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CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS

QUARTERLY PROGRESS REPORT
OCTOBER-DECEMBER 1982

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Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Contract No. DE-AC02-76CH00016

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Manuscript Completed - January 1983
Date Published - February 1983

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Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Regulatory Research
Contract No. DE-AC02-76CH00016
FIN NO. A-3236

SUMMARY

During this report period a resin core sample from Epicor-II liner PF-3 was received from Battelle-Columbus Laboratories. Preliminary characterization of this material has begun. Visual observations of the resin do not suggest gross physical degradation.

Irradiation induced formation of acidic species has been studied for IRN-77 resins in different cation forms. With the exception of H^+ form, the pH of the supernate over irradiated resin is relatively insensitive to cation form although iron may reduce the extent of functional group scission. The supernate over irradiated Fe^{++} and Fe^{+++} form resin contains a mixture of ferrous or ferric sulfates and sulfuric acid. Data on sodium form resin imply that the salt-to-acid ratio is increased (i.e., the acidity is decreased) by ion-exchange processes following radiolytic attack. These processes, and the limited dissociation of bisulfate ion, may account for some of the similarity in pH found with resin irradiated in different counter ion forms.

Radiolytic attack on the functional group in cation resin as evidenced by sulfate formation, is promoted by moisture in the resin. Hydrogen peroxide formation is apparently not a rate-limiting step in this mechanism. Radiolytic attack may be enhanced by resin swelling or aqueous transport effects, which reduce back reactions.

Acidic conditions result from the heavy irradiation of mixed bed resins in the HOH and NaCl form; the decomposition products of the anion and cation components do not neutralize each other. Highly acidic (pH ~1) free liquids are produced in both forms by an irradiation of $\sim 2 \times 10^8$ rad. The liquid is released by the anion component, which undergoes shrinkage; the acidity of this liquid results from decomposition products of the cation resin. On a percentage basis, radiolytic sulfate yields in the cation components are not strongly influenced by the presence of the anion component.

First order kinetic rate constants are reported for oxygen scavenging by irradiated resins. Following a dose of less than 10^7 rad, the atmosphere over irradiated resin should be highly anoxic. Only a small fraction of the oxygen uptake results in CO_2 generation.

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1. INTRODUCTION

Brookhaven National Laboratory (BNL), under contract to the United States Nuclear Regulatory Commission (NRC), is presently carrying out a research program entitled, "Characterization of TMI-Type Wastes and Solid Products." The present document is the fifth progress report issued under this contract. Subsequent reports will be issued on a quarterly schedule.

1.1 Background and Program Objectives

The objective of this program is to develop a data base applicable to NRC licensing considerations for the storage and disposal of ion-exchange media subjected to high internal irradiation doses as a result of heavy radionuclide loadings.

The project incorporates four separate tasks. Task 1 involves a characterization of field samples of heavily loaded ion-exchange media. This is intended to provide a basis for comparison of laboratory and field results. Task 2 is a parametric study of the radiation induced degradation of organic ion-exchange media. In Task 3, radiation effects on solidified forms and high integrity container materials for waste ion-exchange media are to be characterized. Task 4 will assess mechanistic issues specifically dealing with qualifying test procedures for assessing the significance of radiation effects on the use, storage and disposal of ion-exchange media under field conditions.

2. SURVEY/CHARACTERIZATION OF FIELD EXPERIENCE WITH HEAVILY LOADED ION-EXCHANGE MEDIA (K. J. Swyler and W. Becker)

2.1 Monitoring Efforts on Epicor-II Liner Characterization

During this report period, a core sample from Epicor-II liner PF-3 was received at our laboratory. The withdrawal and preparation of this core at Battelle-Columbus Laboratories (BCL) has been described previously (Swyler and Dayal, 1982a). The samples were received at BNL on November 12, 1982. The shipment consisted of 15 separate polyethylene bottles, each containing a separate two-inch section of the core.

These sample bottles were removed from the shipping casks in our hot cell facilities and transferred to lead pigs for storage. Subsequently, small samples were withdrawn from the polyethylene bottles and placed in storage for subsequent analysis. Radionuclide assays and chemical characterization of the resin samples is currently under way and will be described in detail later. Some preliminary observations are as follows:

- The gamma activity is localized in the upper portion of the core. Contact radiation level readings on the various samples, provided by BCL and confirmed in our laboratory, are given in Table 2.1.

Table 2.1

Contact Radiation Levels in Epicor-II Core Sections

Sample Number	Core Section (Inches From Bottom)	Contact Radiation Level (mr/h)
1	0-2	50
2	2-4	50
3	4-6	30
4	6-8	50
5	8-10	50
6	10-12	120
7	12-14	250
8	14-16	300
9	16-18	400
10	18-20	1300
11	20-22	10,000
12	22-24	20,000
13	24-26	30,000
14	26-28	15,000
15	28-30 (top)	25,000

The table indicates that the activity is concentrated in a zone extending about 12 in. downward from the top of the core. This zone (Swyler and Dayal, 1982a) contains a layer of whitish material at the top, and, below it, a band of darker material about 10 in. thick. Since the radiation dose is localized to some extent in this darker material, part of the coloring might reflect radiation damage. As noted earlier, however, at least some of the coloring also reflects intrinsic material properties.

- Most of the samples are dry to the extent that they are somewhat difficult to handle - individual beads or particles may be scattered by electrostatic forces. Resin observed during the coring operation appeared reasonably moist - it seems that some dehydration of the samples may have occurred during sampling or storage operations at BCL. In transferring the resins from the polyethylene bottles to small sample jars there was no evidence of any gross physical deterioration (agglomeration, etc.) of the resin.

- Initial radionuclide assay data on beads from sample 15 indicate Cs-137/Cs-134 activity in the ratio of ~14:1. Absolute curie contents are presently being determined.

3. PARAMETRIC STUDY OF RADIATION-INDUCED DEGRADATION OF ORGANIC ION-EXCHANGE MEDIA (C. Dodge, B. A. Karlin, and K. J. Swyler)

During the report period, long-term irradiation of IRN-77 resin continued. Additional results were obtained describing the effect of resin loading and moisture content on the decomposition of IRN-77 resin. Further analyses were carried out on IRN-150 mixed bed resin, and the kinetics of radiolytic oxygen scavenging were determined. Results are described below.

3.1 Effect of Resin Loading on the Radiolytic Attack and Acid Product Formation in Sulfonic Acid Cation Resin

Experiments at high irradiation dose rate (1.5×10^6 rad/h) were carried out to further investigate the effect of resin loading on radiolytic damage and acid product formation. Irradiations of resin in the Cs^+ form, Fe^{++} form, Fe^{+++} form and NH_4^+ form were carried out in sealed glass tubes according to the procedures described earlier. Supernatant solutions were analyzed for radiolytic decomposition products, including sulfate ion and counter ions released. Results are shown in Figures 3.1 and 3.2.

The data in Figure 3.1, indicate the same general trends observed in H^+ form and Na^+ form resin; supernatant pH decreases with increasing radiation dose in all cases, indicating the radiolytic formation of acidic species. In comparison with the Na^+ form resin, the supernates of Cs^+ , Fe^{++} , Fe^{+++} and NH_4^+ form resin are somewhat more acidic. The difference is not large however, and over the range indicated in Figure 3.1. The supernatant pH is not particularly sensitive to resin loading.

For the Fe^{++} resin, ion balance (Table 3.1) indicates that, at high total dose, roughly two-thirds of the sulfate can be accounted for as FeSO_4 , and one-third as H_2SO_4 . At the solution pH, approximately 50% of the SO_4 will be associated with H^+ to form bisulfate ion. For Fe^{+++} form resin, about half the sulfate can be accounted for as $\text{Fe}_2(\text{SO}_4)_3$ and half as H_2SO_4 . Again, a large fraction of the $\text{SO}_4^{=}$ will be incorporated in bisulfate ion. This preliminary analysis assumes that the iron is not in a mixed oxidation state, and that all the H^+ is either in solution or incorporated in bisulfate ion. Interestingly, the analysis indicates that in the irradiated resin, ferrous iron is not oxidized to ferric iron. Soluble sulfate "yields" in the Fe^{++} and Fe^{+++} forms are substantially lower than those in Na^+ forms. In particular, for the Fe^{+++} form, sulfate levels are less than 50% of those found in the Na^+ form suggesting that Fe loading retards scission of the functional group. A similar effect has been observed by other workers (Gangwer, Goldstein, and Pillay, 1978).

