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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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Summary

At the request of the Initial Pretreatment Module Project within Westinghouse Hanford Company, Pacific Northwest Laboratory (PNL) conducted this study for the Efficient Separations and Processing Crosscutting Program (ESP) under the task "Develop and Test Sorbents." The purpose of the study was to assess and compare the chemical and radiolytic stability of several cesium-selective ion exchange materials in simulated alkaline Hanford tank waste matrices.

Pretreatment of nuclear process wastes to remove of cesium and other radionuclides by ion exchange was proposed previously as one method of minimizing the amount of high-level radioactive waste at Hanford. In this study, PNL evaluated three cesium-selective materials (SuperLig®644, resorcinol-formaldehyde (R-F), and CS-100) for chemical and radiation stability in 1 M NaOH and a simulated neutralized current acid waste (NCAW). The objective of the study is to investigate the stability of the newly produced SuperLig®644 under a variety of conditions in an attempt to simulate and predict the degradation process. The following specific conclusions and recommendations resulted from the study:

- Following irradiation, all materials tested demonstrated a decrease in cesium selectivity and capacity. The cesium λ value in NCAW decreased by a factor of two to six after exposure to 1.0E+09 rad. The relative stability roughly follows the order CS-100 > R-F > SuperLig®644. All materials were stable up to 1.0E+08 rad.

- Oxygen uptake measurements in 100% O_2 indicate the relative instability of SuperLig®644 as compared to R-F. In 1 M NaOH and NCAW, initial uptake was 17.4 and 7.38 mL O_2 g^{-1} h^{-1} for SuperLig®644. In contrast, the uptake by R-F in the same solutions was 7.50 and 4.22 mL O_2 g^{-1} h^{-1}, respectively. The results portray an extreme situation and should not be considered representative of typical ion exchange process conditions.

- The cesium λ values for SuperLig®644 decreased from 400 to 5 and 30 after 16-h exposure to O_2 in 1 M NaOH and NCAW, respectively.

- During the irradiation of SuperLig®644, R-F, and CS-100 in a simulated NCAW matrix, the following gases (listed by decreasing abundance) were generated: hydrogen, nitrous oxide, nitrogen, and oxygen. The relative amount of these gases produced is consistent with the organic resin material acting as a source of reductant within the system. The irradiated SuperLig®644 evolved more H_2, N_2O, and N_2 and less O_2 than either the R-F or CS-100 resins, indicating the relative instability of the former as compared to the latter.

- Radiolytic O_2 production was deemed insignificant in terms of overall resin oxidation resulting in an estimated 14% decrease in cesium loading after 1.0E+09 rad cumulative dose.

- Analysis of the SuperLig®644 by NMR spectroscopy before and after exposure to oxygen indicated extensive modification of the overall chemical structure during degradation. The data demonstrate the utility of using spectroscopic methods for monitoring changes in the chemical structure of organic resins during oxidation and/or radiolysis.

The data are self-consistent and indicate the relative stability of three organic polymers (CS-100 > R-F > SuperLig®644) under a variety of chemical and radiolytic conditions. It should be noted that the most stable material (CS-100) exhibits the worst performance in terms of cesium loading. Even after 1.0E+09 rad cumulative dose, the R-F and SuperLig®644 materials exhibited greater cesium selectivity and loading than the unirradiated CS-100. Based on the data presented in this report, the chemical and radiation stability of SuperLig®644, R-F, and CS-100 are adequate for processing Hanford tank waste by cesium ion exchange.

Acknowledgments

Pacific Northwest Laboratory is collaborating with universities, national laboratories, and industry to develop and test new materials for the pretreatment of nuclear wastes stored at Hanford. The experimental work described in this report would not have been possible without the encouragement and resources provided by Dr. Teresa B. Fryberger, program manager of the Efficient Separations and Processing Crosscutting Program.

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1.0 Introduction

1.1 Background

The contents of Hanford's 177 underground storage tanks include a mixture of sludge, salt cake, and alkaline supernatant liquid. The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains the bulk of the ^{90}Sr and many of the transuranic radionuclides (TRU). The salt cake, generated by extensive evaporation of aqueous solution, consists primarily of dried sodium salts. The supernate consists of concentrated aqueous solutions of sodium nitrate/nitrite salts with smaller quantities of hydroxide, aluminum, potassium, carbonate, sulfate, and phosphate. The bulk of the water-soluble radionuclides such as ^{137}Cs are contained in the interstitial liquid in the salt cake and supernatant solution fractions.

Although the pretreatment and disposal requirements are still being defined, one of the first steps in most pretreatment scenarios will be a solids/liquid separation of the pumpable waste liquor, followed by ion exchange removal of cesium from the resulting supernatant liquid. Next a salt cake dissolution and sludge wash step will be initiated followed by another solids/liquid separation. Most of the cesium is expected to be in the aqueous liquids from these processes, and it is these solutions that are the focus of the cesium ion exchange removal process. The specific cesium decontamination requirements will depend on the waste being pretreated and future decisions to be made by the U.S. Department of Energy (DOE) with resect to the amount of cesium that will be acceptable in the low-activity waste disposal form. The separated cesium will be concentrated and vitrified with the high-level waste sludge for disposal in the high-level waste repository.

The technology for cesium decontamination of high-level alkaline wastes and sludge wash waters is being developed by Westinghouse Hanford Company (WHC), Richland, Washington (Bray 1989; Bray et al. 1990; Bray et al. 1992; Bray et al. 1993a,b; Brown et al. 1995; Kurath et al. 1994); the Westinghouse Savannah River Company (WSRC), Aiken, South Carolina (Bibler 1991; Bibler et al. 1989; Bray et al. 1990); and the West Valley Nuclear Services Company, Inc. (WVNS), West Valley, New York (Bray et al. 1984; Kurath et al. 1989; Bray and Hara 1991). In addition, several ion exchange materials have demonstrated the ability to remove cesium from various simulated solutions (Marsh et al. 1994a,b,c; Marsh et al. 1995). Using this technology as a starting point, experimental studies are being conducted by Pacific Northwest Laboratory (PNL)(a) under DOE's Efficient Separations and Processing Crosscutting Program (ESP) to evaluate the performance of new technologies for the removal of cesium, strontium, technetium and TRUs from simulated and actual alkaline wastes at Hanford. Ultimately, each process must be evaluated in terms of removal efficiency, process chemical consumption and recycle, chemical and radiation stability of materials, compatibility with other process streams, secondary waste generation, process and maintenance costs, and final material disposal.

(a) PNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract Number DE-AC06-76RLO 1830.

