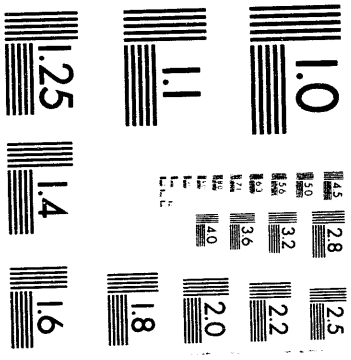
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AN INVESTIGATION OF THE RADIOLYTIC STABILITY OF A RESORCINOL-FORMALDEHYDE ION EXCHANGE RESIN

by

C. L. Crawford, N. E. Bibler and J. P. Bibler

Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29808

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An Investigation of the Radiolytic Stability of a Resorcinol-Formaldehyde Ion Exchange Resin

C. L. Crawford, N. E. Bibler and J. P. Bibler

Savannah River Technology Center
Westinghouse Savannah River Company
Aiken, SC 29808

ABSTRACT

The radiolytic stability of a resorcinol-formaldehyde polycondensation-type cation exchange resin has been investigated for up to 1E09 rads total dose. The resorcinol-formaldehyde resin is a resin developed at the Savannah River Technology Center (SRTC) that has potential cesium decontamination applications at both Pacific Northwest Laboratories (PNL) and the Savannah River Site (SRS). We have determined both radiation and storage effects on the performance of the resin using 101-AW Hanford simulant and ASTM Type-I water. Distribution coefficient determinations, total carbon analysis, and physical observations lead us to conclude that radiation up to 1E08 rads does not significantly affect the performance of the resin. The resin is more stable to radiation in water than in 101-AW Hanford simulant. Also radiation or storage does not affect the thermal stability of the resin. Cas production rates for several resin slurries were found to increase in the order of resin/101-AW Hanford simulant, resin/ASTM water, and resin/0.5 M HNO_3. We have determined that H_2 is produced from radiolysis of resin in 101-AW Hanford simulant with a G value of $G(H_2)$ of 0.11±0.02 molecules/100eV and in 0.5 M HNO_3 with a G value of $G(H_2)$ of 0.27±0.02 molecules/100eV.

INTRODUCTION

Developing and demonstrating waste separations technologies are the principal objectives of the Underground Storage Tank - Integrated Demonstration (UST-ID) Program carried out by Pacific Northwest Laboratories (PNL) at the DOE Hanford site.[1] One planned separation technique utilizes ion exchange for removal of cesium and strontium from high-level liquid supernates. A resorcinol-formaldehyde resin, which is a polycondensation-type cation exchange resin for cesium removal, has been developed at the Savannah River Technology Center (SRTC) and has demonstrated superlative performance in testing at SRS, Oak Ridge and PNL.[2,3] Advantages of this resin relative to other media for cesium removal are its high capacity for cesium and its compatibility with the high pH and aluminum and sodium concentrations of both Hanford and SRS high-level liquid wastes.

PNL plans to perform ion exchange in mobile compact processing units (CPU) close to each underground waste tank.[1] The process will include charging and elution of the resin in ion exchange columns. Additionally, the resorcinol-formaldehyde resin is being considered as a backup or second generation process for In Tank Precipitation (ITP), which is the current or reference cesium decontamination process under development at SRS.[2,4] The radiolytic stability of the resorcinol-formaldehyde resin is an important consideration for both of the applications mentioned above. A review has recently been published that stresses the importance of knowing the effects of radiation of these types of resins used in the nuclear industry.[5] Previous studies on the resorcinol resin have indicated that no significant effects due to radiation are to be expected during the process of Cs-137 removal with the resorcinol/formaldehyde resin.[2,3] Our purpose in this investigation is to determine the effects of ionizing radiation on the resin's overall stability and its ability to maintain its selectivity in removing Cs from solutions of high Na concentration.[6] We have also measured the rate of radiolytic production of gaseous compounds such as H_2 or CO_2. Knowing the rate of H_2 production is especially important since H_2 is flammable.

EXPERIMENTAL

Ion Exchange Resins

The resorcinol-formaldehyde resins used in this study consisted of a potassium (K) form and a mixed sodium-potassium (Na/K) form. Preparation of the resin as well as elemental analyses of each form have been discussed and presented previously.[2,4] The K form results from the condensation reaction between resorcinol and formaldehyde in KOH. This condensation forms the black, insoluble organic resin which contains K ions that exchange with Cs in the process solutions. The Na/K form of the resin was then prepared by washing the K form with excess 2M NaOH. This replaces most of the K ions with Na ions. Both forms of the resin were washed with water to remove excess caustic. The resulting resins were ~40 wt % in both carbon and oxygen and ~ 5 wt % in hydrogen. The resins have an exchange capacity of nominally 2.9 milliequivalents per gram of air-dried resin and bulk densities as determined in 2 M NaOH solution of ~0.36 grams of dry resin per 1 ml of swollen resin.[2]