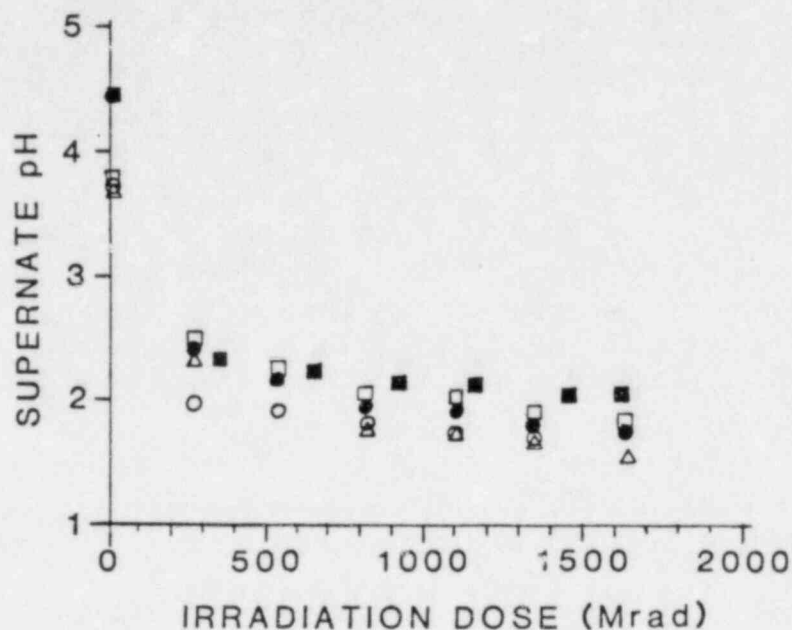


Figure 3.1 Supernatant pH vs irradiation dose for various forms of IRN-77 resin. Dose rate = 1.6×10^6 rad/h. Samples irradiated in sealed environment. ■ - Na⁺ form resin; ○ - NH₄⁺ form; ● - Cs⁺ form; □ - Fe⁺⁺ form; △ - Fe⁺⁺⁺ form.

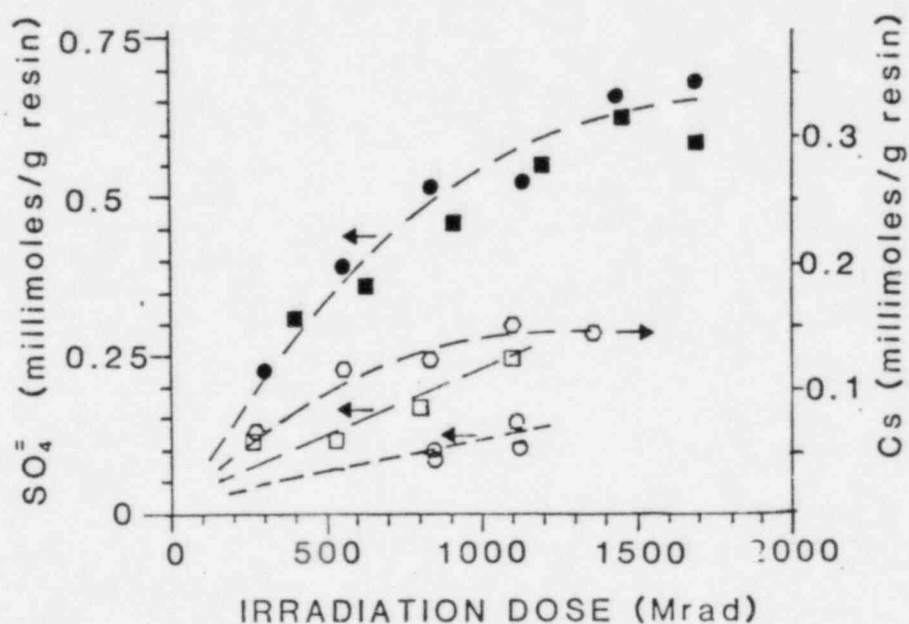


Figure 3.2 Sulfate ion and counter ion supernatate yields (moles per g of resin) vs irradiation dose in different forms of IRN-77 resin. ■ - Na⁺ form; ● - H⁺ form; □ - Fe⁺⁺⁺ form; ○ = H⁺ form, and Na form, dry; ○ - Cs⁺ form.

Table 3.1

Equivalents of Fe, H⁺ and SO₄⁼ in the Supernate of Irradiated IRN-77 Resin

Resin Form	Irradiation Dose (Rad)	Milli Equivalents Per mL of Supernate ^a			
		H ⁺	Fe ⁺⁺	Fe ⁺⁺⁺	SO ₄ ⁼
Fe ⁺⁺	2.7x10 ⁸	9.1x10 ⁻³	5.2x10 ⁻²		4.8x10 ⁻²
	5.4x10 ⁸	2.7x10 ⁻²	8.4x10 ⁻²		1.2x10 ⁻¹
	8.2x10 ⁸	4.1x10 ⁻²	9.6x10 ⁻²		1.5x10 ⁻¹
	1.1x10 ⁹	3.2x10 ⁻²	6.8x10 ⁻²		9.2x10 ⁻²
Fe ⁺⁺⁺	2.7x10 ⁸	1.3x10 ⁻²		4.2x10 ⁻³	4.8x10 ⁻²
	5.4x10 ⁸	2.3x10 ⁻²		2.0x10 ⁻²	4.8x10 ⁻²
	8.2x10 ⁸	3.3x10 ⁻²		3.3x10 ⁻²	6.8x10 ⁻²
	1.1x10 ⁹	4.8x10 ⁻²		4.6x10 ⁻²	1.0x10 ⁻¹

^aThe equivalents for H⁺ are determined from pH data and include a calculated contribution from undissociated HSO₄⁻ at the indicated pH.

The release of certain soluble species in Figure 3.2 also slows down with increasing radiation dose. This effect has been referred to earlier; the primary production of radiation damage may decrease as the extent of radiation damage increases, or the number of decomposition products which enter solution may be limited by solubility constraints. This latter situation is familiar in "static leaching" experiments. Care should be exercised in interpreting the Fe data where species of limited solubility are involved. Presently, there is no evidence that the slower release with increasing radiation dose is a solubility effect. Figure 3.2 indicates that the decrease in yields begins at about 5x10⁸ rad in Na⁺ and H⁺ form resin corresponding to a scission of about 15% of the exchange sites (and a supernatant solution which is 0.07 molar in SO₄⁼). Sodium levels in the supernate at 5x10⁸ rad are roughly 0.1 molar, corresponding to a release of ~20% of the available sodium.

3.2 Effect of Moisture Content on the Radiolytic Attack and Acid Product Formation in Sulfonic Acid Cation Resin

Samples of IRN-77 in the H⁺ and Na⁺ form were irradiated under wet and dry conditions to determine the effect of moisture on radiolytic attack. Irradiations were carried out on dry (7% moisture content) samples in sealed glass vessels and on 2 g resin samples immersed in 10 mL of deionized water. For the samples irradiated under deionized water, the pH was determined periodically by removing the samples from the irradiation facility. Sulfate and pH analysis was performed on the supernatant liquids contacted with 2 g of the dry resin following irradiation. Results are given in Tables 3.2 and 3.3.

Table 3.2

Soluble Radiolysis Products and Acidic Species
in IRN-77 Irradiated in Dry Form

Resin Form	Na ⁺ Dry			H ⁺ Dry	
	pH ^a	SO ₄ ⁼ b	Na ⁺ b	pH ^a	SO ₄ ⁼ b
Radiation Dose (Rad)					
0	5.8	(9.6±0.4)×10 ⁻⁷	(2.5±0.8)×10 ⁻⁷	3.0	3.5×10 ⁻⁶
2.7×10 ⁸	3.7	---	(2.0±1.4)×10 ⁻⁴	2.3	
5.5×10 ⁸	3.3	---	(2.8±0)×10 ⁻⁴	2.0	
8.2×10 ⁸	3.2	(1.9±0.2)×10 ⁻⁴	(3.5±0.7)×10 ⁻⁴	1.8	(2.1±0.2)×10 ⁻⁴
1.1×10 ⁹	3.0	(2.3±0.2)×10 ⁻⁴	(6.5±0.3)×10 ⁻⁴	1.8	2.8×10 ⁻⁴

^apH of supernate formed with 10 mL of water and 1 g of irradiated resin.
^bMoles released per gram dry resin.

