TECHNICAL REPORT

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# LOW-LEVEL WASTE PACKAGE AND ENGINEERED-BARRIER STUDY

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## QUARTERLY PROGRESS REPORT

## OCTOBER-DECEMBER 1987

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APRIL 1988

# NUCLEAR WASTE AND MATERIALS TECHNOLOGY DIVISION

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#### LOW-LEVEL WASTE PACKAGE AND ENGINEERED-BARRIER STUDY

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#### April 1988

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#### ABSTRACT

Gamma-irradiation and sulfate-attack tests were carried out on Portland I, Portland V, and Ontario-Hydro-type cement mortars to determine their suitability as low-level waste barriers. Gamma doses to  $5.0 \times 10^8$  rad do not detrimentally affect compressive strength. For the sulfate-attack studies it was surprising to find that the Ontario-Hydro-type composition, which included silica fume, showed the least resistance to attack.

High-density polyethylene creep tests are being carried out to determine which failure/degradation modes could be important if this material is used for waste containers. Irradiation-embrittlement tests are also being performed on stressed U-bend specimens to estimate the rate of damage.

### CONTENTS

																													Page
ABS LIS LIS ACK	TRACT TOFF TOFT	IGURES ABLES GMENTS	· · · · · · · · · · · · · · · · · · ·	•••••			•••••	•	• • • •	•••••	••••	•••••	•••••	•••••	•••••	•		•		:		• • • •	• • • •	•••••	• • • •	• • • • •	•••••	•••••	iii vii ix xi
1.	INTRO	DUCTIO	DN .															•		•	•								1
2.	MECHAI	NICAL IALS.	AND	CH •	EM.	CAI	L :	ST/	ABI		T)	• •	DF	C8	EME	NT.	-8	BAS	SEC.		STF	200	сти •	JR/	۱L •				3
	2.1	Sulfa Gamma	ate- a-lr	Att rad	ack	t To	est n 1	s Tes	sts	•	:	:	•	•	:	:	•	•	:		:	:	:	:	•	•	:	:	3 5
3.	DEGRA	DATION	ME	СНА	NIS	SMS	IN	4 }	HIG	iH-	DE	ENS	SIT	ΓY	PO	LY	EI	THY	LE	ENE	. (	(HC	PE	:)					9
	3.1	Overv	iew	of	Re	se	arc	h	Ac	ti	vi	iti	ies	5.	in	•	•	·	•		• •				•	•	•	•	9
	3.3	Envir	cial	ent	eep	B	eha	ivi	ior	:			:	:	:	•		•	*	•	•			*	•	:	:	:	9 21
4.	BIODE	EGRADA	TIO	N O	F	ON	-E)	(C)	AN	IGE	M	IEC	)IA	١.															33
5.	REFER	RENCES																1											35

### LIST OF FIGURES

Figure	2.1	Typical arrangement for 10 in (25.4 cm) long cement mortar bars immersed in solution for sulfate-attack tests. In this case, Portland V bars are immersed in 2.1% Na <sub>2</sub> SO <sub>4</sub> solution
Figure	2.2	Portland I cement mortar bars after an 8 h oven- drying cycle
Figure	3.1	Appearance of Type I (a), Type II (b), and Type III (c) Marlex C-100 HDPE U-bend specimens gamma irradiated to 2.1 x 10 <sup>6</sup> rad (A), 1.3 x 10 <sup>7</sup> rad (B), and 6.7 x 10 <sup>8</sup> rad (C). Individual unirradiated Type I, Type II, and Type III control specimens are shown at the bottom of the figure. Magnification 0.8 X
Figure	3.2	Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples. Specimens are unirradiated controls. Specimen numbers given above each sketch 12
Figure	3.3	Crack patterns in unirradiated Type I Marlex CL-100 HDPE U-bend samples held at 10°C for 350 d. Specimen numbers given above each sketch
Figure	3.4	Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples prior to gamma irradiation at 1.4 x 10 <sup>3</sup> rad/h. Specimen numbers given above each sketch
Figure	3.5	Crack patterns in Type I Marlex CL-100 HDPE U-bend samples after gamma irradiation to 7.5 x $10^6$ rad at a dose rate of 1.4 x $10^3$ rad/h. Specimen numbers given above each sketch
Figure	3.6	Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples prior to gamma irradiation at $8.4 \times 10^3$ rad/h. Specimen numbers given above each sketch
Figure	3.7	Crack patterns in Type I Marlex CL-100 HDPE U-bend samples after gamma irradiation to 6.0 x $10^7$ rad at a dose rate of 8.4 x $10^7$ rad/h. Specimen numbers given above each sketch

Page

## LIST OF FIGURES (continued)

PAGE

Fig	ure	3.8	Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples prior to gamma irradiation at 4.4 x 10 <sup>5</sup> rad/h. Specimen numbers given above each sketch
Fig	ure	3.9	Crack patterns in Type I Marlex CL-100 HDPE U-bend samples after gamma irradiation to $1.3 \times 10^9$ rad at a dose rate of 4.4 x $10^5$ rad/h. Specimen numbers given above each sketch
Fig	ure	3.10	Fine cracking in Type II Marlex CL-100 HDPE U-bend specimens (top row of 8) irradiated to 6.0 x $10^7$ rad (at 8.4 x $10^3$ rad/h). Note that the cracks are not in the apex region. Magnification 1.7 X
Fig	ure	3.11	Cracking in Type I (bottom row) and Type III (top row) Marlex CL-100 HDPE U-bend specimens irradiated to 6.0 x $10^7$ rad (ct 8.4 x $10^3$ rad/h). Note that the cracks in the Type III specimens are not in the apex region. Magnification 1.7 X
Fig	ure	3.12	Stress-rupture results for Marlex CL-100 HDPE tested at 20°C in various environments
Fig	ure	3.13	Elongations at failure for Marlex CL-100 HDPE tested at 20°C in various environments
Fig	ure	3.14	Creep of Marlex CL-100 HDPE in various environments at 8.27 MPa (1200 psi)
Fig	ure	3.15	Creep of Marlex CL-100 HDPE in various environments at 9.65 MPa (1400 psi)
Fig	ure	3.16	Creep of Marlex CL-100 HDPE in various environments at 10.34 MPa (1500 psi)
Fig	ure	3.17	Creep of Marlex CL-100 HDPE in various environments at 11.03 MPa (1600 psi)

## LIST OF TABLES

Page

Table	2.1	Length increase measurements on cement mortar bars exposed to alternate wet-dry cycling in $2.1\%$ Na <sub>2</sub> SO <sub>4</sub> solution or deionized water
Table	2.2	Compressive strengths for cement-mortar samples gamma irradiated for 48.5 d to 5 x $10^8$ rad
Table	3.1	Test matrix for crack-propagation studies on irradiated Marlex CL-100 miniature U-bend specimens
Table	3.2	Cracking in Type I HDPE U-bend specimens exposed to gamma irradiation and air at 9°C
Table	3.3	Creep test data for Marlex CL-100 HDPE tested in air and deionized water at room temperature
Table	3.4	Creep test data for Marlex CL-100 HDPE tested in various environments at room temperature

ix

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#### 1. INTRODUCTION

Since the publication of NRC Rule 10 CFR 61, "Licensing Requirements for Land Disposal of Radioactive Wastes," and the NRC Technical Position on Waste Form, there has been action by industry to develop improved low-level waste forms, containers, and engineered barriers. Over the last four years the NRC received a large number of Topical Reports for review as a part of license applications for waste forms, containers, and engineered barriers. During review of the reports, it was recognized that the data provided by the vendors are usually insufficient or questionable. It was also recognized that conventional test methods, such as ASTM test procedures, may not be applicable to certain waste package materials and that analytical procedures have not been established to interpret the test data with respect to the performance objectives in the regulation.

The objective of this research project is to develop an adequate data for performance review of low-level waste package materials identified in rendors' topical reports and to provide a basis for technical guidance to states and applicants. This project will also review and improve, if needed, the existing tests methods for application to materials and to the design of waste packages and engineered barrier concepts. Methods will be developed to extrapolate short-term test data to long-term performance of waste packages as required in the regulation.

To date, five research tasks have been specified by NRC and BNL. They include:

- Task 1: Development of Work Plan.
- Task 2: Mechanical and Chemical Stability of Concrete-Based Structural Materials.
- Task 3: Degradation Mechanisms in High-Density Polyethylene (HDPE).
- Task 4: Biodegradation of Ion-Exchange Media.
- Task 5: Development of HDPE Testing Protocol (to be initiated in FY 1988).

Task 1 (Development of Work Plan) has been completed. Work in Task 2 is at an advanced stage, but will be significantly curtailed after this reporting period because of reduced funding. Task 3 is continuing on the long-term creep behavior of HDPE. Data from this study will be used in Task 5 which will shortly commence. Experimental work in Task 4 has been completed and a Topical Report is being prepared.

#### 2. MECHANICAL AND CHEMICAL STABILITY OF CEMENT-BASED STRUCTURAL MATERIALS

Three types of cementitious materials were prepared for this study, including Portland I and V, and Ontario Hydro Cement Mortars (OHCM). These are used for both sulfate-attack and gamma-irradiation tests. Details of specimen preparation and testing were given in the previous quarterly report (Soo, and others, 1987).

#### 2.1 Sulfate - Attack Tests

These are accelerated tests to determine the susceptibility of cementitious harrier materials to deterioration from sulfates which are present in soils in contact with the cement. The BNL procedure is based on that developed by Kalousek (1976). He showed that sulfate attack effects could be accelerated by a factor of eight if alternate wet-dry cycling of samples was adopted in place of continuous immersion in sulfate solution.

The BNL immersion/drying cycle is:

Step 1: Immersion of specimens in 2.1% Na<sub>2</sub>SO<sub>4</sub> solution (or deionized water for the control tests) at room temperature for 16 h.

Step 2: Forced-air drying of the specimens for 7 h 40 min at  $54 \pm 1^{\circ}$ C.

Step 3: 20 min cooling of the specimens in still air.

Step 4: Repeat Step 1.

All testing begins with an immersion cycle with specimens placed in plastic containers of  $Na_2SO_4$  solution (or deionized water). Glass rods are placed on the bottoms of the containers to assure solution contact on all sides of the test bars. During weekends the samples are left in the immersion cycle and they accumulate 64 h of soaking during this period

Four replicate mortar bars were used for both the sulfate-attack tests and their corresponding controls. Each bar measures  $10" \times 1" \times 1"$  $(25.4 \times 2.54 \times 2.54 \text{ cm})$ . Figure 2.1 shows a typical arrangement for samples immersed in either 2.1% NaSO, or deionized water baths. Shown in Figure 2.2 are eight mortar bars that have been placed on a stainless steel cradle prior to being transferred to an oven for the drying portion of the sulfate-attack test. Although difficult to see, the mortar bars do not contact the metal cradle directly, but are supported on quartz rods for efficient air circulation.

To date, the number of cycles accumulated for the Portland I, Portland V, and Ontario Hydro formulations are 60, 50, and 45, respectively. No obvious sample deterioration has been observed for any of the deionized-water-immersed bars, or for the Portland cement mortar bar mixes immersed in the 2.1% NaSO<sub>4</sub> solution. However, this is not the case for the sulfate immersed OHCM bars. Numerous hairine cracks were observed, not only on each surface near the ends of each bar, but also 1 rger and deeper hairline cracking occurred at the center of the bar, radiating in every direction. These OHCM bars will be closely observed over the next several months to monitor the rate of degradation.



Figure 2.1 Typical arrangement for 10 in (25.4 cm) long coment mortar bars immersed in solution for sulfate-attack tests. In this case, Portland V bars are immersed in 2.1% Na<sub>2</sub>SO<sub>4</sub> solution.



Figure 2.2 Portland I coment mortar bars after an 8 h oven-drying cycle.

Length change measurements were performed for the first time during this quarter. The measurements were made on the Portland I, Portland V, and Ontario Hydro formulations after total test times of 71, 69, and 74 d, respectively. The specimens during these periods had accumulated 48, 45, and 44 cycles, respectively. Table 2.1 shows the data obtained. Measurements are in inches based on readings taken from a comparator purchased according to ASTM Standard C490 - "Apparatus for Use in Measurement of Length Change of Hardened Cement Paste, Mortar, and Concrete." The effective initial gagelength of each bar is 10.00 inches.

Portland V cement is specially formulated to resist sulfate attack. As such, it should show significantly superior behavior compared to the more standard Portland I material. This is confirmed from the data in Table 2.1. In the 2.1 pecent  $Na_2SO_4$  solution, Portland V cement mortar shows a length increase which is only about one-fifth of that for Portland I samples. In the deionized water tests the Portland V specimens actually show a small decrease in length.

The most surprising observation is the poor performance of the Ontario Hydro type samples. These contained silica fume to minimize porosity and inhibit water absorption. In the  $Na_2SO_4$  tests, these samples showed length increases approximately double those for Portland I cement, and were approaching the 0.5 percent length increase which is the arbitrary value for failure (Kalousek, 1976). As mentioned above, the Ontario Hydro type samples were starting to crack, which is clear evidence for degradation.

Testing of the specimens will continue for a short time only, after which this Task will be terminated due to reduction of funding.

#### 2.2 Gamma-Irradiation Tests

The test materials are similar to those used in the sulfate-attack tests, but are in the form of 1 in (2.54 cm) cubes to facilitate irradiation and compression testing. Details of sample preparation and irradiation are given in the last quarterly report (Soo, and others, 1987). A sufficient number of samples was made so that compression tests could be carried out on unirradiated control specimens maintained at 6-9°C (the gamma-irradiation temperature) and room temperature (21°C), as well as on the irradiated cubes.

During this quarter, the cubes irradiated in air at a gamma dose rate of  $4.3 \times 10^5$  rad/h had achieved the first target dose of  $5 \times 10^8$  rad. They were compression tested together with the two sets of unirradiated controls. All samples were compression tested with the cube aligned so that its top and bottom surfaces, as cast, were normal to the direction of loading. Prior to mechanical testing, the top and bottom surfaces were "capped" with a special compound to ensure that they were parallel. The compressive strength data are shown in Table 2.2. Reproducibility was quite good.

The following conclusions may be drawn:

 a) Portland V cement samples are stronger than Portland I samples. Ontario Hydro type specimens are much stronger than the Portland cement specimens.

Specimen	Test Solution	Test Time(d)	Number of Cycles	Initial Bar Measurements(in)	Final Bar Measurements(in)	Length Change(in)	1 Change(1)
Portland I							
1	DIW	71	48	0,1810	0.1820	0.0010	0.01
2	DIW	71	48	0,1785	0.1790	0.0005	0.01
4	DIW	71	48	0,1770	0.1775	0,0005	0.01
5	DIW	71	48	0.1740	0.1745	0.0005	0.01
8	Na . 50	71	48	0.0470	0.0715	0.0245	0.25
9	Na SO	71	48	0.0335	0.0580	0.0245	0.25
10	Na 50	71	48	0.1780	0.2000	0.0220	0.22
10	Na 250 4	71	48	0.1800	0.2010	0.0210	0.21
Portland V							
	014	69	45	0 1605	0 1595	-0.0010	-0.01
2	014	69	45	0 1625	0.1615	-0.0010	-0.01
3	DIW	69	45	0.0470	0.0460	-0.0010	-0.01
4	DIW	69	45	0.0340	0.0330	-0.0010	-0.01
45	Na SO	50	45	0 1845	0 1895	0.0050	0.05
6	Na S()	69	45	0.1790	0 1835	0.0045	0.05
7	Na SO	60	45	0.0270	0.0335	0.0065	0.07
0	Na 250 4	60	45	0.0270	0.0605	0.0005	0.06
0	Na 250 4	09	40	0.0550	0.0005	0.0055	0.00
Ontario Hyd	го Туре						
2	DIW	74	44	0.1710	0.1770	0.0060	0.06
4	DIW	74	44	0.0445	0.0515	0.0070	0.07
5	DiW	74	44	0.1600	0.1665	0.0065	0.07
6	DIW	74	44	0.1525	0.1580	0.0055	0.06
7	Na SO	74	44	0.0250	0.0690	0.0430	0.43
8	Na SO,	74	44	0.0410	0.0875	0.0465	0.47
9	Na SO.	74	44	0,1565	0.1900	0.0335	0.34
11	Na SO	74	44	0.0300	0.0800	0.0500	0.50
Note:							

# Table 2.1 Length increase measurements on cement mortar bars exposed to alternate wet-dry cycling in 2.1% Na $_2$ SO $_4$ solution or deionized water.

- b) Irradiation to 5 x  $10^8$  rad does not cause a strength increase for Portland I and Ontario Hydro type materials compared to materials cured at 8°C and 21°C.
- c) Irradiation to  $5 \times 10^8$  rad appears to give a small increase in strength for Portland V cement mortar compared to unirradiated controls.