1.2 Objectives

The overall objective of the Develop and Test Sorbents task of the ESP is to 1) develop and evaluate newly conceived novel materials for the recovery of cesium, strontium, and technetium from alkaline wastes; 2) determine the loading and elution efficiency of these processes; 3) determine the physical life cycle (including radiation and chemical stability) of these materials; and 4) determine if basic ion exchange data can be applied to a broad range of tank wastes. The goal is to provide the technology to produce a LLW effluent with radioactivity suitable for treatment in the LLW glass vitrification facility. The objective of this report is to describe the chemical oxidative and radiolytic stability of the newly synthesized SuperLig®644 sequestering agent in simulated Hanford alkaline waste supernate and compare these results to those obtained for other currently available organic ion exchange materials under similar conditions.

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

- determine the loss of cesium uptake for SuperLig®644 as measured by the batch distribution coefficient as a function of irradiation dose and oxygen uptake
- determine the O_2, N_2, H_2, and N_2O gas generation rate (G values) for SuperLig®644, R-F, and CS-100 as a function of irradiation dose
- determine the oxygen uptake of the SuperLig®644 and R-F resins in a pure oxygen atmosphere
- characterize structural changes to the SuperLig®644 by ^{13}C cross-polarization magic angle spin (CPMAS) nuclear magnetic resonance (NMR) as a function of oxygen exposure.

1.3 Scope

The work described in this report involves the direct comparison of three cesium-selective materials (SuperLig®644, R-F resin, and CS-100) based on the results obtained from oxidative and radiolytic stability experiments. The materials were irradiated to a total dose of 1.0E+09 rad at 1.6E+06 rad h^{-1} in a simulated neutralized current acid waste (NCAW) supernatant liquid, and the evolved gaseous products were identified and quantified. Additional samples were exposed to an oxygen atmosphere for 16 h and analyzed by ^{13}C CPMAS NMR spectrometry to identify structural changes in the materials that could be correlated to radiolytic and oxidative damage. In addition, all samples were analyzed for ion exchange selectivity by cesium batch distribution (K_d) experiments. These four factors (gas generation, NMR analysis, oxygen uptake, and cesium batch K_d) were used to determine the relative stability of the materials tested.

2.0 Experimental Approach

Previous experimental work completed during Fiscal Year (FY) 1994 and FY 1995 for cesium recovery included the bench-scale column loading and elution of the SuperLig®644, R-F, and CS-100 materials in an NCAW simulant (Brown et al. 1995), cesium batch distribution measurements in various simulated alkaline wastes, and limited chemical and radiation stability tests. Because of the cost and limited availability of actual radioactive waste, simulated solutions have been used for the current stability testing. In this report, three materials (SuperLig®644, R-F, and CS-100) were exposed to either oxygen or ^{60}Co gamma radiation in simulated alkaline waste solutions to evaluate their relative oxidative and radiolytic stability. Radiolytic stability was deduced by analysis of the gases generated and cesium batch K_d analysis of each material. Stability toward oxidation was inferred by O_2 uptake measurements, NMR, and K_d analysis of the exposed materials. These activities are in support of the development of cesium ion exchange processes for the pretreatment of Hanford tank waste.

2.1 Ion Exchange Material Selection

The removal of radioactive cesium by column ion exchange is considered to be the baseline pretreatment process for cleaning up most of the waste currently stored at Hanford. In addition to SuperLig®644, several materials can remove cesium from highly alkaline solutions, including organic ion exchange resins (CS-100 and R-F), inorganic zeolites, (IE-95, IE-96, TIE-96) and other materials (crystalline silicotitanates [CSTs]). The SuperLig®644 polymer resin is the latest version of the covalently bound SuperLig® macrocycle family of sequestering ligands from IBC Advanced Technologies (American Fork, Utah) and has been shown to be highly selective for cesium even in the presence of excess sodium or potassium (Brown et al. 1995). CS-100 and resorcinol-formaldehyde (R-F) are two organic ion exchange resins that are currently available and under consideration (Eager et al. 1994; Penwell et al. 1994) for cesium removal from Hanford tank wastes. CS-100 is a granular (20 to 50 mesh) phenol-formaldehyde condensate polymer ion exchange resin that is commercially available from Rohm & Haas (Philadelphia, Pennsylvania) and is considered to be the baseline cesium ion exchange material.[a] R-F, produced by Boulder Scientific (Mead, Colorado), has been shown to exhibit a much greater loading for cesium and selectivity over sodium or potassium than the CS-100 resin (Kurath et al. 1994). The ratio of as-received-to-dry (105°C for 24 h) resin was 0.97, 0.78, and 0.77 for SuperLig®644, R-F, and CS-100, respectively. In the current study, these two organic ion exchange materials were directly compared to the newly developed SuperLig®644 material in side-by-side oxidation and radiation stability experiments. Inorganic ion exchanges were not included in this study because of the relative stability of these materials toward irradiation.

(a) Gallagher, S. A. 1986. *Report of Current NCAW Ion Exchange Laboratory Data*. Internal Letter #65453-86-088, Rockwell International, Richland, Washington.

2.2 Simulant Solution Selection

The NCAW simulant described in Table 2.1 was chosen for the current stability experiments because previous irradiation tests (Bryan et al. 1993; Carlson et al. 1994), Cs batch K_d, and column loading tests were completed using this composition (Bray et al. 1993a; Kurath et al. 1994; Brown et al. 1995). Cesium was absent during material irradiation and oxidation, but was present at levels ranging from 1.0E-0.5 M to 1.0E-02 M during the batch K_d determinations. In addition, the stability of certain materials toward oxidation in 1 M NaOH was tested. With the data collected during this experiment, a direct comparison of the new SuperLig®644 sequestering agent can be made to other commercial organic ion exchange materials (CS-100 and R-F).

2.3 Oxygen Uptake Measurements

The oxidation of SuperLig®644 and R-F was completed under static conditions and involved exposing each resin material in either NCAW or 1 M NaOH to one atmosphere of pure oxygen at room temperature within a sealed reaction vessel. The sealed system allowed convenient measurement of the resin oxygen uptake by direct correlation of the volume change required to keep a constant pressure in

Table 2.1. NCAW Simulant Composition

Species	Molarity, M
Na	5.00
K	0.12
Rb	5.00E-05
Al	0.43
SO_4	0.15
OH (total)	3.40
OH (free)	1.68
CO_3	0.23
NO_2	0.43
NO_3	1.67
F	0.089
PO_4	0.025

the reaction vessel. An important assumption during the test was that the resin was only partially oxidized (e.g., formation of ketone, aldehyde, carboxylic acid functional groups, etc.) and did not generate any gaseous species that might have increased the reaction vessel pressure. Carbon dioxide is extremely soluble in caustic solutions as carbonate and would not contribute significantly to changes in the overall reaction vessel pressure. In addition to these oxygen uptake measurements, the resin degradation as a function of time was evaluated by NMR spectroscopic analysis (Section 2.6) and by cesium batch distribution (K_d) measurements (Section 2.5).