Table 3.3

Supernatant pH for IRN-77 Resin Irradiated Under Deionized Water

pH of Supernatant Liquid (10 mL) in Contact With Resin (2 g) During Irradiation			
Irradiation Dose (Rad)	Na ⁺ Resin	H ⁺ Resin	Deionized Water Control
0	5.4	3.2	6.12±.01
1.2×10 ⁸			5.0 ±.8
2.3×10 ⁸	2.9	1.6	
2.7×10 ⁸			4.3 ±.5
5.1×10 ⁸	2.4	1.1	
5.3×10 ⁸			3.7 ±.3
7.8×10 ⁸	2.2	1.0	
7.9×10 ⁸			3.8 ±.5
1.2×10 ⁹	2.1	1.0	
1.3×10 ⁹			3.5 ±.6

The tables indicate that radiolytic attack on the functional group, as evidenced by soluble sulfate formation, is reduced but not eliminated in the dry resin. The sulfate yields are less than 25% of those for Na^+ and H^+ form resins irradiated in the fully swollen form (Figure 3.2). It is interesting that the oxidized species, $\text{SO}_4^=$ is observed when water is contacted with resins which have been irradiated in the dry state. For the Na^+ form resin, the soluble species is largely Na_2SO_4 . For the hydrogen form resin, the relationship between pH and $\text{SO}_4^=$ agrees fairly well with the expected behavior for sulfuric acid (Swyler and Dayal, 1982b).

For samples irradiated in contact with water, the pH values for the sodium form are close to those found when appropriate amounts of water are contacted with irradiated resins (Swyler and Dayal, 1982b). During irradiation of the Na^+ form samples immersed in water, large gas pockets formed which pushed the resin upward in the irradiation tube. This effect was not observed in the H^+ form resins. Generally, the pH values of the H^+ resin irradiated in water reproduce those obtained for the supernate over resin irradiated in the fully swollen form. The pH data indicate that irradiation in excess water does not produce acidic species at a rate which is markedly different than that found in the irradiation of resins in the fully swollen form. It is also worth noting that irradiation produced a decrease in the pH of deionized water. Under the present experimental conditions (the samples were irradiated in a vented environment), some of the pH decrease could be due to HNO_3 formation. Presumably, this effect could also occur in the pore water of irradiated resins.

3.3 Formation of Soluble Radiolysis Products in IRN-150 Mixed Bed Resin

Experiments were carried out to characterize the formation of soluble radiolysis products in IRN-150 mixed bed resin. A major aim of these experiments is to determine how the radiation damage response of the composite material reflects the interaction between individual components, whose individual behavior has been characterized earlier.

As in the case of IRN-78 anion resin, the mixed bed systems were found to exhibit a free liquid phase upon irradiation. This free liquid was removed for analysis by centrifuging. The resins were then contacted with deionized water and the supernate analyzed. Preliminary rinsing experiments were initiated to determine if any $\text{SO}_4^=$ produced in the decomposition of the cation component is bound in the anion component by an ion-exchange process. Free liquid and supernate analysis results are given for IRN-150 resin in HOH and the NaCl forms in Tables 3.4 and 3.5.

In both HOH and NaCl form resin, acidity of both the free liquid and supernate solutions increases with irradiation dose. Strongly acidic conditions occurring in the HOH form indicate that the acidic species produced in the decomposition of the IRN-77 (H^+) component are not completely neutralized by the basic IRN-78 (OH^-) component. The mixed bed system does not protect against the formation of acidic conditions under heavy irradiation doses.

In the HOH forms, correlations between pH and $\text{SO}_4^{=}$ concentrations in the supernate and free liquid (Table 3.6) indicate that the species present is less acidic than H_2SO_4 . Since H_2SO_4 is the acid produced in the irradiation of IRN-77 (H^+) form resin, some neutralization on uptake of acidic species has apparently occurred in the irradiated HOH mixed bed resin. For the NaCl form, the acidity of the supernate solution is remarkably similar to that found for the IRN-77 (Na^+) resin alone (Swyler and Dayal, 1982). Both the free liquid and the supernate of the NaCl form are more acidic than those derived from the HOH form, reversing the trend found with the Na^+ and H^+ form resins. This behavior provides further evidence for partial neutralization of acidity in the irradiated HOH resin.

Table 3.4

Soluble Decomposition Products in Irradiated H^+OH^- Form IRN-150 Resin

Irradiation Dose (rad) $\times 10^{-8}$	Free Liquid			Supernate Over Centrifuged Resin	
	Amount Released (mL/g)	$\text{SO}_4^{=}$ (mole/g)	pH	$\text{SO}_4^{=}$ (mole/g)	pH
0	.0155 \pm .013	---	---	---	5.5
2.7	0.22	7.4×10^{-6}	4.4	---	4.9
5.4	0.28	6.4×10^{-5}	2.2	2.3×10^{-5}	3.0
8.1	0.28	1.5×10^{-4}	1.6	4.7×10^{-5}	2.6
11	0.29	5.9×10^{-5}	1.5	5.9×10^{-5}	2.5
13	0.36	---	1.4	6.0×10^{-5}	2.4
16	0.37	1.37×10^{-4}	1.3	6.9×10^{-5}	2.3

^aAll values refer to amount produced per gram of uncentrifuged resin.

Table 3.5

Soluble Decomposition Products in Irradiated Na^+Cl^- Form IRN-150 Resin

Irradiation Dose (rad) $\times 10^{-8}$	Amount Released (mL/g)	Free Liquid				Supernate Over Centrifuged Resin				Total Na^+ (mole/g)	Total Cl (mole/g)
		$\text{SO}_4^{=}$ (mole/g)	Na^+ (mole/g)	Cl^- (mole/g)	pH	$\text{SO}_4^{=}$ (mole/g)	Na^+ (mole/g)	Cl^- (mole/g)	pH		
0	0	---	---	---	---	---	---	---	5.7	---	---
2.7	.136	6.9×10^{-5}	---	1.0×10^{-4}	2.0	9.8×10^{-6}	2.6×10^{-4}	2.2×10^{-4}	2.8	---	3.2×10^{-4}
5.4	.243	1.8×10^{-4}	5.0×10^{-4}	3.7×10^{-4}	1.6	5.4×10^{-5}	3.2×10^{-4}	2.9×10^{-4}	2.3	8.2×10^{-4}	6.6×10^{-4}
8.0	.271	2.7×10^{-4}	4.6×10^{-4}	4.8×10^{-4}	1.5	7.5×10^{-5}	3.2×10^{-4}	1.5×10^{-4}	2.2	7.8×10^{-4}	6.3×10^{-4}
11	.311	1.7×10^{-4}	5.2×10^{-4}	2.5×10^{-4}	1.2	9.2×10^{-5}	3.5×10^{-4}	5.0×10^{-4}	2.1	8.1×10^{-4}	7.5×10^{-4}
13	.325	2.0×10^{-4}	5.5×10^{-4}	2.6×10^{-4}	1.1	---	3.6×10^{-4}	4.9×10^{-9}	2.1	9.1×10^{-4}	7.5×10^{-4}
16	.330	1.9×10^{-4}	7.0×10^{-4}	2.6×10^{-4}	1.0	8.4×10^{-5}	4.2×10^{-4}	4.2×10^{-4}	2.0	1.2×10^{-3}	6.8×10^{-2}

^aAll values refer to amount produced per gram of unirradiated resin.