Work on this Task will shortly be terminated due to reduction in funding. However, compressive strength tests will be carried out on samples when they have reached a target dose of  $10^9$  rad.

	Compressive Strength (psi)								
Cement - Mortar Type	Unirradiated Cured at 21°C	Unirradiated Cured at 8°C	Irradiated at 9°C						
Portland I	5310±164(1)	5045±733	5150±71						
Portland V	5380±252	5483±76	5925±248						
Ontario Hydro Type	8320±641	8283±157	8150±71						
Note:									
(1) Standard devia	tion based on tests	on three samples.							

Table 2.2 Compressive strengths for cement-mortar samples gamma irradiated for  $48.5 \text{ d to } 5 \times 10^8 \text{ rad.}$ 

#### 3. DEGRADATION MECHANISMS IN HIGH-DENSITY POLYETHYLENE (HDPE)

#### 3.1 Overview of Research Activities

High-density polyethylene is currently being used as a high-integrity container material for low-level wastes. Because of the need for such containers to maintain their structural integrity for at least 300 years (NRC Technical Position on Waste Form) potential failure/degradation modes must be determined for realistic environmental conditions. These include consideration of mechanical stress, gaseous/liquid environments within and external to the container, and the gamma radiation field.

In some instances it is necessary to test under conditions more aggressive than those anticipated under shallow-land burial conditions so that failure or degradation modes can be more quickly identified and their relative importance assessed.

A combination of simple inexpensive tests (stressed U-bend samples) and more sophisticated longer-term uniaxial creep tests are being used to define the ranges of conditions for which mechanical failure/degradation is important. The test environments include Igepal CO-630, turbine oil and liquid scintillation fluid as well as air and deionized water (DIW), the control environments. Igepal CO-630 is a surfactant specified in standard ASTM tests for environmental stress cracking. Turbine oil is a possible constituent of low-level waste generated at reactor power plants, and is used in the current tests because of its known detrimental behavior to many types of plastic. Liquid scintillation fluids are not likely to be disposed of in burial sites at this time because of more stringent controls on their disposal. However, they are being evaluated here because they are representative of the class of organic solvents containing toluene and xylene. As such they will give valuable insights regarding a type of potential failure or degradation mode of HDPE.

In addition to the above-mentioned test environments, the effect of gamma irradiation on mechanical properties is being studied. Samples of HDPE are being irradiated in the BNL gamma irradiation test facility.

A description of the various subtasks is given below.

#### 3.2 Crack Initiation and Propagation in a Gamma-Radiation Environment

Crack initiation and propagation is important in stressed HDPE containers because of the anticipated embrittlement by gamma irradiation. A simple inexpensive test was developed at BNL involving the use of static "U-bend" samples exposed to air and gamma radiation. Early tests were carried out on relatively large U-bends made by bending strips of HDPE measuring 25 x 2.5 x 0.32 cm (10" x 1" x 0.125"); see the last quarterly report (Soo, and others, 1987). A more comprehensive set of tests was later initiated to obtain more detailed statistical data on crack initiation and propagation. These were on miniature U-bends manufactured from HDPE strips measuring 10.2 x 1.27 x 0.32 cm (4" x 0.5" x 0.125"). Holes were drilled at distances of 1.27 cm (0.5") from each end of the strips so that nuts and bolts could be used to hold the ends of the strip together when the U-bends were made. The specimens were prepared with the outer surfaces of the U-bends in three different conditions:

- Type I the as-received oxidized condition, which will have "natural" cracks present, as a result of bending,
- Type II as above, but with 10 mils of the oxidized surface removed with sandpaper prior to bending. No cracks were formed during bending,
- Type III the as-received "non-oxidized" surface which also does not crack during bending.
- Table 3.1 shows the test matrix for the U-bend irradiation tests.

Table 3.1	Test matrix for	crack-propagati	ion studies	on irradiated
	Marlex CL-100 m	iniature U-bend	specimens.	

	Outer Surface Condition of U-Bend							
Gamma Dose	Oxidized Surf.	Oxidized Surf.	Non-Oxidized					
Rate	Present	Removed	Surf. Present					
(rad/h)	(Type I)	(Type II)	(Type III)					
$0 \\ 1.4 \times 10^{3} \\ B.4 \times 10^{3} \\ 4.4 \times 10^{5}$	8(1)	8	8					
	8	8	8					
	8	8	8					
	8	8	8					

Figure 3.1 shows the U-bend specimens mounted on aluminum frames to facilitate irradiation. At the time the photograph was taken, the batches of specimens (A, B, and C) had accumulated 2.1 x  $10^6$  rad,  $1.3 \times 10^7$  rad, and 6.7 x  $10^8$  rad, respectively. At the time of examination this reporting period, the doses had reached 7.5 x  $10^6$  rad,  $6.0 \times 10^7$  rad, and  $1.3 \times 10^8$  rad, respectively. Figures 3.2 through 3.9 show sketches of cracks in the apex regions of Type I specimens for the various irradiation conditions. Crack patterns immediately after specimen bending are shown together with the patterns after the given irradiation doses. A careful study shows that cracks can both grow, and new cracks can initiate, in both the irradiated and the unirradiated controls. To obtain statistical data on the cracking behavior, the number of cracks in Type I specimens were counted. The results are given in Table 3.2. Large cracks are defined as those with a length greater than one-half of the specimen width (i.e., >0.64 cm). A small crack is one with a length less or equal to one-half of the specimen width. The number of cracks given in Table 3.2 are the totals for each batch of 8 replicate specimens.



Figure 3.1 Appearance of Type I (a), Type II (b), and Type III (c) Marlex CL-100 HDPE U-bend specimens gamma irradiated to 2.1 x  $10^6$  rad (A), 1.3 x  $10^7$  rad (B), and 6.7 x  $10^8$  rad (C). Individual unirradiated Type I, Type II, and Type III control specimens are shown at the bottom of the figure. Magnification 0.8 X.















Figure 3.2 Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples. Specimens are unirradiated controls. Specimen numbers given above each sketch.

















Figure 3.3 Crack patterns in unirradiated Type I Marlex CL-100 HDPE U-bend samples held at 10°C for 350 d. Specimen numbers given above each sketch.















Figure 3.4 Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples prior to gamma irradiation at 1.4 x  $10^3$  rad/h. Specimen numbers given above each sketch.

















Figure 3.5 Crack patterns in Type I Marlex CL-100 HDPE U-bend samples after gamma irradiation to 7.5 x  $10^6$  rad at a dose rate of 1.4 x  $10^3$  rad/h. Specimen numbers given above each sketch.















Figure 3.6 Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples prior to gamma irradiation at 8.4 x 10<sup>3</sup> rad/h. Specimen numbers given above each sketch.



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Figure 3.7 Crack patterns in Type I Marlex CL-100 HDPE U-bend samples after gamma irradiation to 6.0  $\times$  10<sup>7</sup> rad at a dose rate of 8.4  $\times$  10<sup>7</sup> rad/h. Specimen numbers given above each sketch.















Figure 3.8 Crack patterns in as-prepared Type I Marlex CL-100 HDPE U-bend samples prior to gamma irradiation at 4.4 x  $10^5$  rad/h. Specimen numbers given above each sketch.

















Figure 3.9 Crack patterns in Type I Marlex CL-100 HDPE U-bend samples after irradiation to 1.3 x  $10^9$  rad at a dose rate of 4.4 x  $10^5$  rad/h. Specimen numbers given above each sketch.

Two observations from the data are thought to be significant. First, irradiation in general causes an increase in the total number of new cracks which are initiated during test. For the unirradiated batch of U-bends, only eight new cracks were formed. However, for the three irradiated batches, the numbers of new cracks were between 14 and 19. The largest number (19) was for the intermediate gamma dose rate.

					Number of Cracks After Irradiation								
Irrad. Dose (Rad)		Total Cracks Before Irrad.	Large	Small	Total	Full Penet. Cracks	Almost Full Penet. Cracks						
	0			95	90	13	103	0	0				
7.5	× ×	10 <sup>6</sup> 10 <sup>3</sup>	R/h)	84	97	3	100	2	1				
6.0 8.4	× ×	10 <sup>7</sup> 10 <sup>3</sup>	R/h)	80	95	4	99	2	4				
1.3 4.4	××	10 <sup>9</sup> 10 <sup>5</sup>	R/h)	72	82	4	86	0	1				
	7.5 1.4 6.0 8.4 1.3 4.4	7.5 x 1.4 x 6.0 x 8.4 x 1.3 x 4.4 x	rad. Dose (Rad) 0 7.5 x 10 <sup>6</sup> 1.4 x 10 <sup>3</sup> 6.0 x 10 <sup>7</sup> 8.4 x 10 <sup>3</sup> 1.3 x 10 <sup>9</sup> 4.4 x 10 <sup>5</sup>	0 7.5 x 10 <sup>6</sup> 1.4 x 10 <sup>3</sup> R/h) 6.0 x 10 <sup>7</sup> 8.4 x 10 <sup>3</sup> R/h) 1.3 x 10 <sup>9</sup> 4.4 x 10 <sup>5</sup> R/h)	Trad. Dose (Rad)Total Cracks Before Irrad.095 $7.5 \times 10^6$ $1.4 \times 10^3$ R/h)84 $6.0 \times 10^7$ $8.4 \times 10^3$ R/h)80 $1.3 \times 10^9$ $4.4 \times 10^5$ R/h)72	Trad. Dose (Rad)       Total Cracks Before Irrad.       Large         0       95       90         7.5 x 10 <sup>6</sup> 1.4 x 10 <sup>3</sup> R/h)       84       97         6.0 x 10 <sup>7</sup> 8.4 x 10 <sup>3</sup> R/h)       80       95         1.3 x 10 <sup>9</sup> 4.4 x 10 <sup>5</sup> R/h)       72       82	Trad. Dose (Rad)Total Cracks Before Irrad.Number0959013 $7.5 \times 10^6$ $1.4 \times 10^3$ R/h)84973 $6.0 \times 10^7$ $8.4 \times 10^3$ R/h)80954 $1.3 \times 10^9$ $4.4 \times 10^5$ R/h)72824	Trad. Dose (Rad)Total Cracks Before Irrad.LargeSmallTotal09590131037.5 x $10^6$ 1.4 x $10^3$ R/h)849731006.0 x $10^7$ 8.4 x $10^3$ R/h)80954991.3 x $10^9$ 4.4 x $10^5$ R/h)7282486	Number of Cracks After IrTrad. Dose (Rad)Total Cracks Before Irrad.LargeSmallTotalFull Penet. Cracks095901310307.5 x $10^6$ 1.4 x $10^3$ R/h)8497310026.0 x $10^7$ 8.4 x $10^3$ R/h)809549921.3 x $10^9$ 4.4 x $10^5$ R/h)72824860				

#### Table 3.2 Cracking in Type I HDPE U-bend specimens exposed to gamma irradiation and air at 9°C.

Second, the number of small cracks is largest (13) for the non-irradiated controls. The reason for this is that when gamma irradiation is absent, the small cracks that are formed during bending, or during test, do not grow to large-crack status. On the other hand, for the irradiated specimens, most of the small cracks grew large because of irradiation-induced embrittlement.

Another observation from Table 3.2 is that the specimens which have the greatest number of deep cracks (full-penetration or close-to-full-penetration) are those irradiated at the low and intermediate dose rates. It seems clear that for the unirradiated specimens the lack of embrittlement by gamma irradiation prevents deep cracks from forming. The lack of deep cracks in specimens irradiated at the highest dose rate may be explained on the basis of irradiation-induced chain scission which would cause stress relaxation in the U-bend (Soo, and others, 1987). Rapid irradiation would cause rapid stress relaxation and this would lower the rate of crack propagation.

When deep cracks are formed, it was a surprise to find that they usually reside at locations away from the apex regions of the U-bends (see Figures 3.5 and 3.7). It was expected that these apex regions, of supposedly highest stress, would be prime locations for deep cracks. A possible explanation is that a combination of high stress and gamma-induced chain scission causes more rapid stress relaxation in the apex regions. At the highest gamma dose rate

the stress could fall to a value sufficiently low that deep cracks cannot form. Another factor that would tend to prevent deep cracking in the apex region is the generally higher crack densities in this area at the start of testing. Competition between the many cracks would cause them all to grow at a slow rate. Figures 3.5 and 3.7 show that the deep cracks are usually formed in regions of low crack density. Thus, the local stress causing them to grow will be relatively high.

This quarter, cracking was also detected for the first time in Type II and Type III U-bends (Figures 3.10 and 3.11). The cracks in both of these types of specimens are, again, remote from the apex regions. Rapid stress relaxation at the apex still offers the best explanation for this phenomenon. Cracking is more prominent in Type III U-benus.

The U-bend specimens are currently being re-irradiated and will be examined in the future to check for additional cracking.

#### 3.3 Uniaxial Creep Behavior

Creep tests are continuing at a test temperature of 20°C (68°F) using a simple dead-load system. Strains are measured using LVDTS (linearly variable differential transducers). Rates of creep, ductility-at-failure, and weight increase in the specimens caused by the absorption of the test liquids during creep are all measured. Tables 3.3 and 3.4 show the results accumulated to date. The data for the "old HDPE" were obtained from an earlier batch of material, and the remainder are for a newer supply purchased about 2 years ago. All current work is on the newer material.

Figures 3.12 and 3.13 summarize the failure times and ductilities of "as-received" HDPE as a function of stress and environment. Air and water appear to give similar creep properties. For scintillation fluid, turbine oil, and Igepal, however, there is a significant loss in rupture strength, especially in the low and intermediate stress ranges (Figure 3.12). As the stress level is increased, the curves in Figure 3.12 intend to converge, as expected, since the time to failure becomes primarily stress dependent. This is because failure tends to occur so quickly that time-dependent environmental effects do not have time to become important. Note, also in Figure 3.12, that there appears to be stresses below which creep-type failure is unlikely. The "threshold" stress for oil and Igepal is about 8.27 MPa (1200 psi) and for scintillation fluid it is about 6.89 MPa (1000 psi). One might suppose that if the stress levels in a waste container are kept significantly below 6.89 MPa then HDPE should be immune to a creep-type failure mode.

The ductility of HDPE at high stresses is about 60 percent for all test environments (Figure 3.13). This, again, is a result of failure being controlled by the stress rather than the environment. To a good approximation the ductilities over a stress range of about 8 to 13 MPa (1150 to 1900 psi) are the same for all environments except scintillation fluid. At stresses below about 10.34 MPa (1500 psi) the ductilities in this fluid are very much larger. This seems to be caused by blunting of cracks in the oxidized HDPE surface by chemical dissolution (Soo, and others, 1987). When this occurs, deformation does not concentrate as strongly in the cracked regions, and more uniform strain along the specimen gagelength results. This leads to higher







Cracking in Type I (bottom row) and Type III (top row) Marlex CL-100 HDPE U-bend specimens irradiated to  $6.0 \times 10^7$  rad (at  $8.4 \times 10^3$  rad/h). Note that the cracks in the Type III specimens are not in the apex region. Magnification 1.7 X. Figure 3.11

Test	Specimen	Test	Str	ess	Failure	Elong. at
Number	Condition	Environment	(MPa)	(psi)	Time (h)	Break (%)
381	As rec.	Air	13.79	2000	4.0	56.0
382	As rec.	Air	13.79	2000	0.98	56.6
367	As rec.	Air	13.10	1900	6.8	56.8
369	As rec.	Air	13.10	1900	5.8	46.6
374	As rec.	Air	12.76	1850	5.4	46.2
365	As rec.	Air	12.41	1800	41.0	74.6
359	As rec.	Air	12.41	1800	11.3	>33.6
360 1	As rec.	Air	12.10	1750	52.5	76.0
362	AS IEL.	Air	12.00	1740	28.5	>49.0
358	As rec.	Air	11.72	1700	80.3	79.6
361	As rec.	Air	11.03	1600	457	79.7
360	As rec.	Ai -	10.86	1575	212	85.4
350(a)	As rec.	Air	10.62	1540	166	72.9
350(b)	As rec.	Air	10.62	1540	502	55.0
300	As rec.	Air	10.34	1500	662	61.6
315	As rec.	Air	10.34	1500	761	58.2
363	As rec.	Air	10.17	1475	4023	60.4
357	As rec.	Air	10.00	1450	3821	55.1
380	As rec.	Air	10.00	1450	2455	66,8
377	As rec.	Air	9.83	1425	5173	53.5
316	As rec.	Air	9.65	1400	5378	36.6
364	As rec.	Air	9.31	1350	1819	71.9
391	As rec.	Air	9.13	1325	Ongoing	
355	As rec.	Air	8.96	1300	3'00	37.0
390	As rec.	Air	8.96	1300	Ongoing	
321	As rec.	Air	8.27	1200	7740	16.2
388	As rec.	Air	7.93	1150	Ougoing	
322	As rec.	Air	7.24	1050	Ongoing	1.1.1
384	Old HDPE	Air	13.79	2000	1.8	67.6
375	Old HOPE	Air	12 75	1900	10.6	10.5
351	OLA HOPE	Air	12.50	1000	5.0	22.0
344	Old HOPE	Air	11 72	1700	47	127 6
343	OLA HOPE	Air	11 03	1500	127	80.0
342	OLA HOPE	Ain	10.34	1500	2544	06.3
317	Old HOPE	Air	10.34	1500	7514	59.2
318	Old HOPE	Air	9.65	1400	Oconing	00.2
386	Old HOPE	Air	8.27	1200	Ongoing	1.1
387	(1)	Air	13.79	2000	Ongoing	
385	(1)	Air	12.41	1800	Ongoing	
338	(1)	Air	11.03	1600	2319	585
323	(1)	Air	10.34	1500	7704	248.9
320	(1)	Air	8.27	1200	Ongoing	
337	As rec.	DIW	11.03	1600	112	58.6
347	As rec.	VIO	10.69	1550	57	54.6
301	As rec.	DIW	10.34	1500	2027	95.5
302	As rec.	DIW	9.65	1400	5854	54.5
334	As rec.	DIW	8,27	1200	Ongoing	
339	(1)	DIW	11,03	1600	200	221.6
327	(1)	DIW	10.34	1500	452	85.2
326	(1)	DIW	8.27	1200	Ongoing	
306	(2)	DIW	10.34	1500	1154	57.5
310	(2)	DIW	9,65	1400	6264	53.5

# Table 3.3 Creep test data for Marlex CL-100 HDPE tested in air and deionized water at room temperature.

2. 10 mils removed from non-oxidized surface of specimen.