During the oxidation process, between 0.8 and 1.3 g of each "as-received" resin was separately suspended in 100 mL of either 1 M NaOH or the aqueous NCAW simulant solution. Before starting the oxidation experiments, the apparatus was evacuated and purged a minimum of three times with pure oxygen. The sample flask was attached to the vacuum line and purged with pure oxygen for 15 minutes. The system pressure was increased to atmospheric pressure with O_2. The quantity of oxygen consumed as a function of time was determined by continuously adjusting the elevation of the manometer to ensure a constant reaction chamber pressure and calculating the volume change. After oxidation, the solid samples were separated from the liquid by vacuum filtration and saved for additional NMR and cesium K_d analysis.

2.4 Sample Irradiation

To evaluate the radiation stability of SuperLig®644, R-F and CS-100, the materials were exposed to high-dose ^{60}Co gamma radiation within a sealed stainless steel reaction vessel. The sealed system allowed convenient measurement of gaseous decomposition products generated from solution and resin radiolysis. Gases released during the experiment were measured and identified by mass spectrometry. In addition, the distribution coefficient (batch K_d) for ^{137}Cs uptake (Section 2.5) was determined and used as an additional indicator of radiation damage to the resin material. The materials were exposed to a total radiation dose of approximately 1.0E+09 rad at 1.6E+06 rad h^{-1} over the course of several weeks.

The Gamma Irradiation Facility is operated by PNL and contains 37 stainless steel irradiation tubes positioned in a stainless steel tank 7 ft in diameter by 13 ft, 8 in. deep. 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 3-1/2-ft high concrete wall surrounds the top of the tank. The irradiation tubes, which are sealed on the bottom, vary in length and diameter from 16 ft to 18 ft and 1.8 to 6 in., respectively. The irradiation flux of the tubes range from 2.0E+06 rad h^{-1} to 2.0E+02 rad h^{-1}. The uniform flux region varies from ~6 in. for the tubes closest to the sources to greater than 12 in. for the tubes farthest from the sources. All flux measurements of the tubes are traceable to the National Institute for Standards and Technology.

All materials and test systems were lowered into the irradiation tubes manually and were left in the tubes for the specific amount of time (6.25E-01, 6.25E+00, 6.25E+01, 6.25E+02 h) to achieve the required exposure (1.0E+06, 1.0E+07, 1.0E+08, 1.0E+09 rad). No activation is associated with the gamma irradiation, so the materials were transported to other facilities for cesium batch K_d evaluation (Section 2.5) after removal from the tubes. The temperature of the test was approximately 15°C to 20°C based on the recorded ambient temperatures in the gamma facility.

Approximately 25.6 g of NCAW simulant and 4.40 g of "as received" materials (i.e., R-F, CS-100, and SuperLig®644) were accurately weighed on an analytical balance (±0.0001 g) and placed into separate 30-mL stainless steel irradiation chambers (1.6 cm i.d. x 15 cm). The limiting factor was the least dense material (SuperLig®644) because it is important that the total mass of material be constant for each irradiation. The total volume of the solution and resin could not exceed 25 mL to allow for resin expansion and expulsion of the generated gases during irradiation and gas sampling. The sample vessels were sealed with gas-tight fittings (copper metal knife edge vacuum flanges), pressure tested to 40 psi, and repeatedly evacuated and purged with high-purity argon to remove all residual gases. The vessels were removed from the radiation field and each gas sample was collected by purging the headspace above the resins into previously evacuated gas sampling devices. After the gas samples had been collected, a small quantity (ca. 0.1 g) of material from each sample vessel was removed and stored in a refrigerated environment for later cesium batch K_d analysis (Section 2.5). The sample vessels were resealed and purged repeatedly as previously described before additional radiation exposure. Gas samples were analyzed for CO_2, CO, He, H_2, N_2, O_2, N_2O, NO_x, NH_3, CH_4, C_2H_6, and other hydrocarbons by mass spectrometry at each irradiation dose. From these data the cumulative gas generation rates (moles of gas per resin mass) were calculated.

2.5 Cesium Batch Distribution

The batch distribution coefficient (K_d) is an equilibrium measure of the overall ability of the solid phase ion exchange material to remove an ion from solution under the particular experimental conditions that exist during the contact. The batch K_d is not necessarily the affinity of a material for a particular ion, but can be used to indicate the selectivity, capacity, and affinity of a particular ion for an ion exchange material in the presence of a complex matrix of interfering ions. The addition of a small quantity of ion exchange material into a small volume of supernatant solution is an extremely rapid and cost-effective method to compare a wide variety of ion exchange materials. However, this method does not provide information about ion exchange kinetics and is only useful for measuring the equilibrium behavior under the particular test conditions. Accurate comparison of K_d results requires identical experimental conditions (mass:volume ratio, equilibrium solution composition, material pretreatment,. temperature, duration, etc.) because all of these factors are known to affect K_d.

$$K_d = \frac{(C_0 - C_1)}{C_1} * \frac{V}{M * F} \tag{1}$$

In most batch K_d tests, a known quantity of ion exchange material is placed in contact with a known volume of solution (e.g., complexant concentrate [CC], NCAW, or double-shell slurry feed [DSSF]) containing the particular ions of interest. The material is allowed to contact the solution at a constant temperature for sufficient time to reach equilibrium, after which the solid ion exchange material and liquid supernate are separated. The concentration of the species of interest is determined in the solution and in the solid phase. In this report, the batch K_ds were achieved by contacting 0.1 g of each solid material with 15 mL of supernate liquid. In practice it is easier to measure the concentration of the particular ion of interest in the solution instead of in the solid. Therefore, the equation for the determination of the batch distribution can be simplified by determining the concentration of the analyte before and after contact and calculating the quantity of analyte on the ion exchanger by difference (Equation 1). C_0 is the initial concentration of the ion of interest in the feed solution before contact, C_1 is the concentration after contact, V is the solution volume, M is the exchanger mass, and F is the mass of dry ion exchanger divided by the mass of wet ion exchanger (F-Factor). K_d represents the theoretical volume of solution (mL) that can be processed per mass of exchanger (dry weight basis) under equilibrium conditions. Lambda, the theoretical number of bed volumes of solution that can be processed per volume of exchanger, is obtained by multiplying K_d by the exchanger bed density, ρ_b (g of resin per mL of resin) as shown in Equation 2

$$\lambda = K_d * \rho_b \tag{2}$$

The lambda value provides a method of comparing the ion exchange performance of a wide variety of materials on a volume basis. Brown et al. (1995) reported that this method is biased against low bed density materials (e.g., SuperLig®644 ρ_b = 0.22 g/mL; R-F ρ_b = 0.45 g/mL). However, from an engineering perspective, the volume basis will more accurately reflect column sizes required. Cycle time or cost per cycle would also be important for process engineering.

