboratories in 1991.^(a) The clumping phenomenon was not observed for the remainder of the BSC-187 testing, nor did it occur during the BSC-210 irradiation testing.

(a) Westinghouse Hanford Company Internal Memo 28110-PCL91-011 Rev. 1. 1991. Results from Batch Tests of Savannah River Laboratory and Duolite CS-100 Ion Exchange Resins. From J. S. Buckingham to B. C. Landeene.

Figure 3.1. Cesium Batch K_d for CS-100 as a Function of Gamma Dose - Static and Dynamic Contact with NCAW Solution

Figure 3.2. Cesium Batch K_d for BSC-187 as a Function of Gamma Dose - Static and Dynamic Contact with NCAW Solution

Figure 3.3. Cesium Batch K_d for BSC-210 as a Function of Gamma Dose - Static and Dynamic Contact with NCAW Solution

Figure 3.4. Clump Observed in BSC-187 Irradiation Testing After 10^8 R Exposure

During column elution testing (Kurath et al. 1994), the BSC-187 material showed a tendency to agglomerate during the neutralization of the column, causing the resin to shrink away from the side of the column. When the newer BSC-210 material was tested, agglomeration was not observed and the column settled during the neutralization. It is possible that the same phenomenon caused the clumping observed in the flowing irradiation test.

3.3 Gas Generation for Cation Exchange Resin and NCAW Supernate

The RF and CS-100 resins were irradiated within NCAW simulated waste supernate under flow (NCAW flow at 0.5 column volumes/h) and static conditions at 2×10^5 R/h for up to 4000 h gamma exposure (^{60}Co gamma source) for a total of approximately 1×10^9 R. In order to determine the gas generation for the supernate solution in the absence of resin, NCAW simulated waste supernate was irradiated under static conditions at a dose rate of 1.5×10^5 R/h (^{60}Co gamma source) for a total of 2270 h for a total dose of 2.4×10^8 R.

The gas generation of the static tests was monitored by pressure increases within the vessel and mass spectral analysis if the gas products accumulated throughout the duration of the experiment. In all cases the thermal generation of gases (when no gamma dose was applied) was negligible. G values calculated for the formation of gaseous products as a function of gamma dose for the RF resin and CS-100 resin tests, as well as the NCAW only irradiation test, are presented in Table 3.1.

Gas generation data for static testing of the BSC-187, BSC-210, and CS-100 resins immersed in NCAW supernate are summarized in Figures 3.5 to 3.7. For these tests, hydrogen was the most abundant gas produced and had the highest measured G value. Nitrogen and nitrous oxide were measured in approximately equal quantities.

Oxygen was not measured at a significant level for the system containing RF resin, in contrast to the similar system containing CS-100 resin. Figure 3.8 contains the oxygen gas generation with time for these resins under irradiation conditions. $G(\text{O}_2)$ for the BSC-187 and BSC-210 RF resin (3.3×10^{-5} and 3.5×10^{-5} respectively) is approximately 2 orders of magnitude lower than $G(\text{O}_2)$ for CS-100 (3.3×10^{-3}). This difference in oxygen production can be attributed to the higher reactivity of the activated resorcinol functionality of the RF resin (compared to the phenolic function of CS-100) towards the hydroxy radical formed in the radiolysis of the resin-NCAW system. A major difference between the RF resin and the CS-100 resin is the amount of crosslinking in the polymer chains. Since there is hinderance for the crosslinking in the resorcinol, more nonsubstituted sites are available in the aromatic ring, which gives rise to the higher reactivity of the resorcinol to oxidation. The reaction and capture of the hydroxy radical prevents its eventual formation of molecular oxygen by other reaction pathways.