Irradiation Methods and Systems

Resins were irradiated in either distilled ASTM Type-I water or the 101-AW Hanford simulant. ASTM Type I water is a highly purified water. It was prepared by passing distilled water through special ion exchange resins that remove all the remaining ionic impurities. The 101-AW Hanford simulant has the composition of the caustic supernate in the 101-AW tank at Hanford. This is the first tank expected to be processed in the UST-ID at Hanford.[1] The composition is given in Table 1. (Table 1 also presents the composition of a caustic simulated HLW supernate that was used to determine the performance of the resin after irradiation.) For most of the irradiation tests the ratio of resin to solution in the slurries to be irradiated was 0.10 to 0.15 gram of resin to 1 ml of liquid. For the gas evolution studies 0.5 grams of resin were irradiated for each milliliter of liquid. To determine the possible effects of reactions such as hydrolysis occurring in the absence of radiation that could degrade the resin, slurries identical to those being irradiated were stored in the 101-AW Hanford simulant or ASTM water for times identical to the irradiation times. These slurries were then analyzed along with the irradiated slurries. Irradiations were performed in either glass or stainless steel vessels using a Co-60 gamma ray source submerged beneath 25 ft. of water. The temperatures during the irradiation were ~40°C due to gamma heating. The dose rates used in this study ranged from 0.7 to 2.6 Mrad/hr. These were determined with thin film dosimeters containing a radiometric dye.[7] Optical densities of the thin film dosimeters were measured on a Hitachi model 200 UV/VIS spectrophotometer. After a mixture was irradiated, the irradiated and unirradiated slurries were treated identically. The resin was separated from the liquid by vacuum filtration. The supernates were collected for analysis and the resins were rinsed with 60 ml of ASTM Type-I water. The rinses were also collected for analyses. The resins were further rinsed and dried under vacuum filtration, typically overnight, prior to further analyses such as distribution coefficient determination, moisture content and bulk density. Experiments involving continuous pressure monitoring with dose were made using 45 ml sealed stainless steel vessels. These were connected via 4 ft. of 1/8 in. O.D. stainless steel tubing and 28 ft. of 1/8 inch O.D. nylon pressure tubing to pressure transducers (Sensotec 0-25 psia) outside the radiation field. The transducers were equipped with digital readouts. In these tests resin/liquid and liquid only samples were irradiated in identical systems simultaneously. Prior to sealing the system, no attempts were made to purge air from the slurry or the void volume of the system. A gas sampling septum was located 4 ft. above the steel vessels at the stainless steel/nylon pressure tube interface. After the irradiation gases were sampled and analyzed in 5 cc increments using loc-tight gas chromatographic syringes. In separate calibration verification tests, the 0-25 psia gauges attached to the systems showed excellent linear agreement between pressure and the amount of gas added to the sealed system for up to 30 cc of atmospheric gas. The two electronic pressure transducers were also calibrated in the SRS standards laboratory using NIST traceable methods.

Distribution Coefficient Determinations

Distribution coefficients (Kd) for the irradiated and unirradiated resins were determined using two different test solutions. The value of the Kd is a measure of the ability of the resin to remove Cs from the test solutions. One test solution was a 1.5 M NaOH solution containing 4.5 M $NaNO_3$ along with a trace of nonradioactive and radioactive cesium. The other was a caustic simulated HLW supernate containing a total Na^+ concentration of 5.6 M, a nonradioactive cesium concentration of 2.5 E-4 M, and a trace amount of Cs-137. Composition of this solution is given in Table 1. To determine the Kd, a weighed, air-dried sample of resin was equilibrated by shaking it with a measured volume of the test solutions. The Cs-137 concentration in each test solution was analyzed by gamma counting before and after the shaking to determine the initial Cs Concentration, C_o, and the final equilibrium Cs concentration, C_f. The Kd values were then calculated from the following expression:

$$Kd = [(C_o/C_f)-1]*[\text{ml of test solution/grams of air-dried resin}]$$

Analytical Methods

Total inorganic and organic carbon measurements were made on 60 ml rinses of the resin irradiated or stored in 101-AW Hanford simulant of ASTM water. The instrument used was a O. I. Co. Total Carbon analyzer. Both types of carbon were determined by converting the carbon to CO_2 and measuring the amount of CO_2 produced. Inorganic carbon (carbonate and bicarbonate) was converted to CO_2 by acidifying the sample in the instrument with phosphoric acid. Organic carbon was then determined by oxidizing the remaining carbon compounds to CO_2 using sodium persulfate and measuring the CO_2 produced. Gases produced from the radiolysis of the resin/liquid mixtures in the sealed steel vessels attached to pressure transducers were analyzed by gas chromatography with a Varian Model 3400 gas chromatograph. This chromatograph was equipped with both a thermal conductivity detector and a flame ionization detector. The columns used were a Chromosorb-101 column and a molecular sieve 13X column with argon as the carrier gas. Gases detected and analyzed for were H_2, O_2, N_2, N_2O, CO, CO_2, and CH_4. The presence of N_2O was confirmed by Fourier transform-infrared spectrophotometry using a Nicolet 20DX spectrophotometer with a 10 cm gas sample cell.

Thermogravimetric analysis (TGA) was applied to the irradiated and stored resins in the manner of Marsh.[8] The purpose of the TGA testing was to determine if degraded resin was less stable thermally than undegraded resin. TGA tests were carried out using a TA Instruments 951 Thermogravimetric Analyzer and 2100 Thermal Analyzer. For these analyses the resins were air-dried, the sample chamber was sparged with moist air (~ 50 ml/min), and the temperature was increased from 25 to 600 °C at a uniform rate of 10°C /min. Each test was run with approximately 10 milligrams of small particles of the resin. Differential scanning calorimetry was used to measure the exotherms and endotherms that occurred as the irradiated and unirradiated resins were heated in the presence of air.