Table 3.6

Correlation of $[\text{SO}_4^{=}]^a$ and $[\text{H}^+]^b$ in Liquids
Contacting Irradiated IRN-150 Resin

Resin Form	Irradiation Dose (rad)	Free Liquid (meq/mL)		Supernate (meq/mL)	
		$[\text{SO}_4^{=}]$	$[\text{H}^+]$	$[\text{SO}_4^{=}]$	$[\text{H}^+]$
HOH ⁻	0	---	---	---	---
	2.7x10 ⁸	6.8x10 ⁻²	4.0x10 ⁻⁵	---	---
	5.4x10 ⁸	4.6x10 ⁻¹	9.6x10 ⁻²	1.3x10 ⁻³	1.5x10 ⁻³
	8.1x10 ⁸	1.1	4.0x10 ⁻¹	2.6x10 ⁻²	5.1x10 ⁻³
	1.1x10 ⁹	4.0x10 ⁻¹	1.8x10 ⁻¹	3.4x10 ⁻²	6.5x10 ⁻³
	1.3x10 ⁹	---	---	3.8x10 ⁻²	9.3x10 ⁻³
	1.6x10 ⁹	7.2x10 ⁻¹	3.5x10 ⁻¹	4.4x10 ⁻²	1.4x10 ⁻²
Na ⁺ Cl ⁻	0	---	---	---	---
	2.7x10 ⁸	1.0	2.5x10 ⁻¹	4.6x10 ⁻³	1.8x10 ⁻³
	5.4x10 ⁸	1.5	5.4x10 ⁻¹	2.8x10 ⁻²	9.3x10 ⁻³
	8.1x10 ⁸	2.0	7.7x10 ⁻¹	4.0x10 ⁻²	1.5x10 ⁻²
	1.1x10 ⁹	1.1	5.4x10 ⁻¹	5.2x10 ⁻²	1.7x10 ⁻²
	1.3x10 ⁹	1.3	6.4x10 ⁻¹	---	---
	1.6x10 ⁹	1.2	6.2x10 ⁻¹	5.0x10 ⁻²	2.2x10 ⁻²

^aThe value for $[\text{SO}_4^{=}]$ is total sulfate concentration and may include species such as NaHSO_4 , HSO_4^- etc., which are not dissociated in the undiluted solution.

^bDetermined from pH measurements, including the computed amount of H^+ incorporated in bisulfate at the measured pH.

In the HOH resin, the yield of $\text{SO}_4^{=}$ in the free liquid and supernate increases with irradiation dose up to about 8×10^8 rad. Beyond this point, which produces about 1.5×10^{-4} mole of SO_4 in the free liquid and about 6×10^{-5} moles in the supernate (per gram of resin), additional irradiation no longer produces a systematic increase in sulfate release. Generally similar behavior is observed for $\text{SO}_4^{=}$ and Cl^- in the NaCl form resin. In the free liquid, $\text{SO}_4^{=}$ and Cl^- yield saturate at about 2.0×10^{-4} and 2.5×10^{-4} moles (per gram of resin). In the supernatant liquid, $\text{SO}_4^{=}$ yields reach about 9×10^{-5} moles/g while Cl^- yields level off at about 4×10^{-4} moles/g.

On a fractional basis, maximum unbound $\text{SO}_4^{=}$ yields in the mixed bed system are roughly equivalent to those measured in the pure cation resin (Figure 3.3). In the NaCl form, although a significant fraction of the ion-exchange groups remain on the resin, practically all the available sodium is released after a dose of $\sim 5 \times 10^8$ rad - it is possible that the cations originally present in the IRN-77 component are released in an exchange process

involving positive ions produced by radiolytic scission of the functional groups in the IRN-78 component. [In contrast, preliminary data suggest that less than 10% of the $\text{SO}_4^{=}$ is bound in the anion resin as an exchangeable ion at high total doses. This is in agreement with the previous observation that the functionality of the anion resin is largely destroyed at a dose of 5×10^8 rad.] In the supernate, sulfate and chloride releases are fairly well balanced by sodium ion release (Table 3.7).

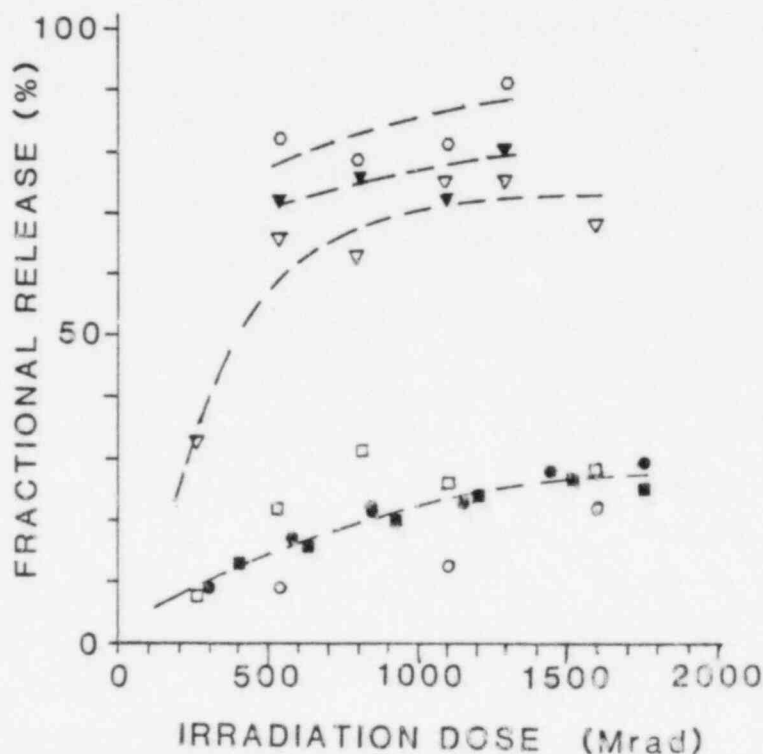


Figure 3.3 Fractional release of functional group decomposition products and exchangeable ions. \circ - Na^+ , IRN-150, NaCl form; ∇ - Cl^- , IRN-78 Cl^- form; \blacktriangledown - Cl^- IRN-150, NaCl form; \square - $\text{SO}_4^{=}$ IRN-150, NaCl form; \circ - $\text{SO}_4^{=}$ IRN-150, HOH form; \blacksquare - $\text{SO}_4^{=}$ IRN-77, Na^+ form; \bullet - $\text{SO}_4^{=}$ IRN-77 H^+ form.

Table 3.7

Ion Balance in Liquids Contacting Irradiated IRN-150 (Na^+Cl^-) Resin^a

Irradiation Dose (rad)	Free Liquid		Supernate	
	$\text{SO}_4^{=} + \text{Cl}^-$	$\text{Na}^+ + \text{H}^+$	$\text{SO}_4^{=} + \text{Cl}^-$	$\text{Na}^+ + \text{H}^+$
2.7×10^8	---	---	0.24	0.27
5.4×10^8	0.73	0.63	0.39	0.40
8.1×10^8	1.02	0.67	0.30	0.43
1.1×10^8	0.59	0.69	0.68	0.48
1.4×10^8	0.66	0.77	---	---
1.7×10^8	0.64	0.73	0.58	0.46

^aAll values given in meq/g resin; H^+ values from pH, including calculated contribution from H^+ incorporated in HSO_4^- at measured pH.

As mentioned earlier, amines (e.g., trimethyl amine) have been identified as decomposition products of irradiated anion resin (c.f., Gangwer et al., 1978; Swyler and Dayal, 1982b). In acidic solution these could be converted to ammonium forms. Table 3.7, however, provides no evidence to indicate that positive ions other than Na^+ and H^+ are present in significant quantities.

In Figure 3.4, the free liquid release in NaCl form and HOH form IRN-150 resin is compared with that observed earlier in Cl^- form IRN-78 resin. This analysis indicates that release of free liquid from the anion resin may be promoted in the acidic environment provided by the decomposition of the cation resin since the mixed bed resin is only about 57% anion resin by weight. The shrinkage is (and subsequent liquid release) confined almost entirely to the anion component, as shown in Figure 3.5.