Table 3.1. G Values for the Production of Gases for Several NCAW Simulated Waste Supernate Solutions Containing RF Resin, CS-100 Resin, and NCAW Supernate Only

G Values (molecules per 100 eV)					
Sample	$G(\text{H}_2)$	$G(\text{N}_2)$	$G(\text{O}_2)$	$G(\text{N}_2\text{O})$	gamma dose rate
RF Resin BSC-187	1.65×10^{-2}	3.94×10^{-3}	3.30×10^{-5}	3.76×10^{-3}	2.1×10^5 R/h
RF Resin BSC-210	1.30×10^{-2}	3.30×10^{-3}	3.53×10^{-5}	3.18×10^{-3}	2.2×10^5 R/h
CS-100	1.05×10^{-2}	3.55×10^{-3}	1.98×10^{-3}	3.31×10^{-3}	2.7×10^5 R/h
NCAW	1.59×10^{-2}	1.47×10^{-3}	7.54×10^{-2}	4.41×10^{-5}	1.5×10^5 R/h

Gas Generation from R-F Resin in NCAW Supernate Under Irradiation and Control Conditions

Figure 3.5. Gas Generation from BSC-187 RF Resin in NCAW Supernate Under Gamma Irradiation and Control Conditions

Gas Generation from R-F Resin in NCAW Supernate Under Irradiation and Control Conditions

Figure 3.6. Gas Generation from BSC-210 RF Resin in NCAW Supernate Under Gamma Irradiation and Control Conditions

Gas Generation from CS-100 Resin in NCAW Supernate Under Irradiation and Control Conditions

Figure 3.7. Gas Generation from CS-100 Resin in NCAW Supernate Under Gamma Irradiation and Control Conditions

Comparison of Oxygen Gas Generation Using CS-100 and RF Resins in NCAW Supernate

Figure 3.8. Comparison of Oxygen Gas Generation from CS-100, BSC-187, and BSC-210 Resins in NCAW Supernate Under Gamma Irradiation Conditions

In order to assess the amount of gas generation induced by the presence of added organic resin, NCAW supernate without added resin material was irradiated. Figure 3.9 contains data for the moles of gases generated during radiolysis of the NCAW supernate. The $G(O_2)$ for the production of oxygen (Table 3.1) is one to three orders of magnitude higher than any of the experiments containing organic resins. Evidently, one of the radiolysis products which is a precursor for oxygen is reacting with the organic resins before it can produce oxygen. This effect is more pronounced in the RF resins than in the CS-100 resins. 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 the reduction of nitrite and nitrate in solution.

Hydrogen and oxygen are expected radiolytic products and result from the homolysis of the O-H bond of water forming $H\cdot$ and $OH\cdot$ radicals. The molecular decomposition of pure water gives H_2 and O_2 in a stoichiometric ratio of 2:1. In the aqueous system containing organic resins (RF and CS-100), the radiolytic hydrogen to oxygen ratio is much higher than that for the NCAW solution alone due to the presence of a source hydrocarbon material which is effective at scavenging $OH\cdot$ to reform water. This prevents its recombination with another hydroxyl radical to form H_2O_2 and its 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 both observed molecular decomposition products in all of the irradiated static tests of NCAW simulated waste, whether organic resins are present or not. The nitrogen-containing products are produced in a higher yield for the systems with organic resins than for the NCAW system only. The resins are the primary thermodynamic source of reductant. These nitrogen containing gases have been produced in similar systems containing nitrite and nitrate with organic carbon present (Bryan et al. 1992, 1994). 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 from 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). Although ammonia has not been observed in this system, the organic is believed to be acting as the reducing agent toward nitrite and nitrate to form nitrogen and nitrous oxide. Even in the NCAW system with no added organic resin, some nitrogen and nitrous oxide is formed, presumably from the direct reduction of nitrite and nitrate ions by $H\cdot$ radical.

3.4 Corrosion

Stainless steel corrosion coupons were placed in the test vessels during resin stability testing to assess steel corrosion under test conditions. Coupons were placed within the test vessels containing the CS-100 and BSC-187 RF resins. Corrosion coupons were used in the flow and static tests, in both the control and irradiated tests. The stainless steel coupons were machined from a single sheet of 304L stainless (1.2-mm thick) and uniquely stamped for identification. Standard American Society for Testing and Materials (ASTM) and National Association of Corrosion Engineers (NACE) methods were employed for cleaning and weighing the corrosion coupons prior to testing. The average surface area of each coupon was approximately 11 cm². Three coupons were used per test vessel, and evenly spaced within the resin. The total steel surface area in each test was approximately 200 cm²/Kg resin.