RESULTS AND DISCUSSION

Tests with the Na/K Form of the Resin

The Na/K resin form was irradiated and stored in both ASTM Type-I water and the 101-AW Hanford simulant. Both the irradiated and unirradiated samples were contained in glass vials that were covered with aluminum foil to prevent liquid evaporation during irradiation or storage. Storage and irradiations times ranged from 0.5 to 451 hours. Radiation doses were in the range of 0.5E06 to 1.2E09 rads. The distribution coefficients, Kd values, for Cs as a function of both dose and resin/liquid storage time were determined for the irradiated resin and the resin stored in the liquids, respectively. These results for two test solutions are shown in Table 2 for the 101-AW Hanford simulant and Table 3 for the ASTM water. Based on the data in Tables 2 and 3 we conclude that radiolysis to doses below 1E08 does not affect the performance of the resin. We also conclude that the resin is more resistant to radiation in ASTM water than the 101-AW Hanford simulant.

Results for the 101-AW Hanford simulant will be discussed first. The data indicate a significant decrease in Kd values measured from the Na/K resins irradiated to doses of ~2E+8 rads compared to the Kd values determined for the resin stored in unirradiated 101-AW Hanford simulant. However, the Kd values in the unirradiated simulant do decrease for the long storage times but not as significantly. This indicates that resin degradation is also occurring from exposure to the 101-AW Hanford simulant for times greater than time nominally 260 hours. This observation is supported by the appearance of the solutions irradiated to the three highest doses or stored up to 248 and 451 hours. These three irradiated solutions were a deep brownish color that increased with dose. The remainder of the irradiated solutions were a light yellow color characteristic of the original 101-AW Hanford simulant. The solutions stored over resin for 248 and 451 hours also had an increased brownish appearance but much less than the irradiated solutions. The 101-AW Hanford simulant is very caustic and it has been postulated that the resin can degrade when exposed to caustic solutions for long periods of time.[9] There is another visual observation worth noting. In the resin samples irradiated in the 101-AW Hanford simulant to >2.5E08 rads white solids appeared. These were separated from the irradiated resin and analyzed. They were comprised mostly of Si indicating that at the large doses, the caustic simulant in the presence of radiation was leaching the glass container. After this was discovered, all future irradiations were performed in stainless steel.

For the resins irradiated or stored in ASTM water, the Kd's also decreased at large doses and long storage times. The decrease is not as great and appears to be nearly the same for the irradiated and unirradiated solutions. On this basis there is a decrease in performance of the resin, but it appears to be caused by degradation in the water rather than radiolysis. It was noted that the pH of the water increased to ~10.5 almost as soon as the resin was added to the water. This probably resulted from excess KOH or NaOH leaching from the resin. Consequently this caustic could have caused the degradation of the resin and introduced organic degradation products into the solution. Three observations concerning the color of the water solutions over the resin are worth noting. First, the color of the water stored for the the shortest time or irradiated to the lowest dose was yellow similar to the 101-AW Hanford simulant. We suggest that this color is due to soluble organic degradation products from the resin. Second, for the unirradiated solutions, the yellow color became darker and eventually became brownish as the length of storage time increased indicating further degradation. Third, the last four irradiated solutions became essentially colorless suggesting that radiolysis destroyed the organic in the solutions that was causing the color.

Another measure of the overall stability of the resins to radiolytic or hydrolytic degradation is the amount of carbon that could be leached from the resin after it is irradiated or stored. After the resins had been stored or irradiated in the two solutions, the solutions were filtered. The resin remaining on the filter paper was then rinsed with 60 ml of ASTM water. The rinses were then analyzed for total organic carbon and inorganic carbon (carbonate and bicarbonate) content. Results are shown in Figures 1 and 2. Radiation dose is given in the bottom of the Figures and storage time for the unirradiated systems given at the top. The data are somewhat scattered but the trends indicated by the curves in both Figures are clearly evident. Resin irradiated in 101-AW Hanford simulant to large doses have large amounts of leachable organic. At low doses the amount of carbon leached is small. At doses >2E08 we find a significant increase in total carbon leached indicating radiolytic decomposition of the resin at these larger doses. The amount leached from the resin stored in 101-AW Hanford simulant but not irradiated also increases over the amount leached from resins stored at shorter times. This confirms that there is increasing degradation with storage time; however, this increase is not as great as in the presence of radiation.

Total carbon amounts leached from the resin/ASTM water mixtures were low (0-70 ppm) throughout the entire dose range and storage times. This indicates little decomposition of the resin to form water soluble compounds or ions even though the Kd values decreased. Note also that radiolysis in ASTM water did not enhance degradation over that observed in resin just being stored. This supports the conclusion that the resin is more stable to radiation in water than in 101-AW Hanford simulant.

The moisture contents were determined of the air-dried Na/K resins throughout the dose range and storage times for both 101-AW Hanford Simulant and water. The moisture contents are in the range of 24-27% for both the resin/water and resin/101-AW Hanford simulant systems. These values were obtained from heating the resins in a convection oven at 98°C until no further mass change was observed, typically for ~4 days. The moisture content of the as received or dry Na/K resin was determined from a triplicate analysis to be slightly lower (20.5 ± 0.1%) . These results indicate that neither radiation or storage of the resin in either 101-AW Hanford simulant or ASTM water significantly affects the resin's water retention properties.

Thermogravimetric analysis (TGA) was performed on some of the irradiated and unirradiated resins. In this study resin stored or irradiated in 0.5 M HNO_3 was also included. This represents resin in presence of acid that is eluting the Cs from the column. Results are shown in Figure 4. All resins analyzed showed a similar gradual weight loss over the full temperature range. None of the Na/K resins displayed >50 % weight loss at the maximum temperature of 600°C. (The residual weight is due to K and Na oxides on the TGA pan.) The results in Figure 3 indicate that radiolysis or hydrolysis does not decrease the thermal stability of the resin or form explosive compounds. Differential Scanning Calorimetry (DSC) analyses were also performed. An endotherm indicating a loss of water occurred for all resins in the range of 100 to 110°C. This was followed by a slow exotherm starting at ~400°C as the resin burned. In agreement with the TGA results, there was no evidence for any large exotherms or formation of explosive compounds.