Tert Number	Specimen Condition	Test Environment	(MPa)	ess (psi)	Failure Time (h)	Elong. at Break (%)	Weight Change (% per test day
370 305 345 348 352 325	As rec. As rec. As rec. As rec. As rec. As rec.	011 011 011 011 011 011 011	11.03 10.34 8.96 8.96 8.62 8.27	1600 1500 1300 1300 1250 1200	45.9 128 102 168 198 1502	92.1 60.3 43.4 51.1 84.1 36.3	0.19 0.06 0.02 0.04 0.01
396 379 378 395 308 309 341 333 383 394	As rec. As rec. As rec. As rec. As rec. As rec. As rec. As rec. As rec.	LSF LSF LSF LSF LSF LSF LSF LSF	12.41 11.72 11.38 11.03 10.34 9.65 8.27 7.24 6.89 6.72	1800 1700 1650 1600 1500 1400 1200 1050 1000 975	7.9 9.6 10.5 33.1 14 35 50 340 1602 0ngoing	85.0 94.8 49.3 89.9 83.5 98.0 98.5 98.5 95.8 80.6	0.72 1.47 0.34 0.25 0.15 1.40 0.02
330 332 331	(1) (1) (1)	LSF LSF LSF	9.65 8.27 7.24	1400 1200 1050	29 85 Ongoing	76.0 216.0	:
313 311	(2) (?)	LSF LSF	10.34 9.65	1500 1400	12 31	55.0 77.0	0.28 0.21
42 55 62	01d HDPE 01d HDPE 01d HDPE	LSF LSF LSF	10.34 9.65 8.27	1500 1400 1200	12 35 280	86.1 37.8 100.7	:
392 393 371 303 304 346 324 389	As rec. As rec. As rec. As rec. As rec. As rec. As rec.	Igepal Igepal Igepal Igepal Igepal Igepal Igepal	12.41 11.72 11.03 10.34 9.65 8.96 8.27 8.10	1800 1700 1600 1500 1400 1300 1200 1175	3.1 17.7 45.6 65 106 128 1194 Ongoing	52.3 51.8 54.7 49.1 54.8 47.3 22.0	0.27 0.23 0.13 0.06 0.03 0.02
106 105 107 108 72 113 114 84	Old HOPE Old HOPE Old HOPE Old HOPE Old HOPE Old HOPE Old HOPE Old HOPE Old HOPE	Igepal Igepal Igepal Igepal Igepal Igepal Igepal	12.41 12.41 11.72 10.34 10.34 10.34 10.34	1800 1800 1700 1700 1500 1500 1500	8 9 50 47 216 366 372 95	74.8 69.2 87.4 54.6 68.7 62.2 79.2 115.3	
340 329 328	$(1) \\ (1) \\ (1)$	Igepal Igepal Igepal	10.34 9.65 8.27	1500 1400 1200	312 476 Ongoing	97.3 59.4	0.04
314 212	(2) (2)	Igepal Igepal	10.34 9.65	1500 1400	56 106	71.4	0.09

# Table 3.4 Creep test data for Marlex CL-100 HDPE tested in various environments at room temperature.



Figure 3.12 Stress-rupture results for Marlex CL-100 HDPE tested at 20°C in various environments.



Figure 3.13 Elongations at failure for Marlex CL-100 HDPE tested at 20°C in various environments.

elongation at failure. The different effect that scintillation fluid has on HDPE compared to oil and Igepal is reflected in the weight-gain data for samples tested in these environments (Table 3.4). Scintillation fluid is much more easily absorbed into the specimen, indicating a strong environmental effect on the bulk of the specimen, as opposed to a surface effect.

Figures 3.14 through 3.17 show creep curves for the various test environments at four stress levels. Air always gives the slowest rate of creep, and scintillation fluid the fastest. The non-air environments cause more rapid deformation, earlier failure, and usually higher ductility.

Creep studies are continuing with prime emphasis on lower stresses to simulate, as closely as practical, realistic stress conditions.

An abstract on the creep work was submitted to the University of Arizona to be considered for inclusion in the Waste Management '88 proceedings.


Figure 3.14 Creep of Marlex CL-100 HDPE in various environments at 8.27 MPa (1200psi).



Figure 3.15 Creep of Marlex CL-100 HDPE in various environments at 9.65 MPa (1400 psi).



Figure 3.16 Creep of Marlex CL-100 HDPE in various environments at 10.34 MPa (1500 psi).



Figure 3.17 Creep of Marlex CL-100 HDPE in various environments at 11.03 MPa (1600 psi).

# 4. BIODEGRADATION OF ION-EXCHANGE MEDIA

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This study has been completed experimentally and a summary of the findings was given in the last quarterly report (Soo, and others, 1987). Data have been comprehensively tabulated and preparation of a topical report has commenced.

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An abstract of a paper was prepared on this work and submitted to the University of Arizona for inclusion in the Waste Management '88 proceedings.

Kalousek, G. L., and others, "Past, Present, and Potential Developments of Sulfate-Resisting Concretes," J. Testing and Evaluation, 4, 347, 1976.

Soo, P., and others, "Low-Level Waste Package and Engineered Barrier Study," Quarterly Progress Report, July - September 1987, WM-3291-5, December, 1987. NUREG/CR-3383 BNL-NUREG-51691

# IRRADIATION EFFECTS ON THE STORAGE AND DISPOSAL OF RADWASTE CONTAINING ORGANIC ION-EXCHANGE MEDIA

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**TOPICAL REPORT** 

K.J. Swyler, C.J. Dodge, and R. Dayal

October 1983

# NUCLEAR WASTE MANAGEMENT DIVISION DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY UPTON, LONG ISLAND, NEW YORK 11973



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**TOPICAL REPORT** 

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#### EXECUTIVE SUMMARY

Polystyrene-divinylbenzene (PS-DVB) based ion exchangers are commonly used in water demineralization or decontamination operations at nuclear facilities. Self-irradiation from sorbed radionuclides may affect the properties of radwaste containing these ion-exchange media. The effects of external irradiation on anion, cation, and mixed bed PS-DVB ion exchangers have been investigated under conditions relevant to radwaste storage and disposal. Three effects are emphasized in the present report: (1) release of acids, radionuclides or chemically aggressive species through radiolytic attack on the functional group, (2) radiolytic generation/uptake of corrosive or combustible gases, (3) effect of irradiation on solidification of resins in cement. Special consideration was placed on external variables such as radiation dose rate, resin chemical loading and moisture conditions, accessibility to atmospheric oxygen, and interactions in multicomponent systems. Such variables may affect the correspondence between laboratory results and field performance.

For sulfonic acid cation resin, sulfate ion is produced in the radiolytic scission of the functional group. The products released are a mixture of sulfuric acid and sulfate salts of the counterion. In fully-swollen sulfonic acid resin, sulfate ion may be largely due to direct radiolytic scission of the functional group, and subsequent hydrolysis of the radical products. This process is not strongly dependent on pH environment, monovalent cation resin loading, and radiation dose rates. This insensitivity to external parameters makes the sulfate yield a convenient measure of radiation durability for regulatory considerations and simplifies the application of laboratory data to field performance. In particular, the present results indicate that, in a sealed environment, accelerated testing at high radiation dose rates is a valid procedure.

In the field the amount of acidity which results from a given sulfate yield will depend on the regin loading. The acidity will be reduced first by a protective ion exchange efffect in which H<sup>+</sup> ion is exchanged for cation at undamaged resin sites. Second, some of the sulfate may be produced by a mechanism in which H<sup>+</sup> ion is not generated in the oxidation of  $SO_3^{=}$  to  $SO_4^{=}$ . In any event, the acidity is substantially reduced for loadings other than H<sup>+</sup>. The acidity however is by no means eliminated. Acidity and radiolytic attack can also be reduced (but not eliminated) by drying the sulfonic acid resin. Reducing the moisture content from 50 to 5% decreases radiolytic sulfate yields by 75%. For dry resins irradiated in a closed environment, a probable radiolytic reaction is one in which one functional group is oxidized and the other reduced.

For doses in excess of  $\sim 5 \times 10^8$  rad, no real protection against radiolytic acidity formation is gained by using IRN-77/78 resins in mixed bed form (at a cation/anion caracity ratio of 1:1). Most importantly, the irradiated anion resin releases substantial amounts of free liquid. At  $10^8$  rad, the extrapolated value for free liquid release from IRN-150 NaCl form resin appears to lie above current NRC guidelines for initial free liquid in highintegrity containers at burial.

For the cation resir, radiolytic hydrogen gas yields are not strongly dependent on radiation dose rate; this supports the validity of accelerated testing. Hydrogen yields can be substantially reduced in field operations by drying the resin.

Oxygen gas is removed from the environment of irradiated resins by an efficient radiolytic oxidation process. This occurs for both cation and anion resins in both dry and fully swollen form. In a sealed environment this process quickly depletes atmospheric oxygen initially present, and will prevent the formation of combustible mixtures of hydrogen and radiolytic oxygen. For samples irradiated in a sealed environment, agglomeration of the resin was not observed. This result, and observations on samples irradiated in excess oxygen, suggest that previously reported radiolytic resin agglomeration is partially associated with extensive radiolytic oxidation.

At this point heavy irradiation appears to enhance, rather than degrade the solidification properties of sulfonic acid resin.

# CONTENTS

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.

EXE	CUTIVE	SUMMARY	Y			:				÷.	κ.													iii
CON	TENTS													٠.				÷						v
FIG	URES							1.1	×															vi
TAB	LES .																			÷,				viii
ACK	NOWLED	GMENTS					,		•		•						•	λ.	*	•	*	٠		x
1.	INTRO	DUCTION	,	<u>.</u>						•											÷		÷	1
2.	EXPER	IMENTAL											•		•	•		•		•	•	•		5
	2.1	Resin C	haract	eris	tic	s ar	nd	Sam	ple	P	re	par	at	ior	1			,						5
	2.2	Irradia	tion P	roce	dur	es																		6
	2.3	analyti	cal Pr	aced	ure	s .																		7
		2.3.1.	Gas P	Tess	ure	and	I C	omp	osi	ti	on			1			÷.							7
		2.3.2	Soluh	le D	leco	mpos	it.	ion	Pr	od	luc	ts.				2		2	3	Ç.	÷.	1		8
		2 3 3	Poete	Evo	han	ap (	an	aci	++								1			ĵ.		9		9
		2.3.4	Free	Liqu	id	and	Re	sin	Su	vel	.11	ng	Bel	hav		r					÷	;		9
3.	RESUL	TE AND	DISCUS	SION																				11
	3 1	Padioly	tio Ef	Fort	0 0	n +3		Pro		++ 1		of	c	at	or		An	ic	n		and	1		
	3.1	Marca B	ad Pas	1000	a 0		16		per			~				1			,	5		١.		11
		Mixed D	ed Kes	ins .						·	*			1 1	in.			. 's		à	18.		<i>.</i>	**
		2.1.1	Calt a	ytic	AL	Laci	K O	Po	ne	r t	inc	C.T.O	na	T /	310	hut	-	-	101	u,	De	130	.,	11
			Salt a	ind U	oun	ter	100	Re	lea	ise		• •	•	•	•	•	•	•	•	*	•	•	•	21
		3.1.2	Radiol	ytic	Ga	s Ge	ene	rac	101	1.		: '	. :	. *	*	4	:	1	: .	÷.,		*	*	51
	3.2	Irradia	tion E	ffec	ts	on 1	Kes	11	SO.	110	111	1ca	111	on	ar	DI	Le	eac	ini	nş	5 *	*	.*	44
		3.2.1	Solidi	fica	tio	n of	t 1	rra	dia	ate	be	Kes	in	S.	٠.		٠.	1	*	1	.*	*	*	44
		3.2.2	Leachi	ng B	leha	vio	r o	of F	om	ns	Co	nta	in	inį	g 1	rr	ad	118	ate	be				1.7
			Resins		. •	• •	۰.	• •		*	۰.	• •	•	. 1.		٠.	٠.	٠	*	*	•	٠		47
		3.2.3	Effect	of	Irr	adia	ati	on	on	Re	esi	n S	swe	111	ing	ç E	set	lav	110	r		•	٠	49
	3.3	Mechani	stic S	itudi	es	×	۰.		۰.		٠.				٠	۰.	1	٠	۰.	٠		٠	*	50
		3.3.1	Radiol	ytic	De	grad	dat	ion	Me	ech	an	ism	ıs,				٠	٠	٠.	٠	٠	٠		50
		3.3.2	Role o	of Hy	dro	gen	Pe	rox	ide	e i	n	Rad	lio	1 yı	tic	F	les	ir	1					
			Decomp	osit	ion																$\sim$			51
		3.3.3	Role c	of Ic	n-E	xch	ang	e P	roo	ces	sse	s i	n	Re	lea	ise	0 6	of	Sc	11	ub!	le		
			Specie																			×		55
		3.3.4	Exchar	ige C	apa	cit	уо	of I	rrı	rad	lia	ted	l S	ul	for	nic	2 1	lc i	id	Re	esi	in	٠	56
4.	CONCI	LUSIONS	AND SU	JMMAF	XY.						×		Ģ				ł	•		ł				59
	4. 3	Padda1	utio			n +1	ha	Paa	1.0	F.		+ 1 -		1	an.			1						59
	4.1	Radio1	yere a	icide (	in o	n L	tor	nes	All	- 1	inc	ere	and	* '	Gr C	,u j		1	1	1				64
	4.2	Radiol	ytic (	as (	ene	rat	100					·			1		1.					. *		04
	4.3	Exchan	ge Rer	sins.	luen	· ·					·	. Da	ama	ge .				;a1			.01	*		65
5.	REFE	ERENCES.						έ.			×							÷						69

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# FIGURES

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1.1	Structures of Polystyrene/DVB Sulfonic Acid Cation Resin and Polystyrene/DVB Quaternary Ammonium Anion Resin
2.1	Break-Seal Vessel for Resin Irradiation 6
3.1	Supernate pH vs Irradiation Dose for Irradiated H <sup>+</sup> and Na <sup>+</sup> Form Resin
3.2	Soluble Sulfate Generation vs Irradiation Dose for Fully Swollen IRN-77 $\rm H^+$ Form Resin and Na^+ Form Resin
3.3	SO4 <sup><math>\equiv</math></sup> Yields vs pH in the Supernate of IRN-77 H <sup>+</sup> Form Resin, Subjected to Various Irradiation Doses
3.4	SO4 <sup>=</sup> Yields vs pH in the Supernate of IRN-77 Na <sup>+</sup> Form Resin. Subjected to Various Irradiation Doses
3.5	Supernatant pH vs Irradiation Dose for Various Forms of Fully Swollen IRN-77 Resin. Dose Rate = 1.6x10 <sup>6</sup> rad/h. Samples Irradiated in Sealed Environment
3.6	Sulfate Ion Supernate Yields (Moles per g of Fully Swollen Resin) vs Irradiation Dose in Different Forms of Fully Swollen IRN-77 Resin
3.7	Photomicrograph of IRN-78 Resin Beads Before and After Irradiation to 1x10 <sup>9</sup> rad at 1.6x10 <sup>6</sup> rad/h. The Beads Were Centrifuged Prior to Photographing to Remove Free Liquid Released During Irradiation
3.8	Fractional Release of Functional Group Decomposition Products and Exchangeable Ions
3.9	Free Liquid Release vs Irradiation Dose in IRN-78 and IRN-150 Resins
3.10	IRN-150 (HOH) Form Resin Before and After Irradiation to 1 x 10 <sup>9</sup> rad
3.11	Hydrogen Pressure Over Irradiated IRN-77 H <sup>+</sup> Form Resin
3.12	Sample Cell Pressure vs Irradiation Time at Different Dose Rates for Na <sup>+</sup> Form IRN-77 Resin
3.13	Gas Pressure Over IRN-78 Resin vs Irradiation Time at 1.6 x 10 <sup>6</sup> rad/h

# FIGURES, Continued

3.14	Gas Generation in IRN-150 Resin Irradiated at 1.6x106 rad/h 3	9
3.15	Gas Pressure over H <sup>+</sup> Form IRN-77 Resin During Irradiation at $8 \times 10^6$ rad/h. The Sample Originally Contained 6.4 psi of $0_2$	2
3.16	Linear and Semilogrithmic Plots of the Difference Between the Data and the Fitted Straight Line in Figure 3.14 4	3
3.17	Resin-Cement Forms Made With Irradiated and Univradiated Resin After Soaking for 28 Days in Deionized Water	6
3.18	Cumulative Fractional Cesium Release From 2 in. x 2 in. Resin- Cement Composite Made With Unirradiated Resin 4	7
3.19	Cumulative Fractional Cesium Release From 2 in. x 2 in. Resin- Cement Composite Made With Resin Exposed to 9 x $10^8$ rad 4	8
3.20	IRN-77 Resin in Various H <sub>2</sub> O <sub>2</sub> Solutions and Deionized Water Only	2
3.21	IRN-77 Resin Irradiated in $H_2O_2$ Solutions	4
3.22	Cation Exchange Capacity vs Soluble Sulfate Supernate Yields for	8

.