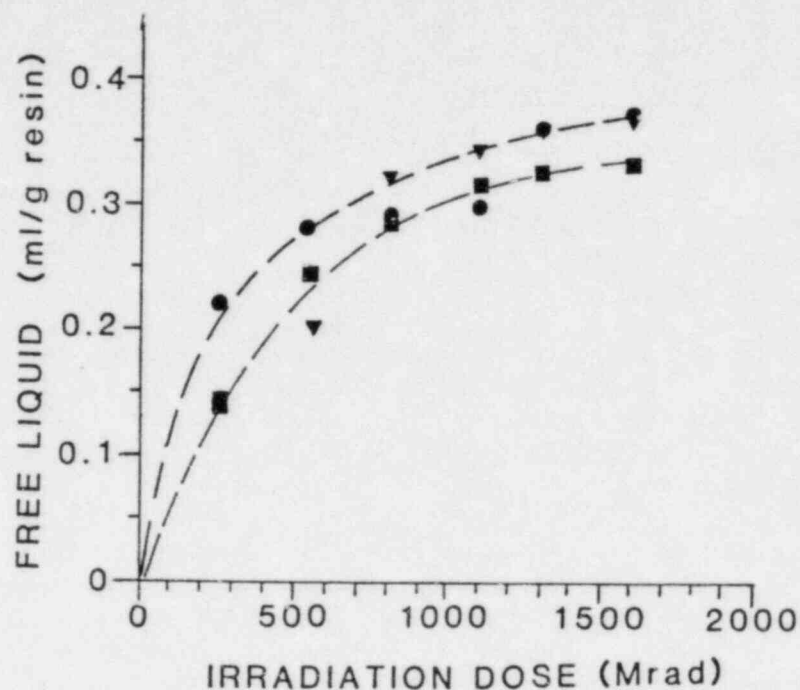


Figure 3.4 Free liquid release vs irradiation dose in IRN-78, ▼ - (Cl⁻); IRN-150, ● - (HOH); and IRN-150, ■ - (NaCl) resins.

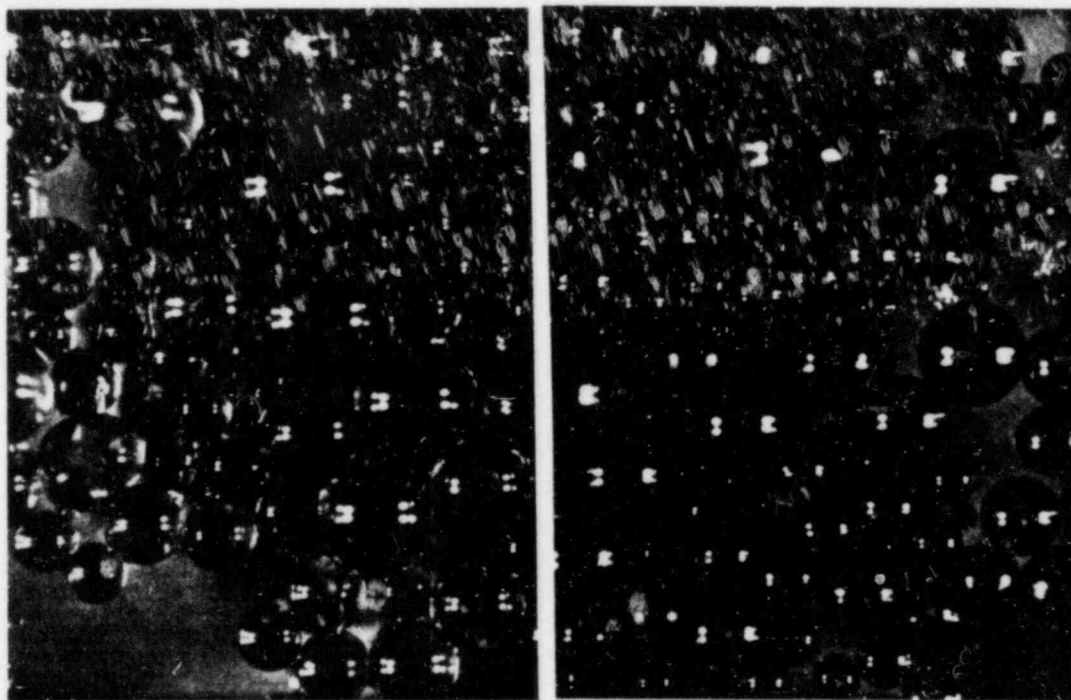


Figure 3.5 IRN-150 (HOH) form resin before (left) and after (right) irradiation to 1×10^9 rad. The cation component darkens under irradiation but does not undergo extensive shrinkage.

3.4 Radiolytic Oxygen Scavenging

Experiments were carried out to study the uptake of oxygen in irradiated resins, and the effect of irradiation atmosphere on resin decomposition. These experiments employed stainless steel irradiation cells, equipped with a pressure transducer. Results for samples irradiated in mixtures of air, helium and oxygen are given in Table 3.8.

The data do not indicate any pronounced variation in hydrogen generation in H^+ form resin with atmospheric composition. G-values for H_2 generation in an inert He environment are $1.03 \pm .19$; for irradiation in an atmosphere originally containing air, $G(H_2) = 1.24 \pm .19$. For samples irradiated in excess oxygen, $G(H_2) = 1.20$ for an initial oxygen pressure (air plus added oxygen) of 6 psi and $G(H_2) = 1.7$ for an initial oxygen pressure of 17 psi. This latter value, however, refers to a measurement at lower radiation dose rate (measurement 10). One atmospheric effect, however, was clearly evident. Samples of the H^+ form resin irradiated in an inert atmosphere showed a release of free liquid, which was not observed for irradiation under oxygen. The maximum free liquid loss was $\sim .04$ mL/g.

Table 3.8
Radiolytic Gas Generation for Resins Irradiated in Various Atmospheres

Sample Form	Radiation Dose (Rad)	Gas Composition									
		Before Irradiation (psi)			After Irradiation (psi)						
		Air	He	O ₂	He	H ₂	O ₂	N ₂	Ar	CO	CO ₂
(1) IRN-77 (H^+)	1.3×10^9	5.3	9.4	---	9.4	7.7	0.01	4.2	.08	.35	2.2
(2) IRN-77 (H^+)	9.7×10^8	---	15.0	---	Not analyzed						
(3) IRN-77 (H^+)	8.0×10^8	.150	---	---	---	5.9	0.06	11.6	.15	.58	1.9
(4) IRN-77 (H^+)	7.2×10^8	---	15.2	---	14.9	4.6	0.06	0.47	0.14	0.58	1.1
(5) IRN-77 (H^+)	8.0×10^8	14.7	---	---	---	7.19	0.04	11.05	0.13	0.05	2.45
(6) IRN-77 (H^+)	9.8×10^8	14.7	---	---	---	4.59	0.02	11.1	0.13	0.17	2.04
(7) IRN-77 (H^+)	9.6×10^8	---	15.7	---	15.20	7.93	---	---	---	0.50	1.961
(8) IRN-77 (H^+)	9.9×10^8	6.2	2.4	5.1 ^a	2.4	8.5	---	4.9	.05	0.67	3.9
(9) IRN-78 (OH^-)	4.2×10^8	---	4.0	13.5	3.9	13.5	---	---	---	0.23	.003
(10) IRN-77 (H^+)	5.5×10^8	---	1.2	17.2	1.30	6.7	.01	.01	---	0.31	1.3
(11) IRN-77 (H^+)	5.5×10^8	---	2.7	16.8	Not analyzed						

^aThe added oxygen in this sample was $^{18}O_2$. $^{18}O_2$ was not detected. $^{12}C^{16}O^{18}O$ was present at a partial pressure of 0.3 psi; $^{12}C^{18}O$ was present at a partial pressure of .07 psi.

For samples irradiated in an oxygen atmosphere, pressure vs time curves can be accurately resolved into a decrease due to oxygen uptake and a linear increase due to radiolytic gas generation. An example is shown below. A straight line is least squares fitted to the linear portion of the curve (Figure 3.6).