The experimental equipment required to complete the batch K_d determinations included an analytical balance, a constant temperature water bath, an oven for F-Factor determinations, a variable speed shaker table, 20-mL scintillation vials, 0.2-μm syringe filters, the appropriate ion exchanger, and simulant solutions. Before initiating the batch contact, each material was converted to the sodium form by pretreatment with two separate 15-mL aliquots of 2 M NaOH for 15 minutes, two aliquots of distilled water, two aliquots of 1 M formic acid, two aliquots of distilled water, two aliquots of 2 M NaOH, and two aliquots of distilled water with a vacuum filtration step between each solution contact. The materials were then air dried for 1 h by vacuum filtering in air. Unfortunately, because of the limited quantity of material available, an F-Factor and bed density could not be obtained for every sample and were estimated from the highest irradiation dose sample. Approximately 0.1 g of each material was contacted with 15 mL of the stock NCAW solution. In addition, the final irradiation samples (1.0E+09 rad) were contacted with several NCAW simulant solutions each containing various cesium concentrations (Na/Cs = 5.0E+02 to 5.0E+05). The sample bottles were placed into a 25°C constant temperature bath shaken lightly for 72 h. The samples were then filtered with a 0.2-μm pore filter to separate the resin material from the solution, and the resulting liquid was analyzed for cesium content by ^{137}Cs gamma counting.

3.0 Results and Discussion

A new class of sequestering agents (SuperLig®) has been developed by IBC Advanced Technologies that can selectively remove various radionuclides (cesium, strontium, etc.) from high ionic-strength alkaline solutions based on molecular recognition technology. Previous tests have demonstrated that one of these materials (SuperLig®644) can remove cesium from simulated Hanford tank waste even in the presence of excess sodium and potassium (Brown et al. 1995). To more accurately assess the potential use of this technology for the pretreatment of nuclear process wastes, the oxidative and radiolytic stability of SuperLig®644 was tested and compared to that of two current baseline materials (R-F and CS-100). The radiation stability of each resin was determined by exposing the materials to ^{60}Co gamma radiation and measuring the evolved gases. A small subsample of each resin was removed after each exposure period and analyzed for cesium selectivity by K_d analysis. Stability towards oxidation was determined by O_2 uptake measurements, structural analysis by NMR, and cesium selectivity by K_d analysis after each oxygen exposure.

3.1 Radiation Stability

3.1.1 Gas Generation

Gases generated during static irradiation of the cesium-selective SuperLig®644, R-F, and CS-100 resins are displayed in Figures 3.1 through 3.3, respectively. The materials were irradiated at 1.6E+06 rad h^{-1}, and the cumulative gas generation (moles of gas per mass of resin) was calculated at each irradiation dose. For all of the materials tested, hydrogen was the most abundant gas produced, followed by nitrogen, nitrous oxide, and oxygen. In addition, a small amount (less than 10% that of oxygen) of carbon monoxide was observed only at a cumulative exposure of 1.00E+09 rad. With the exception of oxygen, all of the gases evolved during the irradiation of SuperLig®644 exceeded those evolved from the R-F or CS-100 resins. The same trends are observed for the R-F resin with respect to CS-100. In general, it appears that gas generation decreases in the following order: SuperLig®644 > R-F > CS-100. In contrast, evolution of oxygen follows the reverse order: CS-100 > R-F > SuperLig®644.

To reduce experimental costs, the normal background measurements were not collected. However, NCAW has been shown previously to evolve H_2, N_2, O_2 and N_2O during radiolysis (Bryan et al. 1993; Carlson et al. 1994). Therefore the data contain contributions from the gas generation of the resin materials and the NCAW solution blank. In addition, previous data also showed insignificant gas generation in the absence of radiation (0.0E+00 rad).

The gas generation G values are displayed in Table 3.1 where G is the number of molecules of each gas produced per 100 eV of energy absorbed. Because gas generation is a function of solution composition, resin material composition, and resin/solution phase ratio, extrapolation of the G values described in this report to other systems may not be meaningful. However, the data are useful for

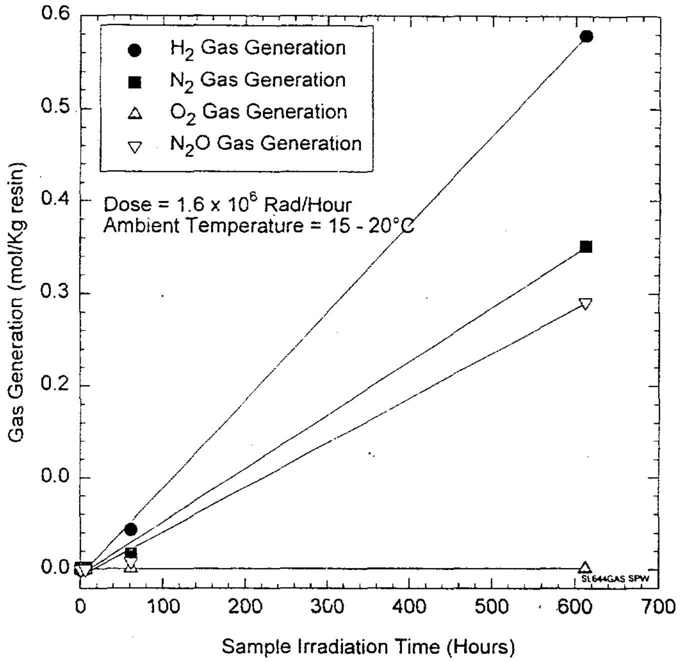

Figure 3.1. Gas Generation (mol/kg resin) During Irradiation of SuperLig®644 Ion Exchanger in Simulated NCAW Supernate at 1.6E+06 rad h^{-1}

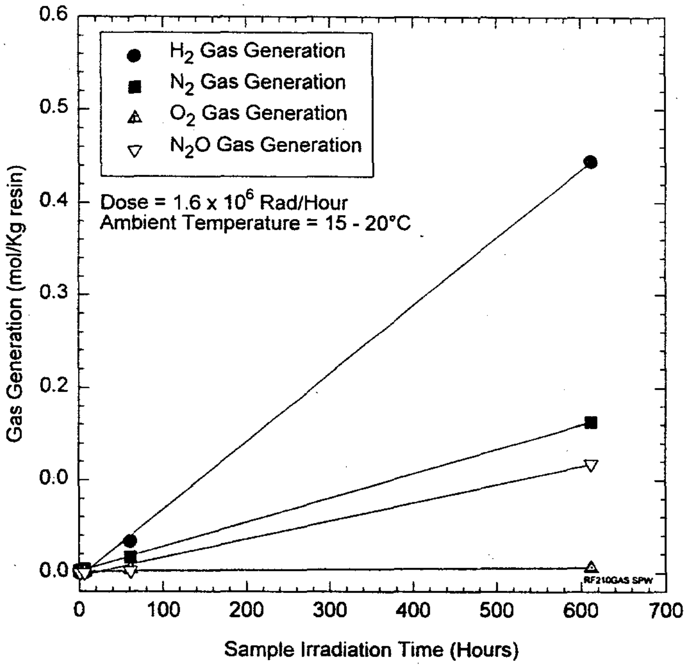

Figure 3.2. Gas Generation (mol/kg resin) During Irradiation of R-F Ion Exchanger in Simulated NCAW Supernate at 1.6E+06 rad h^{-1}