Tests with the K Form of the Resin

Similar experiments to those described above for the Na/K resin were also performed on the K form resin at two intermediate doses of 5.4E+7 and 2.3E+8 rads. Both the irradiated and unirradiated samples were contained in 22 ml stainless steel vessels that were covered with aluminum foil to prevent liquid evaporation. Results for the Kd values are shown in Table 4. The values in Table 4 for both the 101-AW Hanford simulant and ASTM water are in good agreement with the respective values in Table 2 and 3 measured at lower doses and shorter storage times. This agreement indicates that there is no effect of radiation up to 2.3E08 rads or of storage times up to 94 hours on the performance of the resin. This further supports our conclusion that the resin can be used up to a radiation dose at least 1E08 rads.

Final pH values for the ASTM water supernates showed the same trend as for the Na/K resin forms discussed above. All solutions indicated that the pH changed from 10.5 to ~9.6 because of radiolysis. This could be the result of CO_2 production from the radiolysis.

Bulk densities for the K resin forms were determined by soaking a weighed, air-dried resin sample in 2 M NaOH overnight to allow the resin to swell. The bulk density is equal to the ratio of the mass of one gram of dry resin to its volume (ml) in the wetted, swollen form. The bulk densities for the irradiated and blank resin systems were all determined to be less than 0.36 g/ml, which is the nominal value reported for the resin in 2 M NaOH.[2] The value found in this study for duplicate samples of the as received air-dried K form resin in 2 M NaOH was also 0.36 g/ml. For the K resin/water system the bulk densities were in the range of 0.27-0.29 g/ml for the irradiated and stored resins. In the K resin/simulant system the bulk densities were higher (0.33 g/ml) for the stored samples compared to the irradiated samples (0.29 and 0.24). These results indicate that both radiation and liquid storage of the resin increases its swelling capacity.

Gas Production During Radiolysis

Figure 4 shows the pressure produced when slurries of resin were irradiated in sealed vessels. In these tests the resin was irradiated in 101-AW Hanford simulant, ASTM water, and 0.5 M nitric acid. In all three cases gases were produced and the vessels pressurized. Similar results were obtained when these slurries were irradiated in a second series of tests. Each respective solution was also irradiated without resin being present. Very little pressurization was observed for all three solutions. Results for the 101-AW Hanford simulant are shown in Figure 4. For all three solutions in the absence of resin, the only gas detected along with the N_2 and O_2 present initially was a small amount of H_2. When resin was present, nitric acid gave the most gas and 101-AW Hanford simulant the least. Compositions of the gases are given in Table 5. In all three cases, H_2 was produced. Nitrogen was one of the main components in all the gases because it was present with air sealed in the irradiation vessels. With 101-AW Hanford simulant and nitric acid, N_2O was also produced. With water and nitric acid, CO_2 was one of the main gases produced. This gas is produced from decomposition of the resin. It is also probably produced in the 101-AW Hanford simulant but remains in the caustic solution as carbonate. N_2O results from the radiolytic reduction of nitrate when organic is present.[10] N_2O is not produced when the resin was irradiated in water since nitrate was absent. A small amount of CO was produced when the resin was in water or acid. These results indicate that, other than H_2, no hazardous gases were produced (except for the trace of methane detected when the resin was irradiated in water).

Table 6 shows the G values for the various gases produced. The G value is the number of molecules of a gas produced or consumed per 100 eV of energy absorbed by the system. Using the G values one can calculate the gas production rates at other dose rates. The G values were calculated in this manner from the data in Figure 4 and in Table 5. The G value for the total gas was calculated from the slopes of the initial linear portions of the pressure vs. dose curves in Figure 4, the dose rate, the void volume in the system, and the ideal gas law. This G value should be the sum of the G values calculated for the individual gases. The individual G values were calculated from the final composition of the gas, the final dose, the void volume in the system, and the ideal gas law. G values for N_2 and O_2 were calculated from the change in the amounts of these gases caused by the radiation. Negative G values indicate that these gases reacted during the radiolysis. The sum of the individual G values is shown in the last row of Table 6, is indeed nearly equal to the G value for total gas. Oxygen depletion has been observed in other systems and is probably due to O_2 reacting with the organic radicals produced by the radiation.[10] Nitrogen depletion has not been reported previously. The large value for N_2 depletion in the acid system does appear real and not experimental error since it was also found in a second test. Further tests are in progress to investigate this depletion.

The G value for H_2 production is important. During use of this resin in the processing of nuclear waste, it is necessary to know the rate at which H_2 is produced so that one can estimate when a flammable gas mixture may be generated in a closed system. This can be done by using the

G value for H_2 for the processing system (101-AW Hanford simulant or acid) and knowing the dose rate and the gas volume in the system. The average G value for H_2 based on two tests was 0.11±0.02 molecules/100 eV in 101-AW Hanford simulant, and 0.27±0.02 in the 0.5 M HNO_3. It is slightly lower in the 101-AW Hanford simulant due to the presence of 3.9 M nitrate compared to 0.5 M nitrate in the acid. Nitrate ions can scavenge the precursor of H_2.[11] These precursors are H atoms and aqueous electrons produced by the radiolysis of water.[12]

CONCLUSIONS

Based on the data in this study we conclude the following:

1) Resin degrades in the presence of radiation and when stored in caustic solution.
2) Radiation up to doses of 1E08 does not affect the performance of the resin.
3) Storage times in caustic up to ~100 hours does not affect the performance of the resin.
4) Radiolysis in 101-AW Hanford simulant or 0.5 M HNO_3 does not decrease the thermal stability of the resin.
5) H_2 is produced from radiolysis of resin in 101-AW Hanford simulant ($G(H_2)=0.11\pm0.02$) and in 0.5 M HNO_3 ($G(H_2) = 0.27\pm0.02$).