Corrosion coupons were left within the resin during each resin test, flow with and without gamma irradiation, and static with and without gamma irradiation. The total length of corrosion test for each experiment was approximately 2400 h in the CS-100 resin test and approximately 4000 h in the BSC-187 RF resin tests. Corrosion rates based on linearized corrosion rates were calculated at the conclusion of the test.

Gas Generation from NCAW Under Gamma Irradiation

Figure 3.9. Gas Generation from NCAW Supernate Under Gamma Irradiation

The corrosion data (Table 3.2) show that for the CS-100 and RF resin the measured corrosion rate is extremely small. The negative values obtained for the CS-100 tests indicate a precipitation film that could not be removed by the washing procedure prior to measuring the final mass of the test coupon.

A precipitation coating formed on the test coupons for the static-irradiation test for both the CS-100 and RF resin tests, see Figure 3.10. For the static non-irradiation test, no coating layer or visible corrosion was observed. Due to the insignificant mass loss of the test coupons (Table 3.2), it is believed that the observed coating is a precipitated layer onto the steel coupon rather than a corrosion product, due to its appearance and ability to peel away from the coupon exposing an untarnished surface of the test coupon. Initial analysis of the coating layer from the static-irradiated corrosion coupons by infrared techniques indicates that the coating is not composed of an organic hydrocarbon material.

For both experiments using CS-100 and RF resin, flow-irradiated and the flow non-irradiated tests, there was very little observable difference in appearance of the coupons before and after testing, see Figure 3.11. The flow-irradiated corrosion coupons show slight discoloration, while the flow non-irradiated coupons appear new. The small to negligible mass loss observed in the corrosion studies indicate that corrosion of the 304L stainless steel is not a problem in the flow tests under control or irradiated conditions.

In the static-irradiated test (for both the CS-100 and RF resins) there was a coating layer precipitated onto the corrosion coupon, but in the flow-irradiated system, there was no evidence for the formation of the coating layer. The coating material on the static-irradiated tests must originate from the radiolysis of the NCAW waste simulant since there is no evidence of this coating behavior in the static non-irradiated tests. The reaction rate of the irradiation produced coating material must be slow in order to allow the column feed rate of approximately 0.5 column volumes/h in the flow system to be able to sweep out the coating material before it had time to react with, and produce a coating on the coupons.

Table 3.2. Coupon Corrosion Tests Summary for CS-100 and RF Resin. Test coupons were inserted within resin with test vessels during irradiation and control tests.

CS-100 Resin Test Coupons

<u>Test conditions</u>	<u>Corrosion rate (mils per year)</u>	<u>Mass loss (% weight)</u>
irradiated - flow	0.0045 ± 0.002	0.0048 ± 0.002
irradiated - static	-0.0055 ± 0.01	-0.0069 ± 0.01
non-irradiated -flow	-0.00067 ± 0.001	-0.00068 ± 0.001
non-irradiated - static	-0.00067 ± 0.001	-0.00068 ± 0.001

RF Resin Test Coupons

<u>Test conditions</u>	<u>Corrosion rate mils per year)</u>	<u>Mass loss (% weight)</u>
irradiated - flow	0.0042 ± 0.001	0.0093 ± 0.003
irradiated - static	0.0020 ± 0.001	0.0039 ± 0.002
non-irradiated - flow	0.0019 ± 0.00002	0.00039 ± 0.00005
non-irradiated - static	0.0020 ± 0.00006	0.0039 ± 0.00005
blank coupons		0.0027 ± 0.003

Figure 3.10. Stainless Steel Coupons After Static Resin Testing

Figure 3.11. Stainless Steel Coupons After Flowing Resin Tests

Solubility properties of the coating material may be an alternative explanation for the difference between the observed coating on the static-irradiated corrosion coupons and lack of coated material on the flow-irradiated coupons. The solubility of the coating material may be exceeded in the static test where the irradiation produced coating material is continually increasing within solution. In the flow-irradiated solution, the irradiation-produced coating material is continually diluted by fresh NCAW feed (0.5 column volumes/h) and does not build up to a concentration high enough to exceed the solubility limit.