- vii -

TABLES

0

•

12

.

43

.

2.1	Properties of Ion-Exchange Media	5
3.1	G-Values for Sulfate Ion Formation in Irradiated IRN-77 Resins 1	14
3.2	Fraction of Sulfuric Acid in the Supernate of Irradiated H <sup>+</sup> Form IRN-77 Resin vs Irradiation Dose	16
3.3	Equivalents of Hydrogen Ion, Sodium Ion and Sulfate Ion in the Supernate of Irradiated Na <sup>+</sup> Form Resin	16
3.4	Equivalents of Fe <sup>+++</sup> , H <sup>+</sup> and SO <sub>4</sub> <sup>=</sup> in the Supernate of Irra- diated Fe <sup>+++</sup> Form IRN-77 Resin	19
3.5	Soluble Radiolysis Products and Acidic Species in IRN-77 Irra- diated in Dry Form	21
3.6	Supernatant pH for IRN-77 Resin Irradiated Under Deionized Water. 2	21
3.7	Properties of Liquids Contacting Irradiated IRN-78 Resin 2	22
3.8	Physical Changes and Cl <sup>-</sup> Ion Release in Irradiated IRN-78 Resin in the Cl <sup>-</sup> Form	23
3.9	Soluble Decomposition Products in Irradiated HOH Form IRN-150 Resin	25
3.10	Soluble Decomposition Products in Irradiated NaCl Form IRN-150 Resin	26
3.11	Correlation of [SO4"] and [H <sup>+</sup> ] in Liquids Contacting Irra- diated IRN-150 HOH Form Resin	27
3.12	Ion Balance in Liquids Contacting Irradiated IRN-150 (NaCl) Resin	28
3.13	Gas Pressures in the Atmosphere Over Irradiated H <sup>+</sup> Form IRN-77 Resin	31
3.14	Atmospheric Composition Over Irradiated Na $^+$ Form Resins	34
3.15	Radiolytic Gas Generation Data for Various Forms of IRN-77 Resin.	35
3.16	Radiolytic Gas Generation in Dried IRN-77 Resin	36
3.17	Partial Gas Pressures in the Atmosphere Over Irradiated IRN-78 Resins	38

# TABLES, Continued

3.18	Partial Gas Pressures in the Atmosphere Over Irradiated IRN-150
	Resins
3.19	G-Values for Radiolytic Hydrogen Generation 40
3.20	Radiolytic Gas Generation for Resins Irradiated in Various
	Atmospheres
3.21	Compression Test Data on Resin-Cement Waste Forms
3.22	Swelling Force Exerted by Irradiated IRN-77 Resin
3.23	pH and Sulfate Content of Peroxide-Resin Solutions 53
3.24	pH and Sulfate Content of Irradiated and Unirradiated Resin-
	Peroxide Solutions
3.25	pH Elevation of H2SO4 Solutions (10 mL) by Sodium Form
	IRN-77 Resin (2 g)
3.26	Titration Data for Irradiated Na <sup>+</sup> Form Resin
3.27	Exchange Capacity of Irradiated IRN-77 Resins

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- ix -

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1

• 4

#### IRRADIATION EFFECTS ON THE STORAGE AND DISPOSAL OF RADWASTE CONTAINING ORGANIC ION-EXCHANGE MEDIA

TOPICAL REPORT

#### 1. INTRODUCTION

Under certain conditions (particularly in clean-up procedures following off-normal reactor operations), ion-exchange media used in demineralization may incorporate a substantial loading of radionuclides. This study considers how the properties of radwastes containing organic ion-exchange media may be modified by heavy doses of ionizing irradiation from sorbed radionuclides.

Radiation effects of potential significance in the storage and disposal of radioactive ion exchange media have been identified in conjunction with operations at TMI-II (Gangwer and Pillay, 1980; McFarland, 1981; Pillay, 1980; Barletta et al., 1981). A large number of laboratory studies have been carried out on radiation effects in ion-exchange media, particularly in the Soviet Union. Reviews have been given by Egorov and Novokov (1967) and by Gangwer, Goldstein and Pillay (1977). However, as the latter authors point out, most of this work is more relevant to radiation effects on process parameters, such as ion exchange capacity, than to radwaste properties. For example, it is clear from the literature that soluble, chemically aggressive species and combustible gases can be produced in the radiolysis of organic ion-exchange media. In actual storage and disposal conditions, however, radiolysis yields may be affected by factors such as radiation dose rate, chemical loading on the resins, moisture content, and interactions between the ion-exchange media and solidification agents or container components. Consequently, little information was available to relate existing laboratory results to the anticipated effects of irradiation on ion-exchange resin waste under actual storage and disposal conditions.

In general, organic ion-exchange resins consist of functional (ion-exchange) groups attached to a polymer backbone. A wide variety of functional groups and backbone configuration is possible - dozens of physically distinct ion-exchange resins are commercially available. In certain applications, organic ion-exchangers may also be used with inorganic materials such as zeolites or charcoal (Barletta et al., 1981). A comprehensive investigation of irradiation effects in the different generic types of ionexchange media would require a level of effort substantially greater than that contemplated in the present program. However, it is possible to restrict the scope of the study while still retaining some generality: results of recent surveys (Piciulo, 1981; MacKenzie et al., 1982) indicate that the majority of organic ion-exchange resins used by the U.S. commercial nuclear power industry are based on a polystyrene-divinylbenzene backbone, with sulfonic acid (cation) or quaternary ammonium (anion) functionality. The structure of these materials is represented in Figure 1.1.





Figure 1.1 Structures of polystyrene/DVB sulfonic acid cation resin (IRN-77, upper) and polystyrene/DVB quaternary ammonium anion resin (IRN-78, lower).

This report describes a parametric study of radiolysis effects in polystyrene-divinylbenzene based ion exchange media. Three radiolytic effects of potential significance in radioactive waste management are emphasized:

- Release of chemically active soluble decomposition products and counterions.
- · Generation or uptake of combustible or corrosive gases.
- · Effect of radiolytic resin decomposition on solidification properties.

Three functional forms of the resin were studied: sulfonic acid cation exchanger, quartenary ammonium anion exchanger and a mixed bed combination of the two. Sulfuric acid or sulfate salts are expected to result from radiolytic attack on the sulfonic acid functional group (Kazanjian and Horrell, 1974) while basic species such as amines result from decomposition of the

quaternary ammonium group (Hall and Streat, 1963). By examining the behavior of the two components separately and in wixed bed form, the component interactions may be studied. Baumann (1966) has suggested that in a mixed bed system, radiolytically released acidic species may be largely neutralized by the presence of the anion component.

Parameters in the study include external radiation dose dose rate, resin moisture content and chemical loading. Emphasis was placed on determining how these factors may affect the relation between laboratory test results and field behavior of resin wastes. Radiation dose rate effects are particularly important in this context, since laboratory dose rates commonly exceed field values by several orders of magnitude. Where diffusion limited processes are involved in radiolytic attack, experiments at accelerated dose rates may give unrealistic damage yields. Such a situation may occur in radiolytic oxidation (c.f., Gillen and Clough, 1981). Efficient radiolytic oxygen scavenging has, for example, recently been demonstrated in irradiated resins (Barletta et al., 1981). Consequently, radiol/tic resin degradation may depend sensitively on the dose rate and the amount of oxygen present in the environment. Oxidation effects are explicitly examined in this study.

In radiation damage studies on ion-exchange resins, it is common practice to rinse the resin free of soluble decomposition products following irradiation (c.f., Baumann, 1966). The rinses are then examined for particular species of interest. This procedure is useful in studying the effects of radiation damage on process performance. In radwaste storage and disposal applications, however, the resin will most probably remain in contact with its own decomposition products both during and after irradiation. This may result in post irradiation chemical or aging effects on resin properties. Further, during storage or in a disposal environment, significant radionuclide transport may be largely limited to those conditions in which the resin is in quasi-static contact with an aqueous medium. Consequently, we believe that properties of aqueous solutions of irradiated resin, in which ion exchange, slow leaching or chemical aging may occur, are of primary importance in the present context. These properties are stressed in this study.

Radiolytic attack on the resin may be promoted by radiolysis products (e.g., peroxides) formed in the aqueous environment, as discussed by Egorov and Novokov (1967). Also, the release of soluble species may be influenced by the ion-exchange properties of t a tradiated resins. Experiments were carried out to examine the role of each of these processes in the overall radiolytic decomposition mechanisms. Practically, however, radiolysis effects are significant only insofar as they affect the possibility of radionuclide release data are presented for resin-cement composites made with irradiated resin. Extensive studies on corrosion of mild steel container material in irradiated resins have also been carried out. These results are presently undergoing final analysis and will be described in a future topical report in this research program. A preliminary description is presently available (Swyler and Dayal, 1982).

- 3 -

A recent Nuclear Regulatory Commission Technical Position recommends that the radiation dose to radwaste containing organic ion-exchange media be limited to  $10^8$  rad. The technical justification for this limit has been presented by MacKenzie et al. (1981). In the present program, doses far in excess of this level were employed. Th's was done both to make certain radiation damage effects (such as loss of e. hange capacity) more clearly observable for purposes of interpretation, and more importantly, to indicate the effects which must be taken into account if the recommended limit is exceeded under future off-normal operations. The final thrust of this program is to provide a data base which can be used to determine how well laboratory tests simulate radiation effects under actual field conditions.

#### EXPERIMENTAL

All experiments have been carried out with either sulfonic acid cation resins (Amberlite IRN-77)\*, quaternary ammonium anion resin (Amberlite IRN-78)\* or mixed bed containing these two materials (Amberlite IRN-150).\* These resins were chosen as typical of those used in the nuclear industry. IRN-77 contains sulfonic acid functional groups (-SO3-) on a polystyrene/ divinylbenzene polymer backbone. IRN-78 contains quaternary ammonium (-CH\_N(CH\_3)3+) functional groups on the same backbone. Structural formulae are given in Figure 1.1.

# 2.1 Resin Characteristics and Sample Preparation

IRN-77 resin is supplied by the manufacturer in the H+ form, and IRN-78 is provided with an OHT loading. The mixed bed (IRN-150) is supplied in HOH form. Physical data on these materials are given in Table 2.1.

#### Table 2.1

#### Properties of Ion-Exchange Mediaa

Resin	Moisture Content (weight %)	Bulk Density (g/cm <sup>3</sup> )	Specific Gravity (g/cm <sup>3</sup> )	Exchange Capacity (meq)/g
IRN-77 (H <sup>+</sup> )	52-55	0.80	1.25	2.35
IRN-78 (OH-)	58-64	0.63	1.11	1.74
IRN-150 (HOH)	55-58	0.67	1.17	1.0/1.0b

aNominal values for fully-swollen resin. Exchange capacity and bulk density from manufacturer's data. <sup>b</sup>Cation capacity/anion capacity.

Resin samples were prepared with different counterion loadings using ion-exchange procedures to convert the resin from one form to another. Following several rinses, the resins were dewatered by suction. This treatment produced resins in the fully-swollen form. Some reains were further oven dried in air at 70°C. Residual moisture content of the various samples was determined by measuring percentage weight loss following prolonged drying at 100°C or by thermogravimetric analysis (TGA). Moisture content as determined by oven drying and TGA agreed to within ~2%.

\*Amberlite is a trademark of the Rohm and Haas Company, Philadelphia, Pa.

IRN-77 resin samples were prepared in Na<sup>+</sup> form, Fe<sup>++</sup> form, Fe<sup>+++</sup> form and NH4<sup>+</sup> form, from the as-delivered H<sup>+</sup> form. The Na<sup>+</sup> conversions were carried out according to standard batch procedures developed in our laboratory and described eisewhere (Weiss and Morcos, 1980). Conversion to Fe<sup>++</sup>, Fe<sup>+++</sup> and NH4<sup>+</sup> loadings was carried out with solutions of FeSO4, FeCl<sub>3</sub> and NH40H respectively, using column techniques recommended by the manufacturer. Sulfuric acid was added to the FeSO4 solution to adjust the pH to 2.3, so as to maintain the iron in Fe<sup>++</sup> form. IRN-78 samples were converted to Cl<sup>-</sup> form and IRN-150 samples were converted to NaCl form by batch contact with excess NaCl in solution. After each conversion, the resin was rinsed with deionized water until the rinse attained a near-neutral pH. In some cases, the resin was titrated following preparation, providing a check on the extent of conversion. For the Na<sup>+</sup> and NH4<sup>+</sup> form, the conversion was between 98 and 100% complete, as indicated by the residual H<sup>+</sup> content of the resin.

#### 2.2 Irradiation Procedures

In the field, most spent resins are stored or disposed of in closed systems (i.e., not open to the atmosphere). The present results refer largely to irradiations in a sealed environment simulating waste storage. Two sample configurations are used. In one, 6.0-g resin samples are weighed into Pyrex break-seal tubes which are then flame-sealed in air (Figure 2.1). Other irradiations were carried out in a special vessel equipped with a pressure transducer, which allowed gas generation or uptake to be observed during the irradiation. The operation of this apparatus had been described proviously (Barletta et al., 1981).



Figure 2.1 Break-seal vessel for resin irradiation.

The lossed sample tubes are either set aside as zero dose control samples or irradiated in BNL's Co-60 gamma pool to different total doses at a given gamma dose rate. The average dose rates employed in the majority of these experiments are  $1.65 \times 10^6$  rad/h,  $9.6 \times 10^4$  rad/h, and  $3.7 \times 10^4$  rad/h. All these are accurate to  $\pm 10\%$ . Bulk or spatial average dose rates were determined by ferric sulfate dosimetry. Spatial variations and attenuation within the irradiation tubes were checked with radiochromic foils. In arriving at these dose rates it is assumed that, for a given gamma ray flux, the energy absorption per unit mass in water and in hydrocarbon materials is identical (Makhlis, 1975).

#### 2.3 Analytical Procedures

## 2.3.1 Gas Pressure and Composition

Following removal of the resins from the irradiation source, sample cell pressure was determined. For the Pyrex cells, pressure was determined by breaking the sealed sample cell in an evacuated chamber equipped with a pressure transducer. The pressure is determined from the relation

$$P_{s} = F_{f} + (P_{f} - P_{i}) \frac{V_{c}}{V_{s}}$$
(2.1)

 $P_s$  is the sample pressure,  $V_s$  the plenum volume in the sample cell,  $P_i$  and  $P_f$  the pressures in the evacuated chamber before and after breaking the sample vessel, and  $V_c$  the volume of the evacuated cell.