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Table 1. Composition of the Tank 101-AW Hanford Simulant and of a Caustic Simulated HLW Supernate Solution used in the Radiolysis Studies to Determine Kd Values for the Resin.

Component	Concentration (M)	
	101-AW Hanford Simulant[a]	Simulated HLW Supernate[b]
NaOH	5.10	2.90
$Al(NO_3)_3$	0.50	0.38
$NaNO_3$	2.40	1.20
$NaNO_2$	2.20	0.71
Na_2CO_3	0.21	0.20
Na_2SO_4	0.01	0.17
KNO_3	N.P.[c]	0.015
$CsNO_3$	N.P.	2.4E-04
Cs-137	N.P.	trace
KOH	1.10	N.P.

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[a] Simulated waste solution used for some resin irradiations.

[b] Waste solution used as equilibrating solution in some Kd determinations.

[c] N. P. = Not Present.

Table 2. Effect of Radiation and Storage Time in 101-AW Hanford Simulant on the Kd Value for Resorcinol Resin (Na/K Form).[a]

		Kd Value, ml/gram			
		4.5M NaNO3,1.5M NaOH		Sim. Supernate	
Irrad or Storage Time,hr	Dose Rads[b]	Irrad. Resin	Unirrad. Resin	Irrad. Resin	Unirrad. Resin
0.5	5.0E05	1.4E03	1.5E03	3.6E02	4.9E02
1.0	1.0E06	2.5E03	3.5E03	5.3E02	8.1E02
20.	2.0E07	3.0E03	1.8E03	7.7E02	5.7E02
52.	5.3E07	2.6E03	2.9E03	6.7E02	>1.0E03[c]
120.	1.2E08	1.7E03	2.9E03	1.9E02	>1.0E03[c]
96.	2.5E08	4.7E02	1.5E03	6.3E01	2.9E02
258.	6.7E08	1.5E02	6.7E02	2.1E01	1.5E02
451.	1.2E09	8.0E02	6.7E02	1.2E01	7.8E01

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[a] 1.2 grams of air dried resin either stored or irradiated in 12 mL of 101-AW Hanford simulant in glass vessels.

[b] The first 5 doses were at a dose rate of 1.0E06 rads/hr. The latter 3 were at 2.6E06 rads/hr.

[c] In these tests, essentially all the Cs-137 was removed from the final equilibrated solutions. This led to a very high calculated values for Kd.

Table 3. Effect of Radiation and Storage Time in ASTM Water on the Kd Value for Resorcinol Resin (Na/K Form).[a]

		Kd Value, ml/gram			
		4.5M NaNO3,1.5M NaOH		Sim. Supernate	
Irrad or Storage Time,hr	Dose Rads[b]	Irrad. Resin	Unirrad. Resin	Irrad. Resin	Unirrad. Resin
0.5	5.0E05	1.2E03	1.5E03	1.4E02	1.1E02
1.0	1.0E06	1.2E03	1.2E03	1.3E02	1.4E02
20.	2.0E07	1.7E03	2.5E03	1.5E02	3.0E02
52.	5.3E07	2.0E03	1.1E03	2.1E02	1.1E03
120.	1.2E08	2.7E03	2.1E03	>1.0E03[c]	3.8E02
96.	2.5E08	9.2E02	1.0E03	5.4E01	1.6E02
258.	6.7E08	7.5E02	9.0E02	9.7E01	1.1E02
451.	1.2E09	8.8E02	9.7E02	8.3E01	8.4E01

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[a] 1.2 grams of air dried resin either stored or irradiated in 12 mL of ASTM water in glass vessels.

[b] The first 5 doses were at a dose rate of 1.0E06 rads/hr. The latter 3 were at 2.6E06 rads/hr.

[c] In this test, essentially all the Cs-137 was removed from the final equilibrated solution. This led to a very high calculated value for Kd.

Table 4. Effect of Radiation and Storage Time in 101-AW Hanford Simulant or ASTM Water on the Kd Value for Resorcinol Resin (K Form).[a]

		Kd Value, ml/gram			
		4.5M NaNO3,1.5M NaOH		Sim. Supernate	
Irrad or Storage Time,hr	Dose Rads[b]	Irrad. Resin	Unirrad. Resin	Irrad. Resin	Unirrad. Resin
	Irradiated or stored in 101-AW Hanford Simulant				
22.	5.4E07	1.4E03	2.0E03	1.1E02	1.5E02
94.	2.3E08	1.3E03	2.4E03	2.2E02	3.4E02
	Irradiated or stored in ASTM Water				
22.	5.4E07	6.8E02	1.4E03	>1.0E03[c]	4.5E02
94.	2.3E08	1.7E03	1.4E03	2.5E02	4.4E02

---

[a] 1.5 grams of air dried resin either stored or irradiated in 10 mL of 101-AW Hanford Simulant of ASTM water in steel vessels.

[b] The dose rate is 2.5E06 rads/hr.

[c] In this test, essentially all the Cs-137 was removed from the final equilibrated solution. This led to a very high calculated value for Kd.