Consistent with the observations for the corrosion coupons, a similar coating product has been observed to form on the stainless steel mesh grid with spacer pins (Figure 3.12) and interior surface of the test vessel in the static-irradiated test (Figure 3.13), but not for the identical parts in the static non-irradiated tests. No coating material was observed on the stainless steel mesh grid with spacer pins, or stainless steel O-ring, vessel surface on the flow-irradiated or flow non-irradiated tests in agreement with the corrosion coupon results above (Figures 3.14 and 3.15).

3.5 Infrared Analysis of BSC-187 RF Resin

Samples of RF resin BSC-187 were analyzed by infrared spectroscopy to investigate the extent and mechanism of oxidation. Samples of the RF resin were analyzed by surface reflectance infrared analysis and by traditional transmittance infrared analysis to determine the relative effect of oxidation at the surface versus the bulk oxidation of the resin.

A photograph of a BSC-187 sample is shown in Figure 3.16. This photograph was taken through the optics of the infrared microscope at 10X magnification. As can be seen in this figure, thin portions of the resin are translucent, allowing for transmittance infrared analysis of that portion of the sample. Figure 3.17 contains the absorbance infrared spectrum (taken in transmittance mode) of the RF resin. The basic features of this spectrum reveal strong absorbance due to the O-H stretching region at 3700-3000 cm^{-1} region. Also apparent is the strong infrared absorbance bands due to the aromatic ring modes of the RF resin material located at 1595 cm^{-1} and about 1400 cm^{-1} . There is a weak shoulder on the high energy side of the 1595 cm^{-1} band which is in the approximate location for carbonyl bands, an expected air oxidation product of the RF resin material. This band is largely occluded by the predominant aromatic ring bands.

A reflectance infrared spectrum was taken at the same location as the transmittance mode spectrum of the RF resin material. In reflectance mode, the incident infrared signal is reflected off the surface of the sample and directed to the detector. In this manner, the surface structure of a sample can be probed preferentially over the bulk property of the sample. The reflectance spectrum is shown in Figure 3.17. As in the transmittance mode measurement, a prominent absorbance is observed for the O-H band in the 3700 - 3000 cm^{-1} region. A band at 1732 cm^{-1} is also a prominent feature of this spectrum. This is assigned to a carbonyl functionality which is due to the air oxidation of the RF resin. The increase in intensity of this band in the reflectance mode measurement compared to the transmittance mode measurement indicated the oxidation of the resin is more prevalent at the surface of the resin. The bands associated with the aromatic ring modes are also observed in the reflectance measurement, but at a lower relative intensity than the carbonyl band.

3.6 Resin Characterization with NMR

This section summarizes results of spectroscopic characterization of cesium ion exchange resins exposed to ^{60}Co radiolysis. RF and CS-100 resins were exposed to gamma radiation under conditions described in previous sections. Control samples were not exposed to γ -radiation, and test samples were exposed to γ -radiation. Details of supernatant exposure, radiation dose, and duration of exposure are given in the experimental section (2.0). All samples for NMR testing were obtained following the maximum dose for each test.

Figure 3.12. Stainless Steel Screen and Holder After Static Resin Tests

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Figure 3.13. Column After Static Tests

Figure 3.14. Stainless Steel Screen and Holder After Flowing Resin Tests

Figure 3.15. Column After Flowing Tests

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Figure 3.16. Micrograph of BSC-187 RF Resin