The cell and sample volumes used in initial experiments were 196 cm<sup>3</sup> and 14 cm<sup>3</sup>, respectively. The large cell volume was chosen to handle the substantial gas pressure anticipated in H<sup>+</sup> form resin containing corrosion coupons. In later experiments, the cell volume was reduced to 100 cm<sup>3</sup>. Following the determination of P<sub>1</sub> and P<sub>f</sub>, where desired, gas was transferred into an evacuated glass vessel for compositional analysis by mass spectroscopy. The accuracy of the fractional composition determination by this technique is +1% for components with concentration down to 1%. For lower concentration, the accuracy is +5% until a detection limit of .05% is reached. A certain amount of water vapor is also present in the samples. Accurate vapor pressures for resins of different moisture content have not yet beer determined. Taking the vapor pressure of pure water at ambient temperatures as an upper limit gives a moisture content of <2% for the vapor phase initially.\*

<sup>\*</sup>The amount of water present in the vapor phase should be less than 0.25 g, which is about 5% of the resin weight. Consequently, in the absence of radiation and chemical effects, significant evaporative drying of the resin could occur only by virtue of water condensation at cold spots on the tube walls. There is no evidence that such condensation occurred in the breakseal tubes. Following irradiation, weight loss for 6-g samples was typically less than 1%.

In later measurements, prior to evacuating the large chamber into which the sample cell is broken, the chamber was first evacuated and then backfilled with helium; thus any residual gas (He) present in the large chamber following final evacuation cannot be confused with air originally present in the sample cell. Further, prior to each series of measurements, a pressure test was carried out on a standard sample cell at atmospheric pressure to provide assurance that the system was functioning property. These refinements improved the accuracy of the gas generation measurements.

In the gas pressure determination, pressure in the sample vessels was reduced to well below atmospheric. The samples were not pumped on further in order to maintain the sample moisture content. Also, it was felt that strongly sorbed gases should not be artificially removed from the samples, since these might contribute to post-irradiation chemical effects. Several experiments were carried out to determine if gas generation and/or slow gas desorption occurred after the samples were depressurized. One sample, initially containing radiolytic gas at 114 psia was left under vacuum (7.0 psia) for 2.5 days following gas transfer. During this period, the pressure in the vacuum vessel rose to 7.9 psia where it remained stable. This increase would correspond to a pressure change of about 8 psi within the sealed sample tube. This probably represents a maximum desorption yield.

In some cases, the pyrex cells were stored for periods of several weeks before the pressure was determined. In other measurements, pressure following irradiation was directly monitored in the vessel equipped with a pressure transducer. None of these experiments suggested any significant change in the cell pressure following irradiation. Long-term irradiations presently under way will consider this topic in greater detail.

#### 2.3.2 Soluble Decomposition Products

Release of soluble decomposition products was generally determined for resin-water solutions under static conditions. For anion and mixed bed resins, free liquids released from the resins during irradiation were removed by centrifuging. For all resins, a liquid fraction was then formed by contacting 2 g of the resin sample with 10 mL of deionized water. The choice of the resin-to-water ratio is somewhat arbitrary. The object is first to leach out soluble decomposition products for further analysis and second, to provide a static environment in which post irradation aging could be observed. These measurements also provide a basis for comparison with results obtained on resins irradiated while immersed in water.

The various liquid phases were analyzed for pH, decomposition products of functional groups (e.g., SO4<sup>=</sup>) and counterions (e.g., Na<sup>+</sup>) in solution. Sulfate ion concentrations were determined using a Dionex Model 10 ion chromatograph. Na and Fe concentrations were measured by atomic absorption spectroscopy. Cl<sup>-</sup> concentrations were determined by colorometric techniques. In those cases where SO4<sup>=</sup> and Cl<sup>-</sup> were simultaneously present in solution, Cl<sup>-</sup> was removed by precipitation with silver acetate to prevent chromatographic interference.

Results obtained in this way depend to some extent on the contact time of the resin-water solution. A rapid initial release of decomposition products, (manifest, for example by a pH decrease) is generally followed by a more gradual change due to slow chemical reaction or leaching processes. These processes may decrease solution pH by as much as one-half unit in a few weeks. The magnitude of the change depends upon the initial pH and the resin loading. After ~3 weeks contact time, solution pH usually remained fairly stable. For example, in one sample of irradiated Na<sup>+</sup> form resin, the supernatant pH dropped from 3.28 to 2.94 in one week. Subsequently, over 18 months storage time, the pH decreased to 2.78. Results presented in this report, unless otherwise noted, refer to solutions of deionized water and irradiated resins, aged for at least three weeks in sealed polyethylene or pyrex vessels. Aliquots of the supernate were then withdrawn for characterization. In checks on selected samples following the 3-week aging period, sulfate levels in the supernate typically fluctuated less than 20% after one month. The concentration of other soluble species (organics, counterions, etc.) was not closely monitored. Aliquot pH agreed closely with the pH measured in the supernate over the irradiated resin. Samples irradiated in contact with water, were periodically removed from the irradiation facility and the supernatant pH measured by inserting a glass electrode in the open sample tube.

Specific yield data presented in this report refer to the amount of materia' in a given volume of liquid (usually 10 mL) contacting a given mass (usually 2 g) of resin. In general, yields measured in this manner may depend on factors such as resin-to-water ratio, ionic strength of the solution, solubility limits, etc. Consequently, the yields should properly be considered relative rather than absolute values. Examination of concentration effects on yields will be described in a subsequent report. It is worth noting here, however, that in IRN-77 resin under the present experimental conditions, there is no evidence that specific yields of soluble sulfate were significantly restricted by concentration effects or ionic strength in solution.

#### 2.3.3 Resin Exchange Capacity

The measurement of exchange capacity followed the procedure developed by Kunin and Fisher (1955). Unirradiated or irradiated cation resins are first converted to the hydrogen form with HNO3. The resin is then rinsed and dewatered by suction. One gram of the resin is contacted overnight with 200-ml 0.1 N NaOH/10% NaCl solution. Aliquots of the supernatant liquid are then back titrated with 0.1 N HCl to determine the amount of H<sup>+</sup> released by the resin. The resin moisture content is determined separately. Exchange capacity is given by meq H<sup>+</sup> released per g of dry resin.

#### 2.3.4 Free Liquid and Resin Swelling Behavior

Irradiated anion and mixed bed resins were centrifuged following irradiation. This was done to remove a free liquid phase which became evident upon irradiation. In the analysis, 6 g of resin were centrifuged and the free liquid collected. The bulk density of the centrifuged resin was determined by

- 9 -

measuring the tamped volume of 1 g of resin, to study swelling effects. Two grams of the centrifuged resin were then contacted with 10 mL of deionized water, as in the case of cation resin. The free liquid, or "pore water," and the supernate over the resin-D.I.W. mixture were then analyzed for soluble radiolytic decomposition products.

# 3. RESULTS AND DISCUSSION

# 3.1 Radiolytic Effects on the Properties of Cation, Anion, and Mixed Bed Resins

In this section, experimental results are presented which describe radiolysis effects of potential significance in the storage and disposal of highly radioactive organic ion-exchange resins. These include both chemical (e.g., formation of acidic species in solution) and physical (e.g. loss of swelling capacity) changes in the resin which might result from selfirradiation under prolonged storage or disposal conditions. Emphasis is placed upon factors such as radiation dose rate, resin loading and synergistic interactions in multicomponent systems, which could affect the correspondence between laboratory results and field performance.

# 3.1.1 Radiolytic Attack on the Functional Group - Acid/Base, Salt and Counterion Release

Soluble acidic or basic species are produced by irradiation of ionexchange resins. At the same time, exchangeable counterions (possibly including radionuclides) are released or leached from the resin. Most of these effects are due to radiolytic attack on the resin functional group. In this section, characteristic features of this process are described.

### 3.1.1.1 Sulfonic Acid Cation Resins (IRN-77)

# 3.1.1.1.1 Radiation Dose and Dose Rate Effects

Formation of acidic species in irradiated IRN-77 resin is shown in Figure 3.1. The figure gives data for resin in both the sodium (Na<sup>+</sup>) and hydrogen (H<sup>+</sup>) form. Data are shown for irradiation at three different dose rates  $-1.6 \times 10^6$  rad/h,  $1 \times 10^5$  rad/h and  $4 \times 10^4$  rad/h. The pH was determined in aliquots of the supernate formed by contacting 2 g of irradiated resin with 10 mL of deionized water. Irradiations were carried out on fully swollen resin in sealed glass vessels, as described in Section 2.

The H<sup>+</sup> form resin is substantially more acidic than the Na<sup>+</sup> form. The dependence of pH on radiation dose is also different for the two forms. For the hydrogen form resin, the hydrogen ion concentration [H<sup>+</sup>], as determined from pH, increases roughly as  $D^{2/3}$  over the range from ~10<sup>7</sup> to  $10^9$  rad, where D is the '~se in rad. In this relation, there is no evidence for any dependence of radiation damage yield upon radiation dose rate. For the Na<sup>+</sup> form resin, the behavior is more complex. [H<sup>+</sup>] increases roughly as D for low total doses and more nearly as  $D^{2/3}$  for larger doses. In all cases, the cation resin acidity increases steadily with increasing irradiation dose.

Figure 3.2 shows the total sulfate ion concentrations found in the supernatant liquids whose pH values were given in Figure 3.1.



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Figure 3.1 Supernate pH vs irradiation dose for irradiated H<sup>+</sup> (open points) and Na<sup>+</sup> form (solid points) resin. Dose rates (rad/h): o -1.6x10<sup>6</sup>; □ -1x10<sup>5</sup>; Δ -4x10<sup>4</sup>.



Figure 3.2 Soluble sulfate generation vs irradiation dose for fully swollen IRN-77 H<sup>+</sup> form resin (open points) and Na<sup>+</sup> form resin (solid points). Dose rates (rad/h): o -1.6x10<sup>6</sup>; □ -1x10<sup>5</sup>; Δ -4x10<sup>4</sup>.

Scatter in the data may be attributed to several sources. First, as indicated in Section 2, sulfate levels in the supernate over irradiated resins may be affected to some extent by post-irradiation chemical reactions or leaching processes. Second, since sulfate ion formation involves not only a scission of the -SO3 group but an additional oxidation step as well, variation in the sulfate yield may reflect variation in both the extent of initial bond scission and the extent of secondary (oxidative) processes which produce the SO, ". Mechanisms are considered further in Section 4. For the present, solution analysis indicates that SO4" is, indeed, the dominant species found in the supernate liquids. In selected samples, no significant concentration of SO3" was detected by ion chromatography. Certain samples were oxidized with hydrogen peroxide and their SO4 content redetermined. In no case did oxidation increase the SO4" concentration by more than 15%. Gas analysis (Section 3.1.2) indicates that little, if any, SO2 escaped from the samples during irradiation. We cannot entirely rule out the possibility that species such as SO3" present in the sealed irradiated tube are oxidized to SO4" in the sampling process. Instability of SO3" in soils, for example, is well known (Lindsay, 1979) and for irradiation in a sealed .essel, the atmosphere over resins quickly becomes anoxic (Section 3.1.2), which might favor SO3". Sulfate ion, however, is commonly reported as the final decomposition product of radiolytic attack on the sulfonic acid functional group in fully swollen resins (Egorov and Novokov, 1967). We believe (Section 4) that SO4 most probably results from the rapid hydrolysis of radiolytic SO3 during irradiation. Consequently, we interpret the SO4 levels given in Figure 3.2 as a measure of attack (radiolytic scission) on the functional group.

By this measure, radiolytic attack on the functional group of IRN-77 resin is sensibly the same for both H<sup>+</sup> and Na<sup>+</sup> forms, irradiated under the present conditions. Since the supernate pH of the Na<sup>+</sup> and H<sup>+</sup> forms are quite different (see Figure 3.1), the attack on the functional group is not sensitive to pH. A similar behavior has been reported for DOWEX-50 resin irradiated under somewhat different conditions (Kazanjian and Harnell, 1974).

The amount of sulfate produced increases with radiation dose. The yield of sulfate may be expressed by a G-value of number of ions produced per 100 eV absorbed. Data obtained in early scoping experiments (Swyler and Weiss, 1981) and in the present experiment (Figure 3.2) lead to the G-values for sulfate formation under gamma radiation in moist resins given in Table 3.1.

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It is noteworthy that G values for 304<sup>=</sup> formation in the supernate decrease with increasing radiation dose. We cannot entirely rule out the possibility that this represents a radiation dose rate or concentration effect until more long-term data become available. However, other workers have observed or postulated relationships in which radiation damage yields in sulfonic acid ion-exchange media decrease with increasing radiation dose (c.f., Utley, 1959). It presently appears that the decrease in sulfate yield at high total doses is an effect associated with high radiation damage levels (and not radiation dose rate). Mechanisms will be considered in Sections 3.3 and 4.

#### Table 3.1

Data Source	Resin Form	G-Value
(Swyler and Weiss, 1981 3x10 <sup>8</sup> rad, 10 <sup>6</sup> rad/h)	H <sup>+</sup> Na <sup>+</sup>	0.65 + .02 0.60 + .06
Figure 3.2, 10 <sup>8</sup> rad	H <sup>+</sup> Na <sup>+</sup>	0.8
Figure 3.2, 10 <sup>9</sup> rad	H <sup>+</sup> Na <sup>+</sup>	0.3

G-Values for Sulfate Ion Formation in Irradiated IRN-77 Resins

## 3.1.1.1.2 Correlation of pH and Sulfate Levels - Radiolytic Formation of Sulfuric Acid and Sulfate Salts

The correlation between the acidity and sulfate within the supernate of irradiated resins was investigated. Figure 3.3 shows a plot of pH vs total  $SO_4^{\pm}$  levels\* in the supernate of H<sup>+</sup> form IRN-77 resin. A theoretical curve calculated for the dissociation of H<sub>2</sub>SO<sub>4</sub> is also shown. In accord with previous observations, the data agree reasonably well with the anticipated behavior of H<sub>2</sub>SO<sub>4</sub>. A similar plot for Na<sup>+</sup> form IRN-77 resin is shown in Figure 3.4. A calculated curve for the dissociation of NaHSO<sub>4</sub> is also given. The experimental pH is at least one unit greater than would be expected on the basis of NaHSO<sub>4</sub> formation.

The supernates of several samples of irradiated H<sup>+</sup> form resin were titrated with NaOH. At the same time, the supernate was reanalyzed for  $SO_4^=$ . The fraction of the acidity attributable to  $H_2SO_4$  was then determined. This ranged from 60% at a dose of  $2 \times 10^7$  rad to 100% at  $10^9$  rad (Table 3.2). These results confirm that, for the H<sup>+</sup> resin, the primary acidic species in solution is sulfuric acid. At lower doses a weaker acid is also present as indicated both by the total acidity and by the shape of the titration curves.

For sodium form resins, radiolytic acidity estimates made in conjunction with the TMI cleanup have assumed acid salt (NaHSO4) formation (Wallace et al., 1980). In Figure 3.4, however, the supernate is substantially less acidic than would be expected on the basis of acid salt (NaHSO4) solutions. Titration data, sodium, and sulfate levels are given for the supernate of irradiated Na<sup>+</sup> form resin in Table 3.3. The Table also includes data from early scoping experiments described in Swyler and Weiss (1981).

<sup>\*</sup>This assumes a homogeneous distribution of SO4<sup>=</sup> in 10 mL of liquid phase, both within and outside the resin. In the supernate, a certain fraction of the SO4<sup>=</sup> will be incorporated in bisulfate, HSO4<sup>-</sup>. In the measurement technique HSO4<sup>-</sup> is determined as SO4<sup>=</sup>.







Figure 3.4

SO4<sup>=</sup> yields vs pH in the supernate of IRN-77 Na<sup>+</sup> form resin, subjected to various irradiation doses. The dashed line indicates the behavior anticipated for the dissociation of NaHSO4. The crosses indicate measured values for NaHSO4 solutions. The SO4<sup>=</sup> yields include SO4<sup>=</sup> incorporated in HSO4<sup>-</sup> at the indicated pH. Solid points = unirradiated control samples.

#### Table 3.2

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Sulfuric Acid (Percent)	рН	Percent Dissociation
66	2.10	100
85	1.50	63
104	1.05	40
100	0.95	42
	Sulfuric Acid (Percent) 66 85 104 100	Sulfuric Acid (Percent) pH 66 2.10 85 1.90 104 1.05 100 0.95

Fraction of Sulfuric Acid in the Supernate of Irradiated H<sup>+</sup> Form IRN-77 Resin vs Irradiation Dose

#### Table 3.3

Equivalents of Hydrogen Ion, Sodium Ion and Sulfate Ion in the Supernate of Irradiated Na<sup>+</sup> Form Resin

Irradiation Dose (Rad)	[H <sup>+</sup> ] <sup>a</sup>	[Na <sup>+</sup> ] <sup>a</sup>	[S04 <sup>=</sup> ] <sup>a</sup>	рН	Percent Dissociation
5.5 x 10 <sup>7</sup> 3.0 x 10 <sup>8</sup> c 9.1 x 10 <sup>8</sup>	.005 N.M. .041	N.M. <sup>b</sup> 0.11+.02 N.M.	0.03 0.07+.01 0.18	3.0 2.1+.1 2.1	20 N.M. 20
<sup>a</sup> All values in meq 2-g irradiated res <sup>b</sup> N.M. = not measure	per mL. sin. ed.	Supernate for	rmed from 10-m	L deionized	d water and

The data in Table 3.3 confirm that the acidic species in the supernate of the Na<sup>+</sup> resin is not pure NaHSO4. The ratio of H<sup>+</sup> equivalents to SO4<sup> $\equiv$ </sup> equivalents is only about 1:5 rather than 1:2, and the ratio of Na<sup>+</sup> equivalents to SO4<sup> $\equiv$ </sup> equivalents is substantially greater than 1:2. Also only a small fraction (~20%) of the available acid is dissociated at pH 2-3. In contrast, for the H<sup>+</sup> form, roughly half of the acid is dissociated at pH 1, in accordance with the expected behavior for H<sub>2</sub>SO<sub>4</sub>.