Table 5. Final Gas Composition from Resorcinol Resin Irradiated in Various Solution[a]

	Resin Irradiated in		
	101-AW Hanford Simulant	ASTM Water	0.5 M HNO_3
Final Dose, Mrad	86.0	86.0	33.0
Final Press.,PSIA	17.8	26.0	25.9
Component	Volume Percent		
H_2	12.5	38.6	9.1
O_2	13.2	6.6	2.5
N_2	64.9	32.2	18.0
CO	n.d.	2.1	0.4
CO_2	0.1	18.4	49.3
CH_4	n.d.	0.3	n.d.
N_2O	7.8	n.d.	11.8

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[a] 13.5 grams of air dried resin irradiated in 27 mL of solution. Slurries contained air that was sealed in the radiation vessel with the slurry.

Table 6 Calculated G Values for Resorcinol Resin Irradiated in Various Solutions[a]

	Resin Irradiated in		
	101-AW Hanford Simulant	ASTM Water	0.5 M HNO_3
Final Dose, Mrad	86.0	86.0	33.0
Final Press.,PSIA	17.8	26.0	25.9
Component	G Value, Molecules/100 eV		
Total Gas[b]	0.13	0.63	1.52
H_2	0.09	0.49	0.30
O_2	-0.03	-0.06	-0.03
N_2	0.01	-0.15	-0.90
CO	<0.01	0.03	0.02
CO_2	<0.01	0.23	1.60
CH4	<0.01	0.01	<0.01
N_2O	0.05	<0.01	0.39
Sum	0.12	0.55	1.38

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[a] 13.5 grams of air dried resin irradiated in 27 mL of solution. Slurries were irradiated with the air that was sealed in the radiation vessel with the slurry.

[b] Calculated from the least squares determination of the slopes of the linear portion of the curves in Figure 3. All other values calculated from the final pressure, composition, and dose.

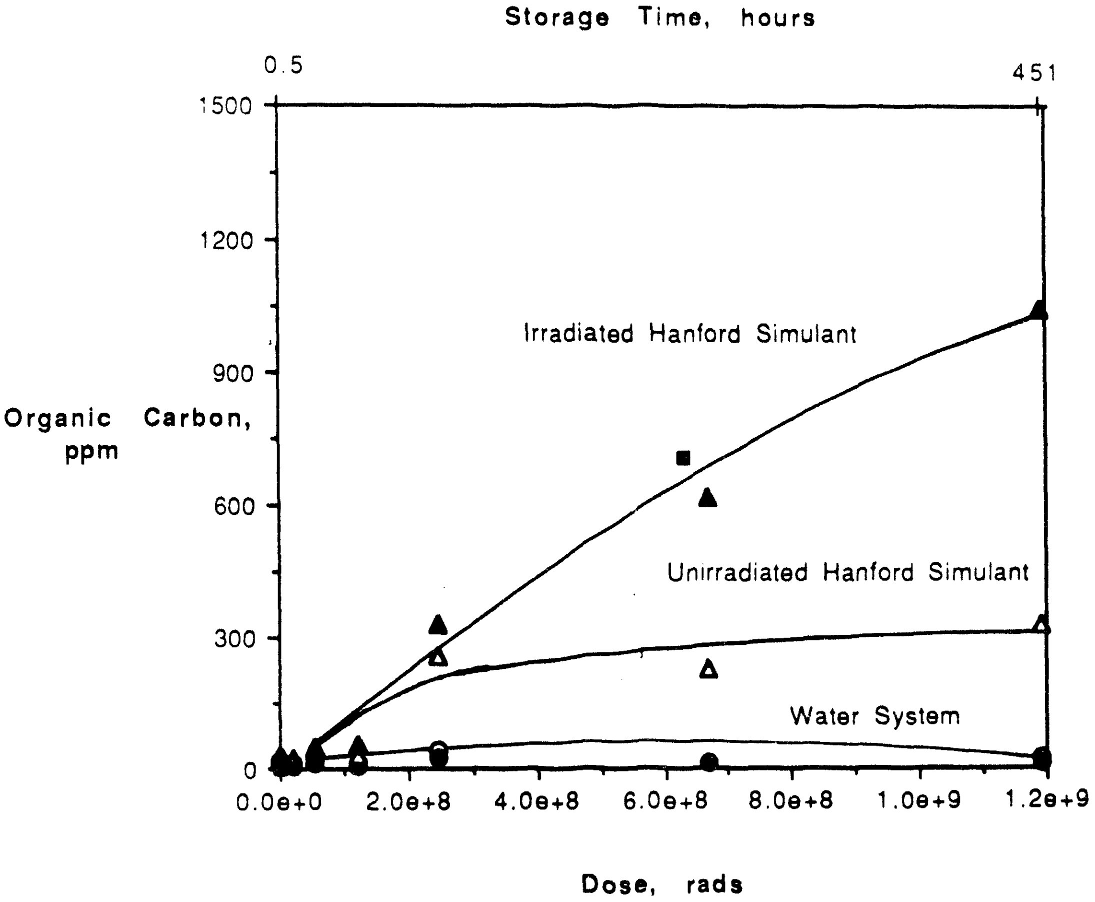

Figure 1. Organic carbon leached by 60 ml ASTM water rinses of samples of Na/K form resin that had been irradiated or stored in Hanford Simulant or Water. Closed symbols are for the irradiated system and open symbols for unirradiated. All results are for resin samples irradiated or stored in glass, except the result shown by ■ , which is the average of duplicate resin samples irradiated in Hanford simulant contained in stainless steel vessels.