Figure 3.17

Figure 3.17. Infrared Spectra of BSC-187 RF Resin

Figure 3.18 shows ^{13}C CPMAS NMR spectra of RF resin in a static (non-flowing) experiment with (a) no γ -radiation (55086-72A), and (b) static (non-flowing) with γ -radiation (55086-72B). The growth of degradation products is clearly evident in (b) (note significant quantities of ketone [185-210 ppm], quinone and/or carboxylate [165-185 ppm], and oxidized methylene bridge groups at 60-90 ppm). Figure 3.19 (c) shows RF resin exposed to flow and γ -radiation (55086-72C), it shows methylene ring bridges (10-50 ppm) at anomalously high intensity compared to phenolic (145-155 ppm) and protonated aromatic (95-140 ppm) resonances. Broad resonances attributed to ketones, quinones, and oxidized bridge groups are apparent. All of these are superimposed on a broad baseline. The anomalous aliphatic intensity is attributed to the presence of high concentrations of stable aromatic free radicals, which selectively broaden aromatic carbons. The second spectrum in Figure 3.19, spectrum (d), is of RF resin subjected to flow but no γ -radiation (55086-72D). It is clearly highly oxidized, and it is apparent that the resin suffered exposure to air during the test, even in the absence of radiation.

Figure 3.20 shows CS-100 in a static test with no γ -radiation (55086-72E), and a static test with γ -radiation (55086-72F). Very little difference is apparent between the two samples, consistent with the much higher resistance of this resin to adventitious oxidation. Small, similar amounts of ketone (185-205 ppm) and quinone/carboxylate (165-185 ppm) functionality are apparent. Figure 3.21 shows the results of flowing and γ -radiation (55086-72G) and flowing with no γ -radiation (55086-72H). The main feature of these two CS-100 resins is the somewhat lower amount of quinone/carboxylate functionality. This could be attributed to elution of some of the soluble carboxylate function from the column. It should be noted that CS-100 is prepared with some p-toluic acid present. Removal of some of this primarily non-bonded material would result in the apparent decrease. In general, the CS-100 samples show only very modest effects of radiation and exposure to flow and supernatant simulant.

55086-72A. RF Resin, Non-flowing Experiment, no γ -Radiolysis

55086-72B. RF Resin, Non-flowing Experiment, γ -Radiolysis

Figure 3.18. ¹³C CPMAS NMR Spectra of BSC-187 RF Resin Samples

55086-72C. RF Resin, Flowing Experiment, γ -Radiolysis

55086-72D. RF Resin, Flowing Experiment, no γ -Radiolysis

Figure 3.19. ^{13}C CPMAS NMR Spectra of BSC-187 RF Resin Samples

55086-72E. CS-100 Resin, Non-Flowing Experiment, no γ -Radiolysis

55086-72F. CS-100 Resin, Non-Flowing Experiment, γ -Radiolysis

Figure 3.20. ^{13}C CPMAS NMR Spectra of CS-100 Resin Samples

55086-72G. CS-100 Resin, Flowing Experiment, γ -Radiolysis

55086-72H. CS-100 Resin, Flowing Experiment, no γ -Radiolysis

Figure 3.21. ^{13}C CPMAS NMR Spectra of CS-100 Resin Samples

4.0 Conclusions and Recommendations

The purpose of this testing was to determine the stability of the organic resins (RF and CS-100) when they are subjected to ionizing radiation. The cesium loading of these resins, as expected, decreased after prolonged exposure to radiation, with the RF resins degrading to a greater extent (as a percentage of the nonirradiated material). During the flowing tests, the degradation was not noticeable until after 10^8 R total dose, so the usable lifetime of the resins appears to be quite good. The RF resin degrades to a greater extent than the CS-100, however, the RF resin which has been exposed to 10^9 R still has a higher K_d for cesium than does nonirradiated CS-100.