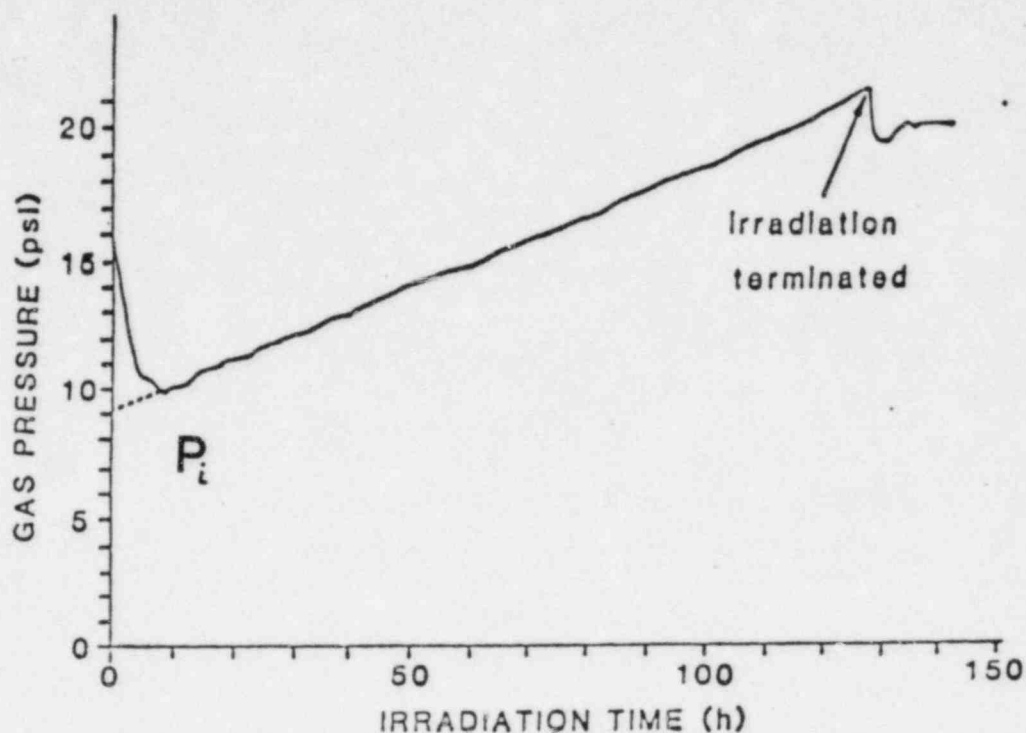


Figure 3.6 Gas pressure over H^+ IRN-77 resin during irradiation at 8×10^6 rad/h. The sample originally contained 6.8 psi of O_2 .

The straight line is then extrapolated to the origin and subtracted from the data. The resulting difference curve (Figure 3.7a) represents the pressure decrease due to radiolytic oxygen uptake, corrected for an assumed linear gas generation which occurs simultaneously. The linear hypothesis is supported by the fact that the pressure defined by the intercept of the fitted straight line (p_i , Figure 3.6) corresponds almost exactly to the total pressure of stable gases (He , N_2 , Ar) determined after the irradiation. Semi-logarithmic plots of the difference curves, (Figure 3.7b) which we take to represent the partial pressure of oxygen in the system, indicate that the oxygen scavenging follows first order kinetics. In Table 3.10, we give the rate constant for oxygen scavenging determined from the analysis.

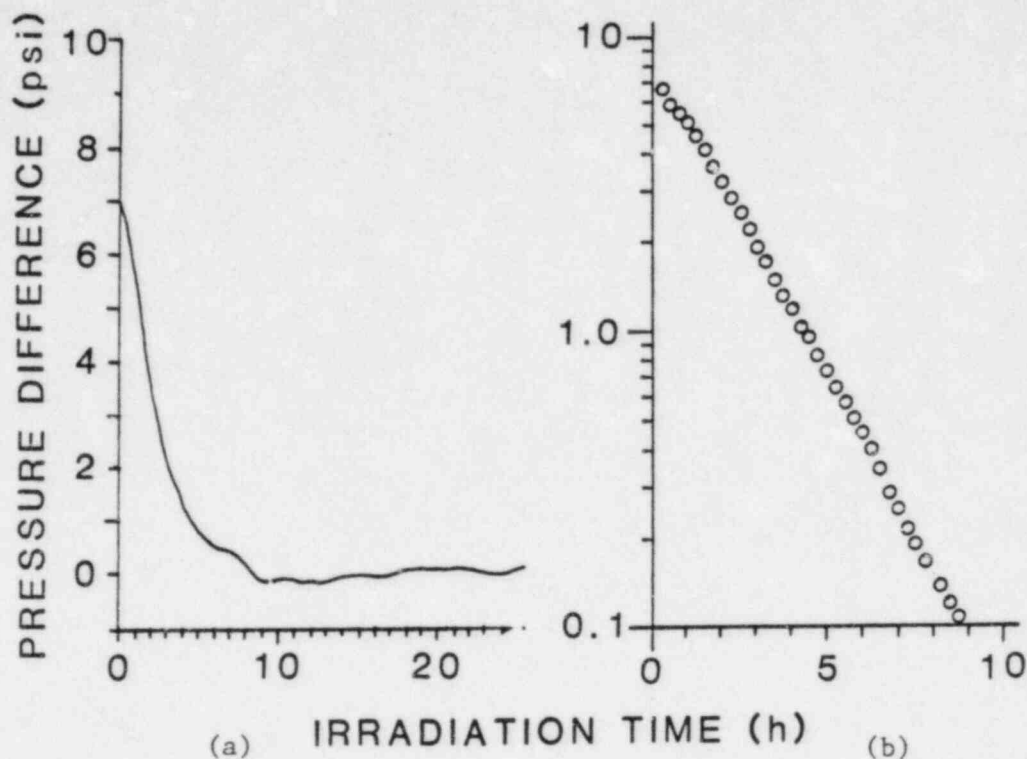


Figure 3.7 Linear (a) and semilogarithmic (b) plots of the difference between the data and the fitted straight line in Figure 3.14.

Table 3.9

Rate Constant for Radiolytic Oxygen Uptake

Resin Form	Amount (g)	Dose Rate (Rad)	K^a (g-Rad) ⁻¹
H ⁺	12	8×10^6	5.3×10^{-9}

^aK is the rate constant in the expression:

$$\frac{d[O_2]}{d} = K m [O_2]$$

Where $[O_2]$ = amount of oxygen in the gas phase over the irradiated resin sample,

m = mass of resin, in grams,

D = radiation dose, in rad.

For the present experimental conditions, K does not depend strongly on radiation dose rate or resin functionality. The maximum oxygen uptake observed in these experiments was $\sim 3.01 \times 10^{-3}$ moles, which corresponds to complete depletion of the oxygen initially present in measurement No. 10 (see Table 3.8). This uptake was accomplished at a dose of $\sim 2.6 \times 10^7$ rad in 12 g of resin. There are approximately 3×10^{-1} moles of carbon (and 3×10^{-2} moles of $-\text{SO}_3\text{H}$) in 12 g of fully swollen resin. If the oxygen scavenging involves only attack at the carbon atoms, a maximum $\sim 1\%$ of the available carbon atoms are oxidized in measurement No. 10.

4. CHARACTERIZATION OF IRRADIATION EFFECTS ON SOLIDIFIED FORMS AND CONTAINER MATERIALS (W. Becker and C. Anderson)

4.1 Solidification of Irradiated Resins

During this report period, no direct measurements on solidified forms were carried out. Plans are being formulated to begin solidification studies on resins from Epicor-II liner PE-16. In addition, mechanistic experiments were carried out which have direct bearing on the ability of irradiated resin/cement waste forms to withstand water immersion. These experiments are described in Section 5.

4.2 Irradiation Damage Studies in High Density Polyethylene

Experiments on the effects of irradiation in various environments on high density polyethylene continued during this report period. This task has been shifted to another NRC program, FIN A-3027, "Properties of Radioactive Wastes and Waste Containers." The progress of this work is reported under the rad-waste and container program.

5. MECHANISTIC STUDIES (W. Becker and C. Dodge)

Certain experiments were carried out investigating the mechanistic aspects of several effects described in Sections 3 and 4. Results of these experiments, and their interpretation are given in this section.