To summarize, while attack on  $\text{H}^+$  and  $\text{Na}^+$  resin functional groups proceeds in a similar manner, the secondary processes which result in free acid formation are quite different. For  $\text{H}^+$  resin, sensibly all the SO4<sup>=</sup> production generates the acidic species H2SO4. In Na<sup>+</sup> form resin, less than 2/5 of the SO4<sup>=</sup> production ultimately results in the analogous acidic species NaHSO4. In fact, this fraction may be considerably lower if it is assumed that the weaker acid which is undissociated at pH 2-3 is a second, possibly organic, component. In other words, in comparison to the hydrogen form resin, the sodium form is significantly protected against formation of free acidic species following scission of the functional group.

#### 3.1.1.1.3 Effect of Resin Loading on Radiolytic Degradation

Experiments at high irradiation dose rate (1.6x10<sup>6</sup> rad/h) were carried out to further investigate the effect of resin loading on radiolytic damage and acid product formation. Irradiations of fully swollen resin in the Fe<sup>++</sup> form, Fe<sup>+++</sup> form and NH 4<sup>+</sup> 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 counterions released. pH data and Fe<sup>+++</sup> form solution analysis results are shown in Figures 3.5 and 3.6, respectively.



Figure 3.5 Supernatant pH vs irradiation dose for various forms of fully swollen IRN-77 resin. Dose rate = 1.6x10<sup>6</sup> rad/h. Samples irradiated in sealed environment. ■ - Na<sup>+</sup> form resin; • - NH4<sup>+</sup> form; □ - Fe<sup>++</sup> form; ▲ -Fe<sup>+++</sup> form. Supernate formed from 2-g irradiated resin and 10-mL deionized water.



Figure 3.6 Sulfate ion supernate yields (moles per g of fully swollen resin)
vs irradiation dose in different forms of fully swollen IRN-77
resin.■-Na<sup>+</sup> form; ●-H<sup>+</sup> form; □-Fe<sup>+++</sup> form.

The data in Figure 3.5 indicate the same general trends observed in  $H^+$  form and Na<sup>+</sup> form resin: supernatant pH decreases with increasing radiation dose in all cases, indicating the radiolytic formation of acidic species. In comparison with the Na<sup>+</sup> form resin, the supernates of Fe<sup>++</sup>, Fe<sup>+++</sup>, and NH4<sup>+</sup> form resin are successively more acidic for a given dose. The difference is not large, however, over the dose range indicated in Figure 3.5; the supernatant pH is not particularly sensitive to resin loading.

For resins loaded with iron (and presumably for other forms as well) sulfate released in radiolytic scission of the functional group effectively produces a mixture of sulfuric acid and sulfate salts of the counterion. For the Fe<sup>+++</sup> resin, ion balance (Table 3.4) indicates that at a total dose of  $10^9$  rad, roughly half of the sulfate can be quantitatively accounted for as Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and half as H<sub>2</sub>SO<sub>4</sub>. This analysis assumes that the iron remains in the +3 oxidation state, and that all the H<sup>+</sup> is either in solution or incorporated in bisulfate ion.

Soluble sulfate "yields" in the Fe<sup>++</sup> and Fe<sup>+++</sup> forms of resin are substantially lower than those in Na<sup>+</sup> forms. In particular, for the Fe<sup>+++</sup> form, sulfate levels are less than 50% of those found in the Na<sup>+</sup> form indicating that Fe loading retards scission of the functiona' group. A similar effect has been noted by others (Gangwer et al., 1978).

### Table 3.4

Irradiation	Milliequiva.	lents per mL of Sup	ernatea
Dose (Rad)	H+	Fettt	S04=
0			
2.7x10 <sup>8</sup>	$1.3 \times 10^{-2}$	4.2x10-3	4.8x10-2
5.4x108	2.3x10 <sup>-2</sup>	2.0x10 <sup>-2</sup>	4.8x10-2
8.2x108	3.3x10 <sup>-2</sup>	3.3x10 <sup>-2</sup>	6.8x10-2
1.1x109	4.8x10 <sup>-2</sup>	4.6x10 <sup>-2</sup>	1.0x10 <sup>-1</sup>

Equivalents of Fe<sup>+++</sup>, H<sup>+</sup> and SO<sub>4</sub><sup>=</sup> in the Supernate of Irradiated Fe<sup>+++</sup> Form IRN-77 Resin

<sup>a</sup>The equivalents for H<sup>+</sup> are determined from pH data and include a calculated contribution from undissassociated HSO<sub>4</sub><sup>-</sup> at the indicated pH; supernate formed from 10-mL deionized water and 2 g irradiated resin.

bFe<sup>+++</sup> equivalents are determined assuming that the measured iron in the supernate is entirely in the +3 state.

In Na<sup>+</sup> form resin,  $5 \times 10^8$  rad results in supernatant sulfate levels corresponding to attack on 15% of the functional groups. In Fe<sup>+++</sup> form resin, the same dose produces (soluble) sulfate levels corresponding to scission of only 6% of the functional groups. Even with this apparent protective effect, however, the supernate is more acidic for the Fe<sup>+++</sup> form (Figure 3.5). This may be due to a number of factors, including the possible formation of insoluble iron hydroxides. However, a relatively straightforward interpretation seems possible.

The average ratio of moles of sulfate to moles of Fe is 3.02 for the last three entries in Table 3.4. This indicates that iron and sulfate are released in the ratio of very nearly 1:3, which is consistent with the fact that there are three  $-SO_3^-$  groups for every Fe<sup>+++</sup> ion in the resin. The average ratio of moles of H<sup>+</sup> to moles of SO<sub>4</sub><sup>=</sup> is 0.96. This means that H<sup>+</sup> is produced on a very nearly 1:1 basis with the scission of the functional group.

This H<sup>+</sup> is required to maintain the charge balance in the conversion of  $-SO_3^-$  to  $SO_4^-$ . There is no evidence that it is subsequently taken up by ion-exchange processes in the undamaged resin. The difference in selectivities between H<sup>+</sup> and Fe<sup>+++</sup> would probably prevent this effect. On the other hand, for Na<sup>+</sup> form resin, more moles of sodium are released to the supernate than moles of sulfate. This "extra" sodium (which could be produced in the Jundamental damage process or released in subsequent ion-exchange
processes on the undamaged resin) removes the 1:1  $H^+SO_4^=$  charge balance requirement observed in the Fe<sup>+++</sup> resin. Consequently, although the  $SO_4^=$  yield is greater for Na<sup>+</sup> resin, the supernate can be less acidic.

# 3.1.1.1.4 Effect of Resin Moisture Content on Radiolytic Degradation

Samples of IRN-77 in the  $H^+$  and Na<sup>+</sup> 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 1 g of the dry resin following irradiation. One gram dry samples were chosen to provide the same amount of solid as that in 2 g of fully swollen resin.

Radiolytic attack on the functional group, as evidenced by soluble sulfate formation, is reduced but not eliminated in the dry resin (Table 3.5). The fractional sulfate yields are less than 25% of those for Na<sup>+</sup> and H<sup>+</sup> resins irradiated in the fully swollen form. It is interesting that the oxidized species,  $S0_4^=$ , is observed when water is contacted with resins which have been irradiated in the dry state. For the Na<sup>+</sup> form resin, the soluble species is largely Na<sub>2</sub>SO<sub>4</sub>. For the hydrogen form resin the relationship between pH and SO<sub>4</sub><sup>=</sup> agrees fairly well with the expected behavior for sulfurie acid.

Generally, the pH values of the H<sup>+</sup> and Na<sup>+</sup> form resins irradiated in water (Table 3.6) reproduce those obtained for the supernate over resin irradiated in the fully swollen form. Irradiation in excess water produces acidic species at a rate which is similar to that for resins irradiated in the fully swollen form. During irradiation of the Na<sup>+</sup> 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<sup>+</sup> form resins. It is also worth noting that irradiation produced a decrease in the pH of deionized water irradiated as a control. Under the present experimental conditions (the samples were irradiated in a vented environment), some of the pH decrease could be due to HNO<sub>3</sub> formation as suggested in other radiolysis experiments (c.f. McVay et al., 1980). Presumably, this effect could also occur in the pore water of irradiated resins, resulting in nitrate formation.

# Table 3.5

Resin Form		Na <sup>+</sup> Dry	6		H <sup>+</sup> Dry
	pHa	$so_4 = b$	Na <sup>+</sup> b	pHa	s04 = p
Radiation <sup>C</sup> Dose (Rad) O	5.8	(9.6+0.4)x10 <sup>-7</sup>	(2.5+0.8)x10 <sup>-7</sup>	3.0	<3.5x10 <sup>-6</sup>
2.7x10 <sup>8</sup>	3.7	N.M.d	(2.0+1.4)×10-4	2.3	N.M.
5.4x10 <sup>8</sup>	3.3	N.M.	2.8x10-4	2.0	N.M.
8.2x10 <sup>8</sup>	3.2	(1.9+0.2)x10 <sup>-4</sup>	(3.5+0.7)x10 <sup>-4</sup>	1.8	(2.1+0.2)x10 <sup>-4</sup>
1.1x10 <sup>9</sup>	3.0	(2.3+0.2)x10-4	(6.5+0.3)x10-4	1.8	2.8x10-4

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

<sup>a</sup>pH of supernate formed with 10 mL of water and 1 g of irradiated resin. <sup>b</sup>Moles released in 10 mL of supernate per gram dry resin. <sup>c</sup>Radiation dose rate:  $1.6 \times 10^6$  rad/h. <sup>d</sup>N.M. = not measured.

# Table 3.6

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 <sup>+</sup> Resin	H <sup>+</sup> Resin	Deionized Water Control						
0	5.4	3.2	6.12 +. 01						
1.2×108	_a	-	5.0 + .8						
2.3x108	2.9	1.6							
2.7x108	-	-	4.3 + .5						
5.1x108	2.4	1.1							
5.3x10 <sup>8</sup>		-	3.7 + .3						
7.8x108	2.2	1.0	-						
7.9x10 <sup>8</sup>	-		3.8 + .5						
1.2x109	2.1	1.0	-						
1.3x10 <sup>9</sup>		-	3.5 + .6						

- 21 -

# 3.1.1.2 Quaternary Ammonium Anion Resin (IRN-78)

# 3.1.1.2.1 Radiation and Resin Loading Effect on Release of Soluble Radiolysis Products

For irradiation doses approaching  $3 \times 10^8$  rad the anion resins lose their ability to retain water, and free liquid was observed. In later analysis, this free liquid was removed by centrifuging, and separately analyzed. The remaining dewatered resin was then contacted with deionized water, in the ratio 2 g to 10 mL, and the supernate analyzed as in previous measurements.

The pH of the free liquid and supernate in the Cl<sup>-</sup> form resin is neutral to slightly acidic following irradiation, indicating that strong acids or bases are not formed by the radiolytic scission of the functional group (Table 3.7). This is in agreement with observation of trimethylamine as a decomposition product of irradiated resin (see Section 3.2).

#### Table 3.7

Properties of Liquids Contacting Irradiated<sup>a</sup> IRN-78 Resin

Sample Type	Irradiation Dose (rad)	Liquid Yield (mL)	Liquid pH	Supernate pH Over Centrifuged Resin
	0	<0.2	N.M.b	6.1+0.7
C1-	2.7x10 <sup>8</sup>	0.84	5.7	7.1
	5.4x108	1.20	6.4	6.8
	8.1x10 <sup>8</sup>	1.93	7.4	5.8
	1.1x109	2.06	7.3	5.6
	1.3x10 <sup>9</sup>	2.13	7.0	5.3
	0	<0.1	N.M.	8.6+0.8
OH-	8.0x10 <sup>7</sup>	N.M.	N.M.	10.4*
	1.6x10 <sup>8</sup>	N.M.	N.M.	10.6*
	3.2×10 <sup>8</sup>	N.M.	N.M.	11.0*
	8.0x108	2.38	10.5	10.6
	1.1x10 <sup>9</sup>	2.49	10.4	10.7

<sup>a</sup>All irradiations carried out at 1.6 x 10<sup>6</sup> rad/h.

Liquid yield - Amount of liquid removed by centrifuging 6 g of resin. Liquid pH - pH of liquid removed by centrifuging.

Supernatant pH - pH of supernatant formed from 2 g centrifuged resins plus 10-mL deionized water. For samples indicated by an asterisk (\*) the free liquid was decanted from the resins, rather than centrifuged.  $b_{\rm N.M.}$  = not measured

The centrifuged free liquid and supernate were measured for Cl<sup>-</sup> concentration. The densities of the liquid and the resin after centrifuging were also determined. This information was employed to determine the shrinkage of the resin caused by release of free liquid, whether or not the centrifuged resin was significantly agglomerated, and the extent of counterion release by the irradiation. Results are shown in Table 3.8. Considering that the exchange capacity of the fully swollen resin is ~1.7 meq/g, Table 3.8 indicates that, for doses >8x10<sup>8</sup> rad, sensibly all the available Cl<sup>-</sup> ion is released into the free liquid and supernate solutions. This suggests that the resin has lost its functionality, although the ion exchange capacity was not measured. Other studies (c.f., Moody and Thomas, 1968; Kazanjian and Horrell, 1975) commonly report extensive loss of capacity below 8 x 10<sup>8</sup> rad.

## Table 3.8

Irradiation	Free Liquid Release	Bulk Resin Density	Cl- Re	lease (Mole	s/g)
Dose (rad)	(mL/g)	g/cm <sup>3</sup>	Free Liquid	Supernate	Total
0	.027+.02	0.63+.01	N.M.b	<10 <sup>-6</sup>	N.M.
2.7x108	0.14	0.62	N.M.	$2.9 \times 10^{-4}$	N.M.
5.4x108	0.20	0.63	N.M.	$3.7 \times 10^{-4}$	N.M.
8.1x10 <sup>8</sup>	0.32	0.62	8.5x10-4	4.1x10-4	1.3x10-3
1.1x10 <sup>8</sup>	0.34	0.69	9.0x10-4	3.6x10 <sup>-4</sup>	1.3x10-3
1.3x109	0.36	0.69	$9.0 \times 10^{-4}$	$3.2 \times 10^{-4}$	1.2x10-3
i. 6x109	0.35	0.78	$1.0 \times 10^{-3}$	3.9x10 <sup>-4</sup>	$1.4 \times 10^{-3}$

Physical Changes and Cl<sup>-</sup> Ion Release in Irradiated IRN-78 Resin in the Cl<sup>-</sup> Form<sup>a</sup>

<sup>a</sup>All per gram quantities refer to 1 g of fully swollen resin.  $b_{N,M}$  = not measured.

For the irradiated OH<sup>-</sup> form resin, free liquid and supernate pH values are more basic than those of control samples (Table 3.7). The free liquid chemistry represents the true chemical conditions in the system follow-ing irradiation. This is analogous to pore water in soil samples. The supernate over irradiated and centrifuged resins contains decomposition products which were not removed with the free liquid. The supernate thus provides a measure of total resin decomposition and applies to those field conditions where excess water may be present. The anion resin supernate data may also be compared to the cation resin data. Per gram of OH form resin, the free liquid is much more concentrated than the supernate. However, the pH of the supernate and the free liquids are similar, suggesting a buffering effect. The OH<sup>-</sup> concentration is maintained at about  $3x10^{-4}$  moles/liter. This is

substantially lower than the concentration  $(3 \times 10^{-1} \text{ moles/liter})$  that would be expected on the basis of complete release and subsequent stabilization of OH<sup>-</sup> ion. Either the released OH<sup>-</sup> is incorporated in a weak base, or is taken up in other radiolytic process.

# 3.1.1.2.2 Effect of Radiation on Free Liquid Release

At  $5 \times 10^8$  rad, about 60% of the moisture originally present in the dewatered Cl<sup>-</sup> resin has been released as free liquid. This release is accompanied by a shrinkage of the resin beads and some increase in bulk density of the centrifuged resin, indicative of structural damage or compaction. From volumetric considerations, a free liquid release of 0.35 mL/g corresponds to a shrinkage or bead volume decrease of 38% since the specific volume of the fully swollen resin beads prior to irradiation is 0.91 mL/g. A photomicrograph of the centrifuged resin beads before and after irradiation to  $1 \times 10^7$  rad is shown in Figure 3.7.