This loss of cesium loading appears to be due more to the presence of oxygen in the system than the irradiation of the resin. The RF resin K_d decreased more rapidly as a function of time/dose than the CS-100, and the oxidation was more rapid for the RF resin than the CS-100. During the radiation of water in the absence of a reducing agent, proportional quantities (2:1 by molar concentration) of hydrogen and oxygen are produced. In the simulant wastes that were used in these studies, nitrous oxide and nitrogen gas were also produced due to the presence of nitrites and nitrates. From the gas analysis, it is seen that not all of the oxygen produced in the radiolysis of the solution is being released to the atmosphere. This oxygen, or oxygen precursors such as the hydroxyl radical, is reacting with the reducing agent present, namely the organic resins. This reaction can be followed by the NMR, which shows the formation of oxidation products such as quinones and carboxylates. The presence of these oxidation products, as shown by the NMR, is greater in the RF resin than in the CS-100. This is the same trend as is observed by the capacities for cesium removal, with the RF resins having a much lower percentage of capacity following irradiation. The FTIR data corroborates the NMR data by showing the reduction in aromaticity of the resin and an increase in the oxidation products. The FTIR data also shows that the degradation is more of a surface phenomena, which would indicate that oxidation is more of a concern than the radiolytic degradation of the resin.

An obvious mitigation for the degradation of the resins, especially the RF resin, would be to rigorously exclude oxygen from the process. Since oxygen is a byproduct of the radiolysis of water, this may prove to be difficult. Another possibility would be to modify the RF resin to make it less susceptible to oxidation. The addition of some functional groups at the most likely sites for oxidation, or increased crosslinking of the resin would decrease the oxidative degradation of the RF resin.

Since it was only observed in the BSC-187 case, the clumping phenomenon could be an artifact of the manufacturing process or due to the conditions of storage. The difference between the processes for making the BSC-187 and BSC-210 should be noted and the newer process used for all batches to be used for removal of cesium onsite. In addition, the optimum length and conditions for storage of the RF resin should be determined. NMR spectrometry or FTIR spectroscopy could be used as a method for acceptance of the RF resins. These techniques would allow for the identification of the artifacts of manufacturing that cause the agglomeration present in the batch and would indicate if the resin has oxidatively degraded.

In addition to the loss of cesium uptake due to the irradiation, another potential problem is the buildup of the inorganic layer on the stainless steel surfaces in the static tests. This buildup appears to be caused by the degradation of the salts in the simulated NCAW solution. If this is a common occurrence during the processing of the Hanford Site tank wastes, it has the potential to cause serious problems for the process equipment leading to plugging, failure of valves, and increase in contamination of the process equipment. The mechanism of this buildup should be examined and possible mitigating action should be considered.

Based on the operation of the process as indicated in the cesium removal flowsheets for CS-100 (Eager 1994) and RF resin (Penwell 1994) it is projected that radiation damage is not likely to be a major factor in the lifetime of the resins (Table 4.1). The data in Table 4.1 shows that the time

Table 4.1. Comparison of Irradiation Times to Processing Times

<u>Resin</u>	<u>Time to reach 10⁸ R (days)</u>	<u>Time to reach 10⁹ R (days)</u>	<u>Time for 5 cycles (days)</u>	<u>Waste</u>
CS-100	126	1260	2.1	NCAW
RF	15	150	14.5	NCAW
CS-100	17,00	17,000	1	DSSF-7
RF	160	1600	11	DSSF-7

required to reach a total dose greater than 10⁸ R generally exceeds the time required to complete 5 load/elute cycles. This suggests that the resins may be useable for more than 5 load/elute cycles.

The data presented in Table 4.1 are based largely on the information in the flowsheets for CS-100 and RF. The surface dose rates for a column loaded with NCAW are 3.3⁴ R/h and 2.7⁵ R/h for CS-100 and RF, respectively. These dose rates are for a fully loaded resin bed with a volume of 2000 L with a 108-cm diameter and a 213-cm length. The internal dose rate is expected to be somewhat higher but probably by less than a factor of 2 and is assumed to be the same for this analysis. Based on the relative concentrations of ¹³⁷Cs and the estimated K_ds the dose rates from loading double shell slurry feed (DSSF) are expected to be lower by a factor of 13.4 (CS-100) and 10.6 (RF). The processing times for 5 resin cycles is based on the processing rates given in the flowsheets, the assumed ¹³⁷Cs concentrations, and a total operating efficiency of 100% (60% was assumed in the flowsheets).

5.0 References

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