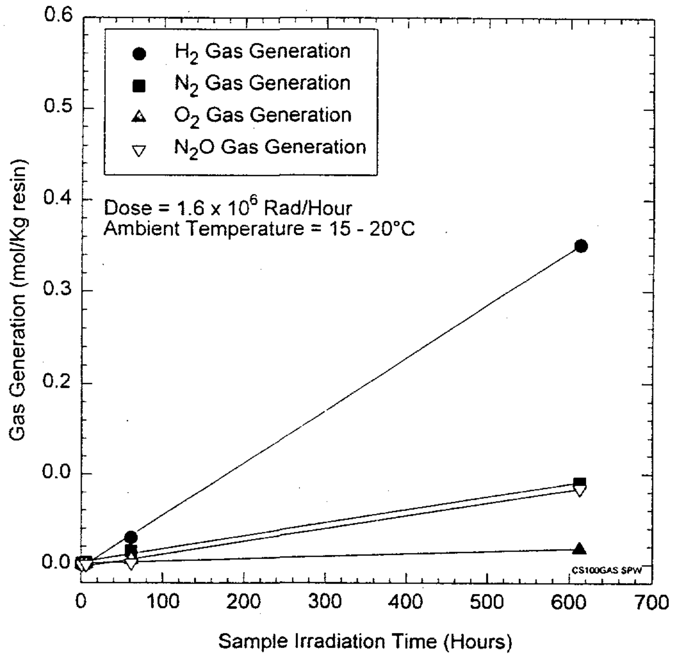

Figure 3.3. Gas Generation (mol/kg resin) During Irradiation of CS-100 Ion Exchanger in Simulated NCAW Supernate at 1.6E+06 rad h^{-1}

Table 3.1. G Values (molecules/100 eV) for Selected Organic Resins in NCAW

	Generation Efficiency				Dose Rate (rad/h)	Phase[(a)] Ratio
Sample Material	$G(H_2)$	$G(N_2)$	$G(O_2)$	$G(N_2O)$		
SuperLig®644	7.6E-02	3.9E-02	8.9E-04	2.8E-02	1.6E+06	5.82
R-F resin	5.9E-02	2.5E-02	3.3E-03	1.1E-02	1.6E+06	5.82
CS-100 resin	4.9E-02	1.8E-02	5.4E-03	7.8E-03	1.6E+06	5.82
NCAW blank	1.6E-02	1.5E-03	7.5E-02	4.4E-05	1.5E+05	∞

(a) Liquid/solid phase ratio is the mass of NCAW solution divided by the mass of the organic resin (dry weight basis).

comparing the relative stability or gas generation efficiency for each material. The trends observed in Figures 3.1 through 3.3 are readily apparent and quantified in Table 3.1. During radiolysis, the SuperLig®644 evolves 1.29 times the H_2, 1.56 times the N_2, 2.55 times the N_2O, but only 0.27 times the O_2 as compared to that given off by the R-F. When compared to CS-100, SuperLig®644 evolves 1.55 times the H_2, 2.17 times the N_2, 3.59 times the N_2O, and only 0.16 times the O_2. The apparent lack of oxygen evolution is not surprising and has been observed previously for the R-F resin (Bryan et al. 1993; Carlson et al. 1994). It can be explained in the following reaction sequence:

$$\gamma + H_2O \rightarrow H\cdot + OH\cdot \tag{3}$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2 \rightarrow 0.5\ O_2 + H_2O \tag{4}$$

$$H\cdot + H\cdot \rightarrow H_2 \tag{5}$$

$$OH\cdot + RH \rightarrow R\cdot + H_2O \tag{6}$$

$$H\cdot + RH \rightarrow R\cdot + H_2 \tag{7}$$

Hydrogen and oxygen are expected radiolytic products and result from the homolysis of the O-H bond of water initially forming H· and OH· radicals (Equation 3). The molecular decomposition products of pure water are H_2 and O_2 in a 2:1 stoichiometric ratio (Equations 4 and 5). In the aqueous system containing either SuperLig®644, R-F, or CS-100, the radiolytic hydrogen to oxygen ratio is much higher than that for pure water because of the presence of a source of hydrocarbon material that is effective at scavenging OH· to reform water (Equation 6). This prevents hydroxyl radical recombination to form H_2O_2 and eventually the molecular decomposition product O_2. The H· radical can react with a like radical (H·) (Equation 5) or directly with the hydrocarbon resin to form H_2 (Equation 7). A reduced concentration of oxygen in the headspace above the resin during radiolysis indicates the relative stability of a material towards oxidation by dissolved O_2, H_2O_2, OH·, or other intermediate. In this case, SuperLig®644 evolves less O_2 than either R-F or CS-100 and therefore must be more susceptible towards oxidation.

Nitrogen and nitrous oxide are both observed molecular decomposition products during the irradiation of SuperLig®644, R-F, and CS-100 in NCAW simulant solutions. These nitrogen-containing gases have been produced in similar systems containing nitrite and nitrate with organic carbon present (Bryan et al. 1992). Because the R-F and CS-100 resins do not contain organic nitrogen, the source of nitrogen in N_2 and N_2O must be from nitrate and nitrite in the NCAW 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. The chemical structure of SuperLig®644 is proprietary, and N_2 or N_2O may originate from the above mechanism or the resin itself if organic nitrogen functional groups are present.

3.1.2 Cesium Selectivity

In addition to analysis of the gases evolved during radiolysis, the cesium selectivity of each material was determined as a function of radiation dose. A plot of the cesium λ value (Section 2.5) against total resin exposure in rad is shown in Figure 3.4. Due to insufficient quantity of sample, the data were collected at the same initial Na/Cs ratio but at different equilibrium Na/Cs ratios. Therefore, there is a slight bias in favor of the higher lambda materials (e.g., R-F > SuperLig®644 > CS-100). Duplicate measurements are displayed on the graph; therefore, the variation in the data at different doses is thought to be significant. It is possible that the chemical structure of the resin is changing continuously during radiolysis and this affects cesium selectivity. Free radicals may be formed within the polymeric structure and create different structures or additional cross-linking that may increase or decrease cesium selectivity and capacity. In the current tests, all three materials demonstrated nearly constant cesium λ values from 1.0E+06 to 1.0E+08 rad. For SuperLig®644 the value decreased at 1.0E+07 rad and increased at 1.0E+08 rad. All three materials exhibited decreased performance at 1.0E+09 rad. In previous experimental studies, lower K_d or λ values have been observed for several materials at a total dose greater than 1.0E+07 rad (Bryan et al. 1993; Carlson et al. 1994).