Figure 3.7 Photomicrograph of IRN-78 resin beads before (upper) and after (lower) irradiation to 1x10<sup>9</sup> rad at 1.6x10<sup>6</sup> rad/h. The beads were centrifuged prior to photographing to remove free liquid released during irradiation. In agreement with the bulk density data, Figure 3.7 shows that the free liquid release is accompanied by a shrinkage in bead size, rather than a wholesale decomposition of the beads themselves. Also, as indicated in Table 3.7, the release of free liquids reaches a saturation or limiting value of about 60% (6.35 mL/g). This value is achieved at about the point where the resin appears to have lost its functionality, suggesting that loss of capability to retain mointure is related to the scission or loss of functional groups; the moisture content of the resin generally depends on the number of intact functional groups (Helfferich, 1962). Alternately, a decrease in swelling capacity (and hence in moisture retention) has been attributed to changes in resin cross-linking (Rohm and Haas, 1967).

# 3.1.1.3 Mixed Bed Resin (IRN-150)

# 3.1.1.3.1 Radiation and Resin Loading Effects on the Release of Soluble Radiolysis Products

The aim of these experiments is to examine how the radiation damage response of the mixed bed reflects the interaction between individual components, whose individual behavior has been characterized earlier.

The mixed bed systems were found to exhibit a free liquid phase upon irradiation. This free liquid was removed by centrifuge and separately analyzed. The centrifuged resins were then contacted with deionized water as described earlier. Solution analysis results are given for IRN-150 resin in HOH and the NaCl forms in Tables 3.9 and 3.10.

Table 3.9

	Fr	ee Liquid		Supernate Over				
Irradiation	Amount			Centrifuge	ed Resin <sup>b</sup>			
Dose (rad) x 10 <sup>-8</sup>	Released (mL/g)	SO4 <sup>=</sup> (mole/g)	pН	SO4 <sup>=</sup> (mole/g)	pН			
0	0.015+.01	N.M.C	N.M.	<10-6	5.5			
2.7	0.22	7.4x10-6	4.4	N.M.	4.9			
5.4	0.28	6.4x10-5	2.2	2.3x10-5	3.0			
8.1	0.28	1.5x10-4	1.6	4.7x10-5	2.6			
11	0.29	5.9x10-5	1.5	5.9x10-5	2.5			
13	0.36	N.M.	1.4	6.0x10 <sup>-5</sup>	2.4			
16	0.37	$1.37 \times 10^{-4}$	1.3	6.9x10-5	2.3			

Soluble Decomposition roducts in Irradiated HOH Form -150 Resin<sup>a</sup>

<sup>a</sup>All values refer to amount produced per gram of fully swollen resin. <sup>b</sup>Supernate formed from 10-mL deionized water and 2 g of centrifuged resin. <sup>c</sup>N.M. = not measured.

		Free Liquid					Supernate Over Centrifuged Resin b					
Irradiation Dose (rad) x 10 <sup>-8</sup>	Amount Released (mL/g)	SO4" (mole/g)	Na <sup>+</sup> (mole/g)	C1" (mole/g)	рН	SO4" (mole/g)	Na <sup>+</sup> (mole/g)	Cl" (mole/g)	pH [	Total Dissolved Na <sup>+</sup> (mole/g)	Total Dissolved Cl <sup>*</sup> (mole/g)	
0 2.7 5.4 8.1 11 13 16	<pre>&lt;0.02 .13 .24 .27 .31 .32 .33</pre>	N.M.C 6.9x10-5 1.8x10-6 2.7x10-4 1.7x10-4 2.0x10-4 1.9x10-4	N.M. S.0x10-4 5.2x10-4 4.6x10-4 5.5x10-4 7.0x10-4	N.M. 1.9×10-4 3.7×10-4 4.8×10-4 2.5×10-4 2.6×10-4 2.6×10-4	N.M. 2.0 1.6 1.5 1.2 1.1 1.0	<10 <sup>-6</sup> 9.8×10 <sup>-6</sup> 5.4×10 <sup>-5</sup> 7.5×10 <sup>-5</sup> 9.2×10 <sup>-5</sup> N.H. 8.4×10 <sup>-5</sup>	<10 <sup>-5</sup> 2.6x10 <sup>-4</sup> 3.2x10 <sup>-4</sup> 3.2x10 <sup>-4</sup> 2.5x10 <sup>-4</sup> 2.3x10 <sup>-4</sup> 2.3x10 <sup>-4</sup> 2.8x10 <sup>-4</sup>	<10 <sup>-6</sup> 2.2x10 <sup>-4</sup> 2.9x10 <sup>-4</sup> 1.5x10 <sup>-4</sup> 3.4x10 <sup>-4</sup> 3.3x10 <sup>-4</sup> 4.2x10 <sup>-4</sup>	5.8+0. 2.8 2.3 2.2 2.1 2.1 2.0	9 N.M. N.M. 8.2x10-4 8.4x10-4 7.1x10-4 7.8x10-4 9.3x10-4	N.M. 3.2x10-4 6.6x10-4 6.3x10-4 5.9x10-4 5.6x10-4 5.6x10-4 5.4x10-4	

Table 3.10 Soluble Decomposition Products in Irradiated NaCl Form IRN-150 Resin<sup>a</sup>

"All values refer to amount produced per gram of unirradiated resin.

<sup>b</sup>Supernate formed from 10-mL deionized water and 2-g centrifuged resin.

CN.M. = not measured.

In both HOH and NaCl form resin, acidity of the free liquid and supernate solutions increases with irradiation dose. IRN-150 resin is a mixture of IRN-77 and IRN-78 resin in a ratio of 43:57 by weight. The resin contains cation and anion equivalents in a 1:1 ratio. For these conditions, acidity occurring in the HOH form indicates that the acidic species produced in the decomposition of the IRN-77 (H<sup>+</sup>) component are not completely neutralized by the basic IRN-78 (OH<sup>-</sup>) component. Thus, the mixed bed system did not prevent the formation of acidic conditions under heavy irradiation doses.

Again, the free liquids represent the chemical environment which would occur in the absence of additional water. The supernate liquids reflect the additional species which would be released if excess water were present, and provide a measure of total resin degradation.

## 3.1.1.3.2 Correlation of pH, Radiolytic Sulfate and Counterion Yields

Correlations between  $H^+$  and  $SO_4^=$  concentrations in the supernate and free liquid of HOH form resin (Table 3.11) indicate that the liquids are 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 has occurred in the irradiated HOH mixed bed resin, possibly due to formation of trimethyl ammonium sulfate. However, this neutralization is incomplete.

For the NaCl form, the acidity of the supernate solution is remarkably similar to that found for the IRN-77 (Na<sup>+</sup>) resin alone (Figure 3.2). 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<sup>+</sup> and

H<sup>+</sup> form resins. This behavior provides further evidence for partial neutralization of acidity in the irradiated HOH resin. For the free liquid in NaCl form resin (Table 3.12), at lower doses anion equivalents are greater than those for Na<sup>+</sup> plus H<sup>+</sup>, indicating that another positive ion species (quaternary ammonium ion for example) is present. In the supernate, sulfate formation and chloride release is more closely balanced by sodium release. The liquids can roughly be considered a mixture of sulfuric and hydrochloric acids and their sodium salts.

## Table 3.11

Correlation of [SO4<sup>=</sup>]<sup>a</sup> and [H<sup>+</sup>]<sup>b</sup> in Liquids Contacting Irradiated IRN-150 HOH Form Resin

Resin	Irradiation	Free Liq	uid (meq/mL)	Supernate	(meq/mL)
Form	Dose (rad)	[SO4=]	[H+]	[SO4=]	[H <sup>+</sup> ]
нон	<0.02 2.7x10 <sup>8</sup> 5.4x10 <sup>8</sup> 8.1x10 <sup>8</sup> 1.1x10 <sup>9</sup> 1.3x10 <sup>9</sup> 1.6x10 <sup>9</sup>	N.M. <sup>c</sup> 6.8x10 <sup>-2</sup> 4.6x10 <sup>-1</sup> 1.1 4.0x10 <sup>-1</sup> N.M. 7.2x10 <sup>-1</sup>	N.M. 4.0x10 <sup>-5</sup> 9.6x10 <sup>-2</sup> 4.0x10 <sup>-1</sup> 1.8x10 <sup>-1</sup> N.M. 3.5x10 <sup>-1</sup>	<10 <sup>-6</sup> N.M. 1.3x10 <sup>-3</sup> 2.6x10 <sup>-2</sup> 3.4x10 <sup>-2</sup> 3.8x10 <sup>-2</sup> 3.8x10 <sup>-2</sup> 4x10 <sup>-2</sup>	2x10 <sup>-6</sup> N.M. 1.5x10 <sup>-3</sup> 5.1x10 <sup>-3</sup> 6.5x10 <sup>-3</sup> 9.3x10 <sup>-3</sup> 1.4x10 <sup>-2</sup>

"The value for [SO4"] is total sulfate concentration and may include species such as NaHSO4, HSO4" etc., which are not dissociated in the undiluted solution.

<sup>b</sup>Determined from pH measurements, including the computed amount of H<sup>+</sup> incorporated in bisulfate at the measured pH. <sup>c</sup>N.M. = not measured.

#### Table 3.12

Trradiation	Free Li	quid	Supernate				
Dose (rad)	so = + c1 -	Na + + + +	SO4 + C1 -	$Na^+ + H^+$			
2.7x10 <sup>8</sup>			0.56	0.060			
5.4x108	3.0	2.5	0.099	0.092			
8.1x10 <sup>8</sup>	3.7	2.8	0.082	0.10			
1.1x108	1.9	2.1	0.15	0.08			
1.3x10 <sup>8</sup>	2.0	2.4					
1.6x108	1.9	2.7	0.14	0.10			

Ion Balance in Liquids Contacting Irradiated IRN-150 (Na+Cl-) Resin<sup>a</sup>

<sup>a</sup>All values given in meq/mL resin; H<sup>+</sup> values from pH, including the computed amount of H<sup>+</sup> incorporated in Lisulfate at the measured pH.

# 3.1.1.3.3 Comparative Radiolytic Yields in Single Component and Mixed Bed Resins

Interactions in the mixed bed resin can be studied by comparing the fractional release of radiolytic decomposition products with similar data for the individual components (Figure 3.8).

Maximum fractional  $S04^{=}$  yields in the mixed bed system are comparable with those measured in the pure cation resin.  $S04^{=}$  is evidently not extensively bound in the anion resin as an exchangeable ion. This is in agreement with the previous suggestion that the functionality of the anion resin is largely destroyed at a dose of  $5 \times 10^{8}$  rad. By this measure, incorporating the cation resin in a mixed bed has little effect on radiolytic scission of the sulfonic acid functional group.

In the NaCl form, although a significant fraction of the cationexchange sites presumably remain unchanged, practically all the available sodium is released after a dose of  $\sim 5 \times 10^8$  rad - possibly 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. This ion exchange, facilitated by the free standing liquid, could partially convert the cation component to an ammonium form, for example.



Figure 3.8 Fractional release of functional group decomposition products and exchangeable ions. ○ - Na<sup>+</sup>, IRN-150, NaCl form; ♥- C1<sup>-</sup>, IRN-78 C1<sup>-</sup> form; ♥- C1<sup>-</sup>, IRN-150, NaCl form; □ - S04<sup>=</sup>, IRN-150, NaCl form; o- S04<sup>=</sup>, IRN-150, HOH form; ■- S04<sup>=</sup>, IRN-77, Na<sup>+</sup> form; o- S04<sup>=</sup>, IRN-77, H<sup>+</sup> form.

# 3.1.1.3.4 Relative Free Liquid Re sase in Single Component And Mixed Bed Resins

In Figure 3.9, the free liquid release in NaCl form and HOH form IRN-150 resin is compared with that observed earlier in Cl<sup>-</sup> form IRN-78 resin. The figure also gives results expressed as percent shrinkage of the anion component. This analysis indicates that release of free liquid from the anion resin is promoted in the mixed bed. A similar effect in the shrinkage of irradiated anion resin has been mentioned by Paumann (1966). The shrinkage (and subsequent liquid release) is confined largely to the anion component, as shown in Figure 3.10.



Figure 3.9 Free liquid release vs irradiation dose in IRN-78, ▼ - (C1<sup>-</sup>); IRN-150, ● - (HOH); and IRN-150, ■ -(NaC1) resins.



Figure 3.10 IRN-150 (HOH) form resin before (left) and after (right) irradiation to 1x10<sup>9</sup> rad. The cation component darkens under irradiation but does not undergo extensive shrinkage.

# 3.1.2 Radiolytic Gas Generation

#### 3.1.2.1 Gas Generation in IRN-77 Resin

The results presented in this Section refer to samples of IRN-77 resin prepared and gamma irradiated in sealed Pyrex tubes, according to procedures described previously. Gas generation was studied for different resin loadings and moisture content.

# 3.1.2.1.1 H+ Form Resin - Fully Swollen

The partial pressures of the various gases found in the atmosphere over irradiated IRN-77 H<sup>+</sup> resin have been calculated from the observed total pressure and compositional analysis. The total pressure and various partial pressures are shown in Table 3.13 for different times and at different irradiation dose rates.

			P	ressure	(psi)				1
Dose Rate (rad/h)	Time († )	H2	00	c0 2	N <sub>2</sub>	02	Ar	Total	
0	0	0	0	0	11.5	3.08	0.14	14.7a	-
	165	N.D.b	0.37	2.10	10.4	1.95	0.13	15.3	
	340	N.D.	0.08	0.08	11.0	3.09	0.14	14.4	
	508	0.02	0.12	1.98	10.9	2.20	0.14	15.4	
	675	C						14.6	
	845	0.01	0.74	2.26	9.8	1.52	0.12	14.6	
	1018							14.4	
4x10 <sup>4</sup>	0	0	0	0	11.5	3.08	0.14	14.78	
	165	0.11	0.15	2.31	11.2	0.52	0.14	14.4	
	340	0.24	0.08	2.51	11.0	0.01	0.14	14.0	
	508	0.38	0.50	2.02	10.7	0.07	0.14	13.8	
	675d	0.02	0.35	1.98	9.8	1.89	0.12	14.2	
	845d	0.05	N.D.	0.04	10.6	2.55	0.13	13.4	
	1018	0.69	0.13	1.62	10.7	0.01	0.13	13.3	
1×105	0	0	0	0	11.5	3.08	0.14	16.78	
	165	0.25	0.40	1.87	10.7	0.09	0.13	13.5	
	340	0.63	N.D.	2.83	11.2	0.01	0.14	14.9	
1 A C C C C	508							14.1	
	675	1.03	0.60	1.65	10.5	0.01	0.13	14.1	
	845	1.17	0.19	1.94	10.5	0.01	0.13	13.9	
	1018	1.40	0.26	1.74	10.5	0.01	0.13	14.1	
1.6x106	0	0	0	0	11.5	3.08	0.14	14.78	
	165	4.83	0.86	2.87	10.1	0.01	0.14	18.9	
-	340	9.62	N.D.	4 43	10.0	0.01	0.12	24.3	
×	508	15.8	0.24	6.41	9.7	0.02	0.13	32.4	
	675							38.2	
	845	28.9	0.43	8.88	9.7	0.01	0.13	48 2	
*	1018	35.6	0.52	8.71	9.9	0.21	0.13	55.1	

#### Table 3.13

Gas Pressures in the Atmosphere Over Irradiated H+ Form IRN-77 Resin

Assumes initial composition of standard air at 1 atmosphere. bN.D. = not detected; pressure <0.01 psi. CGas composition not analyzed. dCompositional analysis suspect. For the unirradiated control samples, the pressure does not vary systematically with time. The pressure averaged over all control samples is 14.8 psi and the r.m.s. deviation is +0.41 psi. These values should be taken to reflect, respectively, the average initial pressure for these experiments, and the experimental uncertainty (+3%) in a given pressure determination. The compositional analyses are subject to additional uncertainty. In particular, air may be introduced during sample transfer processes. This seemed to have happened in the samples indicated by (d) in Table 3.13.

The principal radiolytic gas generated is hydrogen. The hydrogen pressure increases in a closely linear manner with irradiation dose over a range of dose rates (Figure 3.11). A least squares  $po^{-2}r$ -law fit to the data indicate that this dependence is linear to within experimental uncertainty. In other words, the G-value for radiolytic hydrogen generation is insensitive to radiation dose rate. Between  $10^6$  and  $10^9$  rad, the G value derived from the fit is 0.13 + .02.