5.1 Role of Hydrogen Peroxide on Radiolytic Resin Decomposition

An experiment was conducted to examine the effect of hydrogen peroxide attack on resin in greater detail, and to isolate and effects due to auto degradation of the peroxide. A series of samples were made up each containing 5 g of resin in the "as delivered" hydrogen form. To each sample was added 20 mL of a serially diluted ACS grade 30.0% (8.8 M) hydrogen peroxide reagent from Fisher Scientific Company. The sample flasks were then swirled and stoppered. Control samples without resin were also made up as a check on auto degradation of the peroxide. In contrast to earlier measurements, where the electrode contacted the resin, pH measurements were made on 10-mL aliquots withdrawn from each sample and measured on a Beckman Model 4500 pH meter using a Beckman combination glass electrode No. 71124. Analyses were made initially after make up and two more times over a 45-day period. The results are presented in Table 5.1.

Table 5.1

pH and Sulfate Content of Peroxide-Resin Solutions

(H ₂ O ₂) ^a Moles/L	pH			(SO ₄ ²⁻) Moles/L			SO ₄ ²⁻ Yield Moles/g Resin		
	Day 1	Day 22	Day 45	Day 1	Day 22	Day 45	Day 1	Day 22	Day 45
0	3.4	3.4	3.1	3.8x10 ⁻⁵	5.7x10 ⁻⁵	8.0x 10 ⁻⁷	1.5x10 ⁻⁷	2.3x10 ⁻⁷	3.2x10 ⁻⁷
8.8x10 ⁻⁶	3.4	3.3	3.2	4.1x10 ⁻⁵	5.0x10 ⁻⁵	5.4x10 ⁻⁵	1.6x10 ⁻⁷	2.0x10 ⁻⁷	2.2x10 ⁻⁷
8.8x10 ⁻⁵	3.6	3.1	3.0	4.0x10 ⁻⁵	6.3x10 ⁻⁵	1.1x10 ⁻⁴	1.6x10 ⁻⁷	2.5x10 ⁻⁷	4.4x10 ⁻⁷
8.8x10 ⁻⁴	3.4	2.9	2.7	3.7x10 ⁻⁵	1.2x10 ⁻⁴	1.5x10 ⁻⁴	1.5x10 ⁻⁷	4.8x10 ⁻⁷	6.0x10 ⁻⁷
8.8x10 ⁻³	3.4	2.7	2.5	5.4x10 ⁻⁵	3.3x10 ⁻⁴	5.1x10 ⁻⁴	2.2x10 ⁻⁷	1.3x10 ⁻⁶	2.0x10 ⁻⁶
8.8x10 ⁻²	3.6	2.7	2.4	6.1x10 ⁻⁵	4.8x10 ⁻⁴	7.5x10 ⁻⁴	2.4x10 ⁻⁷	1.9x10 ⁻⁶	3.0x10 ⁻⁶
8.8x10 ⁻¹	3.3	2.7	2.6	7.4x10 ⁻⁵	3.9x10 ⁻⁴	7.8x10 ⁻⁴	3.0x10 ⁻⁷	1.6x10 ⁻⁶	3.1x10 ⁻⁶
8.8	2.5	1.7	1.44	2.5x10 ⁻⁴	1.5x10 ⁻³	2.9x10 ⁻³	1.0x10 ⁻⁶	6.0x10 ⁻⁶	1.2x10 ⁻⁵

^aSamples made from 5 g of IRN-77 resin plus 20 mL of peroxide solution.

Results for irradiated resin-peroxide solutions are shown in Table 5.2. The trends for unirradiated control samples are generally similar to those in Table 5.1; for the sample containing 8.8 molar H₂O₂, the pH values in Table 5.2 are somewhat greater (2.5 vs 1.7) and SO₄²⁻ yields somewhat less (1.9 x 10⁻⁶ vs 6 x 10⁻⁶ moles/g) than those in Table 5.1.

Table 5.2

pH and Sulfate Content of Irradiated and Unirradiated Resin-Peroxide Solutions^a

Contact Time Irradiation Dose Rate (rad/h)	Supernatant Initial (H ₂ O ₂) (moles/L)	pH		(SO ₄ ²⁻) (moles/L)		SO ₄ ²⁻ Yield (moles/g resin)	
		Day 10	Day 20	Day 10	Day 20	Day 10	Day 20
0	0	3.8	3.2	2.4 x 10 ⁻⁵	5.3 x 10 ⁻⁴	4.3 x 10 ⁻⁸	8.8 x 10 ⁻⁷
0	8 x 10 ⁻³	3.0	—	2.3 x 10 ⁻⁴	3.7 x 10 ⁻⁴	4.0 x 10 ⁻⁷	6.1 x 10 ⁻⁷
0	8.8	2.8	2.5	5.1 x 10 ⁻⁴	1.1 x 10 ⁻³	8.7 x 10 ⁻⁷	1.9 x 10 ⁻⁶
1.5 x 10 ⁶	0	0.8	0.6	0.18	0.32	3.0 x 10 ⁻⁴	5.5 x 10 ⁻³
1.5 x 10 ⁶	8 x 10 ⁻³	0.9	0.6	0.15	0.31	2.5 x 10 ⁻⁴	5.0 x 10 ⁻³
1.5 x 10 ⁶	8.8	0.8	<0.6	0.18	0.31	3.0 x 10 ⁻⁴	5.0 x 10 ⁻³

Solution = 5 mL of H₂O₂ solution contacted with 3-g IRN-77 H⁺ resin for the times indicated.
Half the samples were irradiated at 1.5 x 10⁶ rad/h during contact.

For the experimental conditions of Table 5.2, the pH and SO₄²⁻ yields in irradiated resin are largely independent of H₂O₂ concentration. On a per gram basis, the SO₄²⁻ yields are comparable to those found for resins irradiated in the swollen form at corresponding doses. The pH values are comparable to those found earlier for resins irradiated in deionized water, allowing for the difference in resin-water ratios.

In the present experiments then, any effect of added H_2O_2 on decomposition of the functional group is obscured by the irradiation effects. Samples irradiated in contact with peroxide, however, exhibit a gross physical degradation which was not observed in a sealed environment, or for samples irradiated in deionized water (Figure 5.1).

This information, implies that, during irradiation, hydrogen peroxide formation is not a rate-limiting step in radiolytic attack on the functional group. Hydrogen peroxide clearly attacks the resin backbone during irradiation. A similar attack might be expected for samples irradiated in oxygen-rich environments, - for example, in an open-air system. The additional acidity observed in unirradiated samples contacted with peroxide may be partly attributed to formation of other species, such as sulfonic acid and partly to formation of H_2SO_4 . The balance between the two would reflect the extent of sulfonation reactions (Morrison and Boyd, 1960).

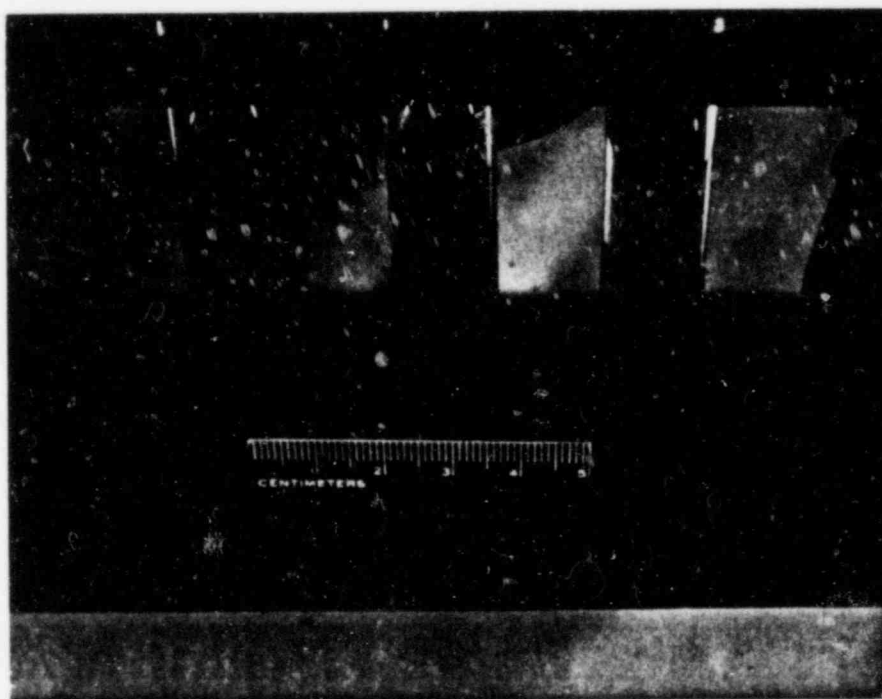


Figure 5.1 IRN-77 resin irradiated in H_2O_2 solutions.
Left - resin + 8 M H_2O_2 ; center - resin + .008 M H_2O_2 ; right - resin + deionized water.