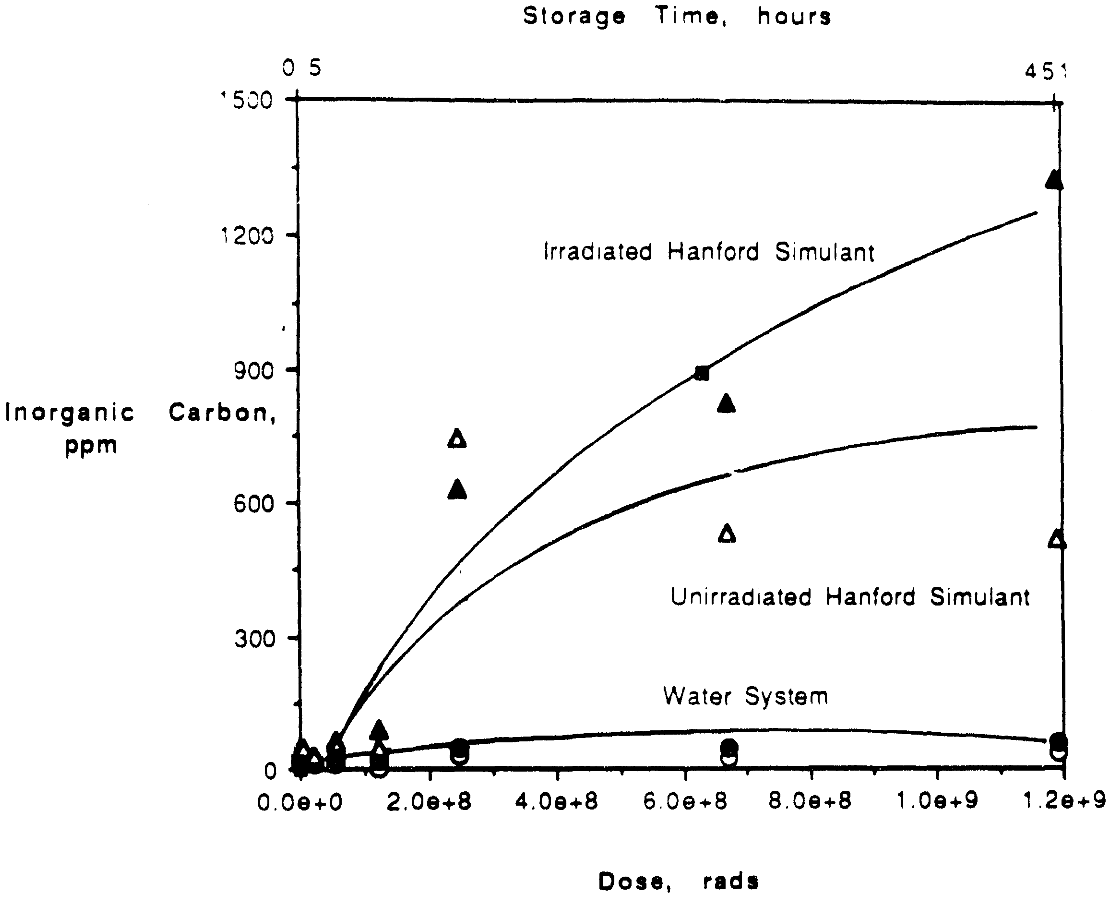

Figure 2. Inorganic carbon leached by 60 ml ASTM water rinses of samples of Na/K form resin that had been irradiated or stored in Hanford Simulant or Water. Closed symbols are for the irradiated system and open symbols for unirradiated. All results are for resin samples irradiated or stored in glass, except the result shown by ■, which is the average of duplicate resin samples irradiated in Hanford simulant contained in stainless steel vessels.