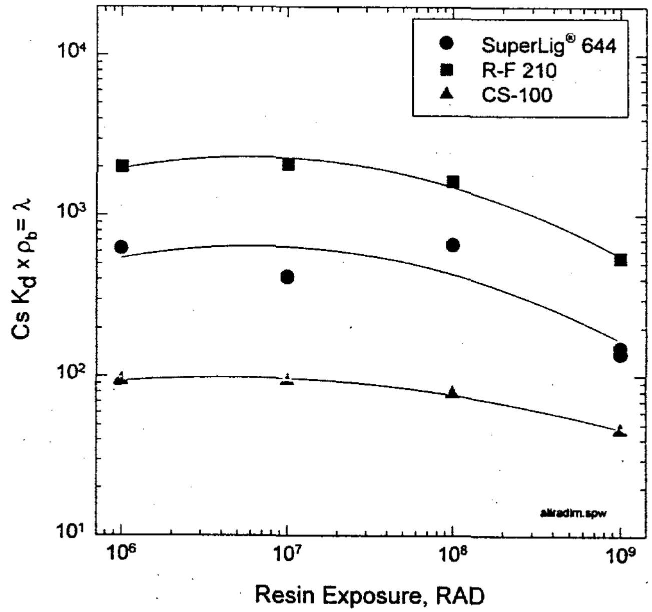

Figure 3.4. Cesium Column Distribution Ratio of SuperLig®644, R-F, and CS-100 in Simulated NCAW Supernate (equilibrium Na/Cs $\approx$ 1.0E+05) as a Function of Radiation Exposure

The extent of this degradation is shown clearly in Figure 3.4. For SuperLig®644, R-F, and CS-100, the performance decreases by approximately 68%, 74%, and 55%, respectively. However, it should be noted that even at 1.0E+09 rad, the SuperLig®644 and R-F materials exhibit higher cesium λ values than CS-100. These doses are based on irradiation with an external ^{60}Co source and may or may not accurately predict resin exposure during actual waste processing. It is estimated that several months of continuous operation would be required to reach the 1.0E+08 rad dose.

After irradiation to 1.0E+09 rad, the radiolysis experiment was terminated, and large amounts of resin materials were available for further testing. These materials were subjected to additional cesium batch K_d experiments at several different initial Na/Cs ratios (5.0E+02, 5.0E+03, 5.0E+04, 5.0E+05) to determine material cesium loading over a wide variety of cesium concentrations. The results are displayed in Figure 3.5 for SuperLig®644, R-F, and CS-100. At the Na/Cs ratio of the standard NCAW simulant (1.0E+04), the SuperLig®644 loading, as indicated by λ, decreased to approximately 41 λ while the R-F resin exhibited an estimated 120 λ. As discussed in Section 2.5, λ approximates the number of column volumes required to reach 0.5 C/C_0 during column loading. Previous column loading experiments in NCAW (Brown et al. 1995) and unpublished data indicated a loading of between 80 and 90 cv for unirradiated SuperLig®644. For R-F and CS-100, these values in NCAW have been estimated to be close to 190 and 35 cv (Kurath et al. 1994). From these data it appears that SuperLig®644 is the least stable material under radiation exposure, followed by R-F and CS-100. However, it should be noted that even after irradiation to 1.0E+09 rad, the cesium loading of the SuperLig®644 and R-F resins is still greater than that of unirradiated CS-100.

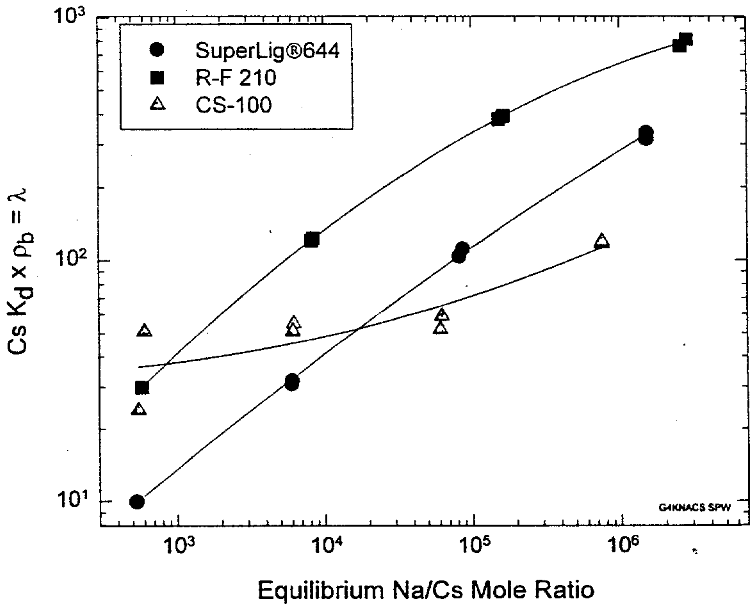

Figure 3.5. Cesium Column Distribution Ratio of SuperLig®644, R-F, and CS-100 in Simulated NCAW Supernate (equilibrium Na/Cs ≈ 5.0E+03 to 3.0E+06) After 1.0E+09 rad Total Exposure

3.2 Oxidation Stability

3.2.1 Oxygen Uptake

The uptake of oxygen by the SuperLig®644 and R-F resins in a simulated NCAW supernate and 1 M NaOH solution was investigated over the course of 16 h. The data, displayed in Figure 3.6, show the relative stability of the R-F over the SuperLig®644. In both solutions, (NCAW and NaOH) the magnitude of initial O_2 uptake for the SuperLig®644 is approximately twice that of R-F. For both materials the O_2 uptake is greater in 1 M NaOH than in NCAW. The reason for this difference is unknown, but may be related to relative oxygen solubility in the two solutions or the chemical composition of the NCAW (nitrate/nitrite equilibria). In addition, this could be caused by chemical interactions associated with additional species in the NCAW (e.g., NO_3^-, NO_2^-, $Al(OH)_4^-$, etc.).

It is interesting to note that the oxygen uptake is roughly linear for all solutions and materials tested except the SuperLig®644 in 1 M NaOH. Because the initial rate of O_2 uptake is much greater than others measured, it is possible that the oxygen supply available for resin degradation is limited by other factors (e.g., O_2 mass transfer). Because O_2 uptake by the resin is calculated by determining the volume change required to keep a constant pressure within a sealed system, it is possible that the O_2 concentration in solution might have decreased as it was consumed during the course of the experiment. If this were the case, the rate of uptake (slope of curve) would decrease as is shown in

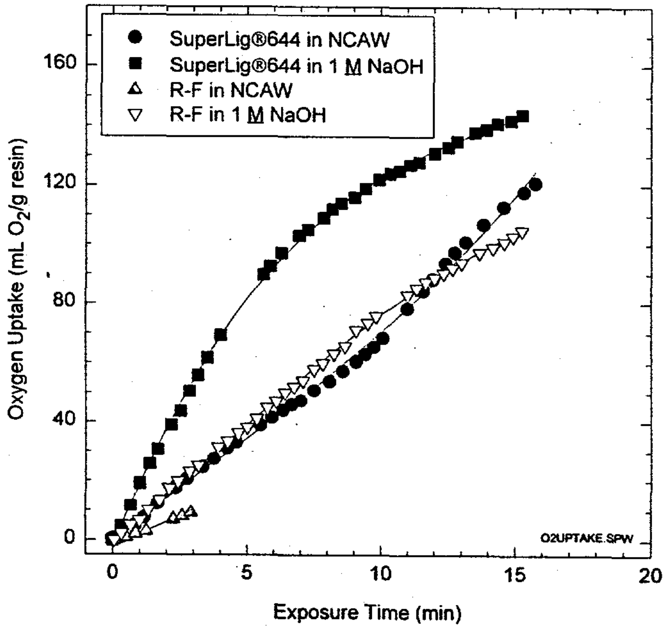

Figure 3.6. Oxygen Uptake by SuperLig®644 and R-F as a Function of Time in 1 M NaOH and NCAW Solutions

Figure 3.6. Also, chemical changes to the resin during oxidation might hinder additional oxidation because all of the easily oxidized sites may have been previously reacted.