5.2 Uptake of Acidic Species by Irradiated IRN-77 Na^+ Form Resin

Generally, if scission of the $-SO_3^-Na^+$ exchange group produces soluble sulfur forms (SO_4^{2-} , etc.), one expects decomposition products such as $NaHSO_4$, containing cation and sulfur in a 1:1 ratio. The additional H^+

ion required by stoichiometry would be presumably produced in the conversion of -SO_3^- to $\text{SO}_4^{=}$, as found in H^+ form resin. As indicated earlier, the data do not fit this picture. We have considered, whether in the sodium form resin, sodium hydrogen sulfate is converted to sodium sulfate by hydrogen-sodium exchange at an undamaged functional site on the sodium form resin:



This would account for the protective effect, relative to radiolytic acid product formation, observed with Na^+ form resin. One attractive feature of this mechanism is that it does not require that Na^+ protect the exchange groups against intrinsic damage. This would be contrary to experience (Egorov and Novokov, 1967).

To directly test the buffering hypothesis, titrations were carried out on irradiated Na^+ form resin. Two grams of this resin had been stored under 100-mL deionized water for several months, following removal from the irradiation tube. The supernatant was removed from the resin and each were titrated separately with 0.1 M NaOH 10% NaCl. Results are given in Table 5.3.

Table 5.3
Titration Data for Irradiated Na^+ Form Resin

Radiation Dose (rad)	Supernatant pH		Meq H^+ /g Resin		
			Supernatant		Resin
	Fresh	Aged	as pH	Titrated	Titrated
0	5.1	5.0	.005	0.037	0.05
4.0×10^7	4.2	4.1	.004	0.009	0.06
1.0×10^8	3.8	3.6	.008	0.020	0.10
1.7×10^9	2.8	2.7	.08	0.16	0.19

In heavily irradiated samples, a substantial fraction (~9%) of the available exchange sites are in the H^+ form. This confirms that the acidity of free liquids contacting irradiated IRN-77 resin is reduced by ion-exchange processes. At pH 2.8, more than 50% of the H^+ is contained in the resin; at lower pH this fraction would presumably be greater. If NaHSO_4 were the only species produced in the scission of the functional group, the ratio of total $\text{SO}_4^{=}$ to total H^+ (free and bound in the resin) should be 2:1. Preliminary values for the $\text{SO}_4^{=}/\text{H}^+$ ratios at 4×10^7 , 1×10^8 , and 1×10^9 rad are 1.8, 2.6, and 3.4, respectively; further analysis is under way.

5.3 Effect of Irradiation on Resin Swelling Behavior

Measurements were carried out to determine the effect of irradiation on the swelling force exerted by irradiated resins upon rehydration. The swelling force was determined by drying resins which had been irradiated in the fully-swollen form and then rehydrating the resins (~1.5 g) in a constant volume equipped with a load cell. The aim is to simulate conditions which might occur when a partially dehydrated resin bead in a cement matrix is exposed to water. Data are given in Table 5.4. A dramatic decrease in swelling force is evident for high radiation dose rates, although the beads did not shrink significantly as a function of irradiation.

Table 5.4

Swelling Force Exerted by Irradiated IRN-77 Resin

Resin Form	Irradiated Dose (rad)	Irradiated Environment	Swelling Force ^a (pounds)
H+	0	----	335 + 43
H+	2.4×10^5	sealed	208
H+	4.5×10^8	sealed	278 + 60
H+	1.0×10^9	sealed	21 + 4
H+	1.0×10^9	vented	7.7 + 2.5
Na+	0	----	257 + 4
Na+	1.0×10^5	sealed	218 + 1
Na+	7.5×10^8	sealed	143 + 41
Na+	1.1×10^9	sealed	33 + 1
Na+	1.0×10^9	vented	14 + 6

^aForce exerted against a 0.5 in.-diam piston upon rewetting the dried resin in a fixed volume.

The rather precipitous decrease in swelling force between $\sim 7 \times 10^8$ and 1×10^9 rad may be due to somewhat different experimental conditions - samples irradiated to 10^9 rad were exposed to different radiation dose rates and resin-oxygen ratios than those at lower doses. Samples irradiated under vented conditions (i.e., exposed to atmospheric O₂) underwent a relatively greater hydration. The increased waste loading latitude found for solidified forms containing irradiated resins (Swyler and Dayal, 1982) may be largely attributable to this decrease in swelling force.

6. DISCUSSION AND CONCLUSIONS

The major results obtained during this report period may be summarized as follows:

Characterization of irradiated resin from Epicor-II liner PF-3 has been initiated. The resin seems relatively dry and does not show any obvious visual evidence of massive degradation. The activity in the core is localized in a zone extending through the upper 1/3 of the core. This zone contains material which is different in both color and texture from the remainder of the core.

Characterization at this point is very preliminary. The fact that the resin may have dried during sampling or storage makes a moisture content determination somewhat ambiguous. This is unfortunate, since moisture is an important parameter in radiation damage formation. The fact that the activity is concentrated in the top 1/3 of the liner, in a band of material which is visually dissimilar from the rest of the core, indicates that the radiation durability of this material will be of particular interest.

With the exception of H^+ , supernatant acidity for heavily irradiated IRN-77 resin is largely insensitive to the counter ion.

For resin in the Na^+ , Cs^+ , NH_4^+ , Fe^{++} , and Fe^{+++} forms, pH values lie within 0.5 units of each other, over the range from 2.6×10^8 to 1.1×10^9 rad. This behavior does not simply reflect the attack on the functional group since $SO_4^{=}$ yields do vary with resin loading. Fe^{+++} , for example, significantly reduces the scission of the functional group (as determined by soluble $SO_4^{=}$ yields) in accordance with the observations of other workers. Ion balances indicate that the supernatant in the Fe form resin contains both sulfate salts and sulfuric acid. Titration data in Na^+ form resin demonstrates that the acid-salt balance may be significantly affected by an ion-exchange process in the undamaged resin. It is not clear yet whether this process, and the limited dissociation of bisulfate ion, can account for the similarity of pH values at different resin loadings. Other alternatives, including formation of organic acids, are under study.

Radiation damage in cation resin (acidity and functional group attack) is reduced but not eliminated when resins are irradiated in the dry form. Cation resins irradiated under water show the same acidity as resins irradiated in the fully swollen (dewatered) form.

Radiolytic attack and/or release of functional group decomposition products is promoted when the resin is irradiated in a moist state. This effect may involve either attack by water radiolysis products, transport of decomposition products within the pore water, or back-reactions and "cage effects" which are dependent on the extent of resin swelling. Such effects have been proposed to explain the dependence of radiation damage formation efficiency and degree of cross-linking (Egorov and Novokov, 1967). The swelling effect may be predominant at least in terms of acid species formation, since once the

resins are fully swollen, excess water present during irradiation does not effect acidity. Certain features of radiolytic resin decomposition can also be produced by contacting the resins with hydrogen peroxide. Hydrogen peroxide formation by water radiolysis, however, is apparently not a rate-limiting step in radiolytic attack on the functional group.

Use of resins in the mixed bed form does not protect against the formation of acidic conditions upon irradiation.

Indeed, the converse may be true in some cases. Preliminary comparison between Na^+ form cation and NaCl form mixed bed resins indicate that, on a percentage basis, acidity, soluble sulfate and cation release, and free liquid formation may be somewhat promoted in the mixed bed. It is possible that this effect involves the release of free liquids by the anion resin. As mentioned previously, however, contact with excess water alone during irradiation does not significantly effect the formation of acidic species. In the irradiated HOH form mixed bed resin, pH is somewhat elevated in comparison to the H^+ form cation, but the resin remains strongly acidic.

7. REFERENCES

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