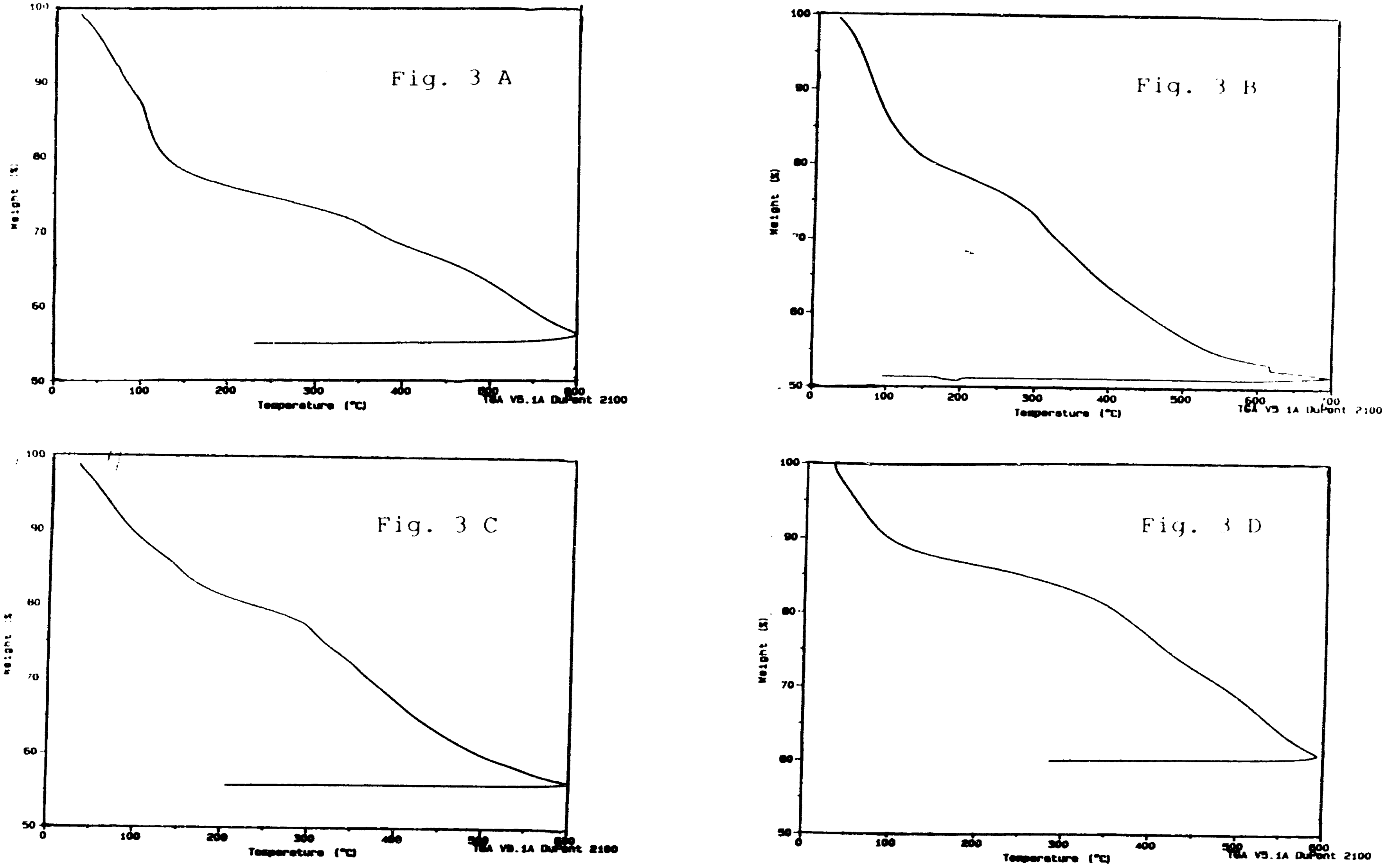

Figure 3. Thermogravimetric Analyses (weight % loss vs.temperature plots) obtained from heating air-dried resins up to 600°C: (A) Dry as received Na/K form resin used in this study; (B) Na/K form resin stored in Hanford simulant for 258 hours; (C) Na/K form resin irradiated in Hanford Simulant to a dose of 7E+8 rads; (D) K form resin irradiated in 0.5 M HNO_3 to a dose of 3E+7 rads. Note that all the plots are identical.

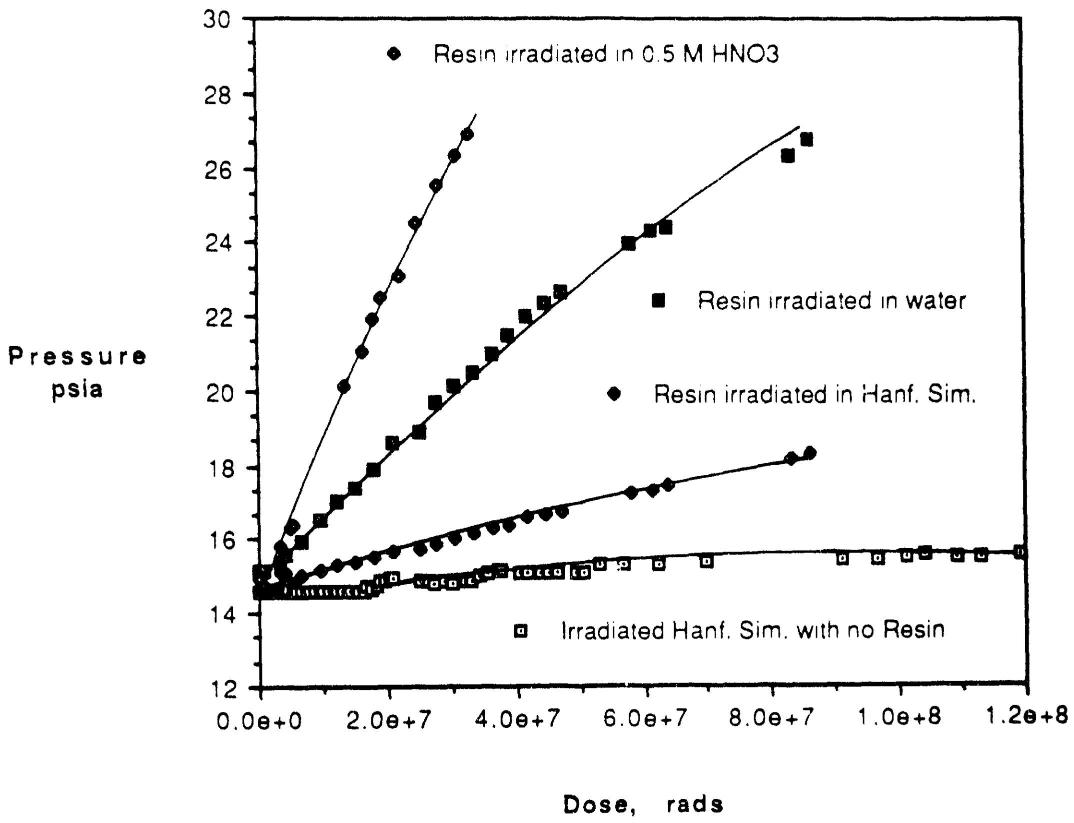

Figure 4. Pressures produced from irradiation of 13.5 grams of resin in 27 ml of 0.5 M HNO3, water, and Hanford simulant in 45 ml stainless steel sealed vessels. The lower curve is from pressures produced from irradiation of 3[illegible] ml of Hanford simulant with no resin present.

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