An estimate of the average rate of O_2 uptake (Table 3.2) can be calculated from the slope of Figure 3.6. In addition, because the SuperLig®644 exhibits nonlinear behavior in 1 M NaOH, an initial, final, and average rate are calculated. Assuming ideal gas law behavior and 100% O_2 at standard temperature and pressure (1 mol O_2 at STP occupies 22.4 L), an estimated oxygen uptake can be calculated in mmol O_2 g^{-1} h^{-1}. These calculations show that in a pure oxygen environment over the course of 16 h of exposure, SuperLig®644 exhibits a significant uptake of oxygen (0.78 mmol O_2 g^{-1} h^{-1}) as compared to the overall capacity (3 mmol g^{-1}) of a standard ion exchange material.

3.2.2 Cesium Selectivity

After exposing SuperLig®644 and R-F to oxygen (Section 3.2), the samples were analyzed for cesium uptake by K_d in an NCAW simulant solution (Table 2.1). The solution had an initial cesium ratio of 1.0E+04, and after contact the equilibrium Na/Cs was approximately 1.0E+05. The K_d value measured for the SuperLig®644 decreased from approximately 1880 mL/g (no O_2 exposure) to 125 mL/g and 25 mL/g for 16-h O_2 exposure in NCAW and 1 M NaOH, respectively. These data have been converted from K_d to λ (Cs K_d x ρ_b = λ) and are displayed in Figure 3.7 as a function of oxygen exposure. The lambda value decreases more than tenfold in the NCAW solution. These results are to be expected based on the data displayed in the previous section (Table 3.2); from these data it can be estimated that over the course of the 16-h exposure, between 3 and 12 mmol O_2 are consumed

Table 3.2. Selected Oxygen Uptake Rates for SuperLig®644 and R-F in Various Solutions

Resin Material	Mass (g)	Solution	Resin Oxygen Uptake	
			mL O_2 g^{-1} h^{-1}	mmol O_2 g^{-1} h^{-1}
SuperLig®644	0.82	1 M NaOH	1.74E+01	7.80E-01(a)
SuperLig®644	0.82	1 M NaOH	4.10E+00	1.83E-01(b)
SuperLig®644	0.82	1 M NaOH	9.30E+00	4.15E-01(c)
SuperLig®644	0.54	NCAW	7.38E+00	3.29E-01
R-F	0.79	1 M NaOH	7.50E+00	3.35E-01
R-F	1.28	NCAW	3.22E+00	1.44E-01

(a) Initial rate averaged from 0 to 1.67 h.
(b) Final rate averaged from 13.3 to 15 h.
(c) Average rate from 0 to 15 h.

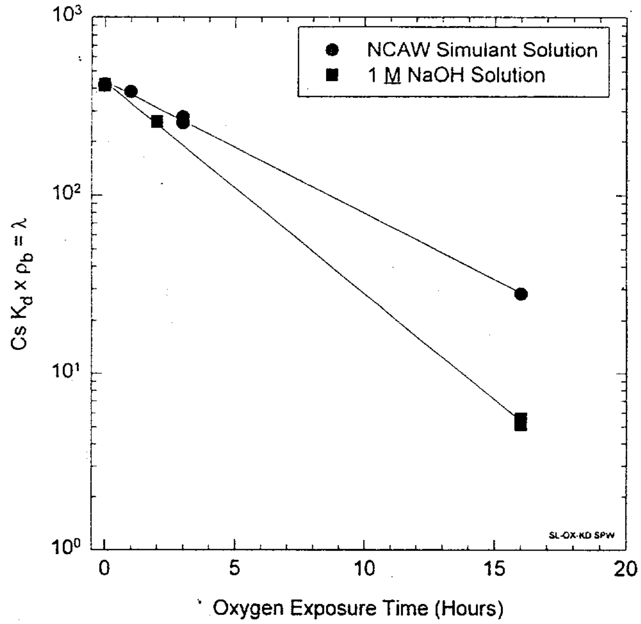

Figure 3.7. Cesium Loading of SuperLig®644 in NCAW (equilibrium Na/Cs ≈ 1.0E+05) as a Function of Oxygen Exposure

per gram of SuperLig®644. This is roughly 1 to 4 times the number of stoichiometric sites on a typical ion exchange resin. Such massive oxygen exposures must undoubtedly change the structure of the organic polymer with potentially detrimental consequences to the exchange capacity.

3.2.3 Spectroscopic Analysis

In addition to O_2 uptake and cesium K_d measurements, the oxidized SuperLig®644 and R-F resins were analyzed by ^{13}C NMR spectroscopy. The spectra for SuperLig®644 roughly illustrate the same patterns of oxidation noted in the previous sections. Because of the proprietary nature of the SuperLig®644 material, the NMR spectra cannot be reproduced in this report. However, general trends observed during the oxygen exposure experiments can be discussed. Two highly oxidized carbon functional groups were identified that were entirely absent from the unoxidized material. The magnitude of these signature peaks increased with exposure time from 0 to 16 hours. In addition, these signals are more prominent in the spectra of the samples exposed to oxygen in 1 M NaOH as opposed to the NCAW simulant. These results generally corroborate the batch K_d results from Figure 3.7, which demonstrated that oxidation is more severe in NaOH than in NCAW solutions. An additional peak was present in the unexposed resin that also increased with O_2 exposure. This indicates that the SuperLig®644 material may be partially oxidized before the start of the oxygen uptake experiments. This is not surprising because no storage conditions were specified by the manufacturer; the material was left in the dried "as received" form and kept under an air atmosphere.

Several peaks decrease during the oxidation process which indicate that certain functional groups are affected by the oxidation process. In addition, several signals were completely removed by oxygen exposure in 1 M NaOH for 16 h. The spectra also indicate that certain functional groups are more susceptible towards oxidation than other groups. It appears that these functional groups are readily reacted in either 1 M NaOH or NCAW. Clearly, these spectra changes indicate extensive modification of the chemical structure of the SuperLig®644 resin during exposure to oxygen. These data also demonstrate the utility of using NMR spectroscopy to monitor the chemical changes that may occur during oxidation and/or radiolysis of organic ion exchange materials. These data can then be used to infer the cesium loading of the resin material.

Spectroscopic analysis of the R-F resin after exposure to oxygen in either 1 M NaOH or NCAW was also completed in a manner analogous to that of the SuperLig®644 (Carlson et al. 1995; Hubler et al. 1995). The spectra also indicate susceptibility towards oxidation and structural modification by oxygen. However, the extent of R-F oxidation is not as great as the degradation observed for the SuperLig®644. These data support the previous oxygen uptake (Section 3.2.1) and cesium batch K_d (Section 3.2.2) results.

3.3 Material Stability During Processing

The radiation (Section 3.1) and oxidation (Section 3.2) stability of several cesium selective organic materials was investigated using nonradioactive simulated waste solutions. Because of the comparative nature of the tests, the data clearly indicate the relative stability of the materials under the experimental conditions investigated. However, one must be careful not to overinterpret the results, and extrapolation of these results to actual waste processing is difficult. For example, the oxygen uptake experiments were completed under an atmosphere of pure oxygen. Undoubtedly, this does not represent a typical ion exchange process conditions and should only be considered an indication of relative stability. However, using the radiation and oxygen stability data, it may be possible to estimate stability during actual processing.

The data demonstrate that oxygen uptake by the organic materials will decrease the cesium loading performance during the ion exchange process. It follows that resin degradation can be minimized by reducing oxygen exposure during storage and processing. However, some concern has been raised because oxygen will be continuously generated on the ion exchange column by the radiolysis of water in the actual waste solution. Using the data described in this report, the radiolytic generation of O_2 can be shown to have an insignificant effect on the SuperLig®644 cesium ion exchange performance in the NCAW simulant.

In Table 3.1, the $G(O_2)$ value in blank NCAW is reported to be 7.5E-02 molecules O_2 generated per 100 eV absorbed. This can be converted to mmol O_2 g^{-1} rad^{-1} as is shown in Equation 8 (per total solution and resin mass) and Equation 9 (per resin mass). Because the typical ion exchanger has between 3 and 6 meq g^{-1} total capacity, the 0.39 mmol O_2 g^{-1} represents degradation of about 5 to 10% of the stoichiometric exchange sites. Using the oxygen uptake data (0.78 mmol O_2 per hour) displayed in Table 3.2, and assuming a total exposure of 1.0E+09 rad, the results from Equation 9 can be converted into equivalent exposure time in 100% O_2 (Equation 10). From Figure 3.7, the estimation of 0.5-h exposure to 100% O_2 can be extrapolated to a worst-case 14% decrease in cesium λ (360 versus 420). Although the method of analysis is rather simplistic, the data suggest that the radiolytic production of oxygen will decrease the SuperLig®644 cesium loading by 14% during several months of process operations (up to 1.0E+09 rad). It is highly likely that other degradation pathways (e.g., chemical) will be more important than oxidation via radiolytic O_2 production during this timeframe.

$$\frac{7.5\text{E}-02 \text{ molec.}}{100 \text{ eV}} \times \frac{6.24\text{E}+11 \text{ eV}}{\text{erg}} \times \frac{100 \text{ erg g}^{-1}}{\text{rad}} = 7.8\text{E}-14 \frac{\text{mol } O_2}{\text{g}^{-1} \text{ rad}^{-1}} \tag{8}$$

$$\frac{7.8\text{x}10^{-14} \text{ mol } O_2}{\text{g rad}} \times \frac{125 \text{ g soln}}{25 \text{ g resin}} \times \frac{1000 \text{ mmol } O_2}{\text{mole } O_2} = \frac{0.39\text{x}10^{-9} \text{ mmol } O_2}{\text{g rad}} \tag{9}$$

$$\frac{0.39\text{x}10^{-9} \text{ mmol } O_2}{\text{g rad}} \times \frac{\text{hour}}{0.78 \text{ mmol } O_2} \times 1\text{x}10^{9} \text{ rad} = 0.5 \text{ h } 100\% \ O_2 \tag{10}$$

4.0 Conclusions and Recommendations

The chemical and radiolytic stability of three cesium-selective materials (SuperLig®644, R-F, and CS-100) was investigated in simulated Hanford alkaline waste by a variety techniques including oxygen uptake, NMR spectroscopy, cesium batch K_d, and gas generation analysis. The results demonstrate for the first time the stability of the newly produced SuperLig®644 with a direct comparison to two other organic ion exchangers. In general, the SuperLig®644 is less stable toward oxidative and radiolytic degradation than either the R-F or CS-100 resins. All three materials appear to be sufficiently stable for cesium ion exchange removal processes in alkaline NCAW supernates up to 1.0E+08 rad cumulative exposure and possibly even 1.0E+09 rad.

Gas evolution analysis during radiolysis also indicated the relative stability of the materials. Experimentally, the SuperLig®644 released more N_2, N_2O and H_2 and less O_2 than either the R-F or CS-100 resins per unit absorbed energy. After irradiation in NCAW to 1.0E+09 rad, the cesium lambda value in NCAW decreased from 400 to 130 (-68%), from 2000 to 520 (-74%), and from 100 to 45 (-55%) for SuperLig®644, R-F, and CS-100, respectively. From O_2 uptake measurements, SuperLig®644 initially reacted with 0.78 and 0.33 mmol O_2 g^{-1} h^{-1} in 1 M NaOH and NCAW, respectively. This is a significant amount of stoichiometric oxidation because a typical ion exchanger has an approximate capacity of 3 to 6 meq g^{-1}. The cesium lambda value ($\lambda = K_d \times \rho_b$) for SuperLig®644 in NCAW decreased from 400 to 5 and 28 after 16 h of O_2 exposure in 1 M NaOH and NCAW, respectively. In contrast, the R-F resin took up 0.33 and 0.14 mmol O_2 g^{-1} h^{-1} in 1 M NaOH and NCAW, respectively.

The loss of cesium ion exchange performance described above is a combination of several factors, including 1) direct energy absorption by the resin during irradiation, 2) resin oxidation by dissolved O_2 present before irradiation, 3) resin oxidation by O_2 generated during the radiolysis of the aqueous waste, and 4) unknown resin degradation (e.g., oxidation by nitrate or nitrite in the aqueous waste). The data suggest that oxygen should be excluded during waste pretreatment to minimize resin degradation. Based on a crude extrapolation of the data collected in this report, the radiolytic production of oxygen accounts for approximately a 14% loss in cesium ion exchange performance for SuperLig®644 after a cumulative dose of 1.0E+09 rad. This reduction is likely insignificant when compared to previously mentioned degradation pathways and the load/elute cycling (pH shock) during normal processing. Additional testing to isolate the separate oxidative pathways is recommended.

The utility of using NMR spectroscopy as a method for determining oxidative and radiolytic degradation of organic resins was also demonstrated.

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