Figure 3.11 Hydrogen pressure over irradiated IRN-77 H<sup>+</sup> form resin. Dose rates (rad/h): 0 - 1.6x10<sup>6</sup>;  $\Box$  - 1x10<sup>5</sup>;  $\Delta$  = 4x10<sup>4</sup>.

A second major radiolytic gaseous component is carbon dioxide. This appears in two stages. In unirradiated control samples and in samples irradiated at 4 x  $10^4$  and  $10^5$  rad/h,  $CO_2$  levels, remains fairly stable with time at roughly 2 psi. For irradiation at  $1.6 \times 10^6$  rad/h, a second stage of  $CO_2$  generation is evident.

In all cases, oxygen is rapidly depleted from the atmosphere over irradiated resins; a dose of >10 Mrad to 6 g of resin is sufficient to remove 100 micromoles of atmospheric oxygen. At high doses, CO2 generation persists long after atmospheric oxygen is consumed. The table also indicates that some autooxidation (or possibly biodegradation) of the resin may be occurring even in unirradiated samples.

# 3.1.2.1.2 Na<sup>+</sup> Form Resin - Fully Swollen

Figure 3.12 shows a buildup of cell pressure vs irradiation time for irradiation of Na<sup>+</sup> form IRN-77 at three different radiation dose rates. Data for an unirradiated control sample is also given.



Figure 3.12 Sample cell pressure vs irradiation time at different dose rates for Na<sup>+</sup> form IRN-77 resin. Irradiation dose rates (rad/h):  $o = 1.6 \times 10^6$ ;  $\Box = 1 \times 10^5$ ;  $\Delta = 4 \times 10^4$ ;  $\bigcirc$  - unirradiated.

For the sodium form resin in this experimental configuration, pressure changes in control samples and in samples irradiated at low dose rates are marginally detectable. The relatively large fluctuation in sample cell pressure in these experiments is due to the use of a large volume evacuated cell in the pressure measurement (Section 2). For irradiation at higher dose rates, fairly substantial pressures are achieved. The G-value for total gas generation determined from a linear fit to the data is approximately 0.25.

Table 3.14 gives the percent composition of the gas phase over the sodium form resins in the various experiments. Again, hydrogen and carbon dioxide are the principal gases generated. The partial hydrogen pressure derived from Figure 3.12 and Table 3.14 increase in an approximately linear manner with irradiation dose. The G-value obtained for H<sub>2</sub> generation (~0.16) is comparable to that for H<sup>+</sup> form resin.

#### Table 3.14

Dose Rate	Time				Perce	ent Com	positic	n		
(rad/h)	(h)	H <sub>2</sub>	02	N <sub>2</sub>	Ar	CO	co2	NOX	SO2	H20
0	1030	N.D.a	20.1	76.6	0.91	0.6	1.68	N.D.	N.D.	.06
$4 \times 10^{4}$	1030	0.56	19.8	76.1	0.91	0.7.	1.79	N.D.	N.D.	.09
$1 \times 10^{5}$	1030									
$1.6 \times 10^{6}$	1030	65.8	0.42	19.9	0.26	N.D.	13.4	N.D.	N.D.	0.17

# Atmospheric Compositions Over Irradiated Na<sup>+</sup> Form Resins (Contact Time 1030 h)

Samples irradiated at low dose rates show an uptake of atmospheric oxygen which is approximately balanced by the formation of  $CO_2$ . In samples irradiated at high dose rates, which show substantial hydrogen generation, the amount of  $CO_2$  present is greater than that anticipated on the basis of conversion of  $O_2$  to  $CO_2$ .

For both the Na<sup>+</sup> and H<sup>+</sup> form samples, oxygen could initially be taken up by the conversion of atmospheric oxygen to  $CO_2$ . At greater doses (or higher dose rates), additional  $CO_2$  is generated by a mechanism which must involve oxygen initially present in the resin or incorporated water.

# 3.1.2.1.3 Fe++, Fe+++, and NH4+ Form Resins - Fully Swollen

Cas generation measurements were also made on IRN-77 resin in Fe<sup>++</sup>, Fe<sup>+++</sup>, and NH4<sup>+</sup> forms (Table 3.15). Gas compositional data for these experiments are less extensive than for H<sup>+</sup> and Na<sup>+</sup> form resins. A number of trends are evident, however. In all cases, hydrogen is the principal gas generated and oxygen scavenging upon irradiation is observed for all resin forms.

Resin	Irradiation Dose	Total Pressure		Partia	1 Pres	sure of	f Compon	ent Ga	ses (p	si)	
Loading	Rad	(psi)	H <sub>2</sub>	02	N <sub>2</sub>	Ar	CO	002	CH4	so2	H20
Fe++	0	13.1+.07									
	2.7×108	16	3.2	.02	9.3	11	1.2	2.5			-
	5.4x108	18									
	8.2×108	2.2	9.9	.01	9.5	.13	.18	2.2			
	1.1×109	28									
	1.3×109	31	19		9.6	1.2		2.0			04
	1.6×109	37	25.	.01	9.0	.12	. 2	2.0			
× ++++		14 411 0					1.0				
	2 2-108	10.071.0	104	6.6	11.0	+10	1.40	2.0			
	4 / XIU	. 17	6.6	110	1114	114	. 21	2.15			
	0.0-10-08	22			10.4						
	1.1.1.09	2.5	0.2		10.5	.13	1.2	3.4	10 M M		***
	1.7.109	33									
	1.JX102	37	24		7 + 1	.10		5.6	***	an inclusion	
	1.6×10,	47	31		9.1	.13	.40	5.8		***	
NH4+	0 1.7×10 <sup>8</sup>	15.2 <u>+0</u> .6 24.5	****	1.7	11.3	.13	.23	2.1	***		
	2.9x108 5.7x108 1.0x109	24.5+.3 29 45	7.6		13.5	.17	0	3.3	.02	***	.03
	1.3×109 1.6×109	51 65	46		10.7	.14	.23	8.5	.12		.04

#### Table 3.15

Radiolytic Cas Generation Data for Various Forms of IRN-77 Resin

Blank entry - not measured; --- not detected; pressure <0.01 psi. Irradiation dose rate:  $Fe^{++}$ ,  $Fe^{+++} = 1.6 \times 10^6$  rad/h;  $NH_4^+ = 2.5 \times 10^6$  rad/h.

The G-values for H<sub>2</sub> generation derived from the data in Table 3.15 for Fe<sup>++</sup> and Fe<sup>+++</sup> forms (0.11 and 0.14, respectively) are comparable to the values found earlier for H<sup>+</sup> form resin. Hydrogen generation is greatest in NH<sub>4</sub><sup>+</sup> form resin; at 1.6 x 10<sup>9</sup> rad, H<sub>2</sub> yields are about twice as large as those for Fe<sup>++</sup> form. SO<sub>2</sub> was not detected for any resin irradiated in the fully swollen form. CO<sub>2</sub> is observed over unirradiated resins. This may be either introduced in the flame sealing process or indicitive of a decomposition mechanism such as biodegradation.

# 3.1.2.1.4 Nat and Ht Form - Oven Dry

Gas generation measurements were carried out on Na<sup>+</sup> and H<sup>+</sup> form resin which had been dried to 7% moisture content prior to irradiation (see Section 2). Data are given in Table 3.16.

#### Table 5.16

Radiolytic Gas Generation in Dried IRN-77 Resin<sup>8</sup>

Resinb	Irradiation Dose	Total Pressure		Partial Pressure of Component Gases (psi)								
Loading	Rad	(psi)	H <sub>2</sub>	02	N <sub>2</sub>	Ar	00	∞2	CH4	SO2	H20	
н+	0 2.7x10 <sup>8</sup> 5.4x10 <sup>8</sup>	13.8+.07 13.3 <del>1</del> .07 14.7	0.5 <u>+</u> .1	0.84.6	10.3+.01	1.22		1.3±.5	c	0.09		
	8.2×10 <sup>8</sup> 1.1×10 <sup>9</sup>	16.5	1.7	0.1	10,1	0.13	***	3.2		0.6		
Na <sup>+</sup>	0 2.7x10 <sup>8</sup> 5.4x10 <sup>8</sup>	14.2+1.6 11.5+.6 11.7+.6	0.6	0.8	9.5	0.11		0.8				
	8.2x10 <sup>8</sup> 1.1x10 <sup>9</sup>	12.0 + .6 13.4 + .4	1.6 2.3	.01	9.2 9.4	0.12 0.10	0.3	0.6		***		

<sup>B</sup>Preasure over 6-g samples irradiated in sealed tubes. <sup>b</sup>All samples dried to 7% moisture content prior to irradiation. <sup>C</sup>--- = none detected. Pressure <0.01 psi. Blank entry = not measured.

Radiolytic gas generation is significantly reduced in the dry resins. Hydrogen pressures are less than 1/10 of those found over 6 grams of fully swollen resin, irradiated under otherwise similar conditions (Tables 3.13 and 3.14). Since 6 g of swollen resin contains roughly half the hydrocarbon mass present in 6 g of dry resin, hydrogen generation in fully swollen resin must be largely associated with the presence of the liquid component. Similar conclusions have been reached by other workers (Mohorcic and Kramer, 1968).

 $SO_2$  and possibly  $CO_2$  are produced when dry H<sup>+</sup> resin is irradiated. The SO<sub>2</sub> results from decomposition of the functional group. The amount produced (~4x10<sup>-6</sup> mole/g at 8x10<sup>8</sup> rad) is negligible in comparison to the SO<sub>4</sub><sup>=</sup> yields found in the supernate over resin irradiated in the dry form (Table 3.6). For the dry Na<sup>+</sup> form, radiolytic SO<sub>2</sub> was not detected under the present experimental conditions.

## 3.1.2.2 Gas Generation in IRN-78 Resin

Curves of radiolytic gas pressure vs irradiation time are shown in Figure 3.13 for IRN-78 resin a. a dose rate of  $1.6 \times 10^6$  rad/h. Gas generation rates do not depend sensitively on the resin form (OH<sup>-</sup> vs Cl<sup>-</sup>) or the presence of corrosion coupons. The total gas generation rate is about five times that observed with IRN-77 cation resin.



Figure 3.13 Gas pressure over IRN-78 resin vs irradiation time at 1.6 x  $10^6$  rad/h. 0 = C1<sup>-</sup> form,  $\Delta$  = OH<sup>-</sup> form.

The partial pressures of the various gases found in the atmosphere over irradiated IRN-78 ORT resin are shown in Table 3.17 for different irradiation times. Hydrogen is the major radiolytic gas generated for both resin forms. The generation rate is somewhat greater for the OHT form resin. Hydrogen G values are 0.62 and 0.34 for OHT and ClT forms, respectively. In all cases, atmospheric oxygen is scavenged.

#### Table 3.17

	Irradiation								
Sample Form	Time (h)	Н2	CO	CO 2	N <sub>2</sub>	02	Ar	CH4	N(CH <sub>3</sub> )
C1-	672	56	0.32	10	11	0.04	0.14	1.10	N.D.
	840	68	0.39	12	11	0.13	0.14	1.42	N.D.
он-	50	4	0.20	N.D.	11	N.D.	0.15	0.11	1.18
	100b	11	N.D.	0.5	11	0.31	0.12	0.16	2.85
	504	73	0.20	N.D.	11	0.02	0.16	0.16	1.60

Partial Gas Pressures in the Atmosphere Over Irradiated IRN-78 Resins

aN.D. = None detected; pressure <0.01 psi. bCorrection made for air introduced in sampling.

For Cl<sup>-</sup> form resin, CO<sub>2</sub> is produced with an apparent  $H_2:CO_2$ ratio of about 5.5:1. Methane formation is also observed.  $CO_2$  is not strongly evident in the atmosphere over OH<sup>-</sup> resin, and trimethylamine is detected. Unirradiated control samples stored for a period equivalent to the irradiation time showed marginal evidence of oxygen uptake and hydrogen generation.

Some caution must be used in interpreting the results in Table 3.17. In particular, at higher radiation doses the samples contained a considerable amount of free liquid. The presence of this free liquid phase may influence gas yields both chrough solubility effects and by permitting the formation of bubbles and vapor pockets within the resin. Formation of such pockets was observed within the irradiated resin both before and after the pressure was released. Finally, some of the gases generated (e.g., trimethylamine) are both dense and soluble. Here, the possibility for stratification of gases in the sampling apparatus exists. This was checked by drawing successive gas samples from several break seal tubes. Thus far, for pressures up to 80 psi, it appears that  $H_2$ ,  $O_2$ ,  $N_2$ , Ar and  $CH_4$  are well distributed in the sampling process. Trimethylamine is either inhomogeneously mixed, in a "heavy fraction", or possibly maintained at a certain vapor pressure over an aqueous solution.

#### 3.1.2.3 Gas Generation in IRN-150 Resin

Total gas pressure vs irradiation time for IRN-150 resin in the HOH and NaCl form resin is shown in Figure 3.14. The gas compositions determined at the end of the irradiation are given in Table 3.18. These data should be regarded as subject to confirmation since as mentioned earlier, formation of gas pockets may occur in samples containing free liquid.





Table 3.18

	Irradiation			Pressu	re (psi	)		
Sample Form	Time (h)	H 2	02	N <sub>2</sub>	Ar	C02	CO	CH4
NaC1	<sub>0</sub> a	0.01	2.9	11.5	0.08	0.1	0.1	N.D.
	168	7.0	0.3	12.7	0.16	N.D.	7.7	0.2
	504	32	N.D.	11.1	0.14	N.D.	7.3	0.6
	840c	51	1.5	11.5	0.15	3.3	7.1	0.9
	1000	58	0.7	11.8	0.16	0.5	7.4	1.1
	<sub>0</sub> a	0.02	2.0	12.6	0.15	N.D.	0.01	N.D.
нон	168	8.5	N.D.	12.5	0.14	N.D.	1.0	0.1
	840	80	0.08	10.1	0.15	N.D.	22	1.0
	1000	111	0.06	11.6	0.14	N.D.	28	1.2

Partial Gas Pressures in the Atmosphere Over Irradiated IRN-150 Resins

<sup>a</sup>All values for unirradiated samples were recorded after the resin had been held in the sample tube for 336 hours. <sup>b</sup>N.D. = not detected; pressure <0.01 psi.

Correction made for air introduced in sampling.

- 39 -

As in all previous experiments, hydrogen is the major radiolytic gas generated and oxygen is rapidly secrenged from the atmosphere over irradiated resins.

The IRN-150 resin is a mixture of IRN-77 and IRN-78 resin in a ratio of 43:57 by weight. Using this information one can consider if the hydrogen gas yield from the mixed bed system is the sum of the yields of the individual components. The predicted yield becomes:

$$G(IRN-150) = G(IRN-77) \times 0.43 + G(IRN-78) \times 0.57$$
(3.1)

Equation (3.1) has been used to calculate the predicted values given in Table 3.19. For the NaCl form and HOH form, the predicted values agree reasonably with measurement. While the calculation is rough, the data indicate that, insofar as radiolytic hydrogen generation is concerned, the yield of a mixed bed system may well be approximated by the (linearly scaled) yields of the individual components.

#### Table 3.19

	G (H <sub>2</sub> )				
Resin Type	Measured	Predicted			
IRN-77 H <sup>+</sup>	0.13+.02				
IRN-78 OH-	0.6	**************************************			
IRN-150 HOH	0.5	0.4			
IRN-77 Na <sup>+</sup>	0.2				
IRN-78 C1-	0.3				
IRN-150 NaCl	0.3	0.3			

G-Values for Radiolytic Hydrogen Generation

In terms of hydrogen generation, the different components of the mixed bed do not interact strongly. This is not true for all gases. The trimethylamine found in the atmosphere over irradiatied OH<sup>-</sup> resin was not observed in the mixed HOH system; this is quite possibly due to differences in pH (and hence in gas solubility) between the irradiated OH<sup>-</sup> and HOH resins (see Section 3.3). There is also an interactive effect on the yields of  $CO_2$ . In the OH<sup>-</sup> form resin, free  $CO_2$  generation was barely detectable. In the mixed bed system, however, more  $CO_2$  is produced in the HOH form than in the NaCl form. Again, one may speculate that  $CO_2$  release is promoted in the acidic environment due to the decomposition of the cation resin component.

# 3.1.2.4 Radiolytic Oxygen Scavenging

Experiments were carried out to study the uptake of atmospheric oxygen by irradiated resins, and the effect of irradiation atmosphere on resin decomposition. These experiments employed stainless steel irradiation cells, equipped with a pressure transducer, as described in Section 2. Results for samples irradiated in mixtures of air, helium and oxygen are given in Table 3.20.

#### Table 3.20

						Gas C	omposi	tion				
Sample <sup>a</sup>		Radiation	Befor	e Irrad (psi)	iation <sup>b</sup>			After	Irradiat (psi)	ion		
Form	Dose (Rad)	Air	Не	02	He	H <sub>2</sub>	02	N <sub>2</sub>	Ar	co	co2	
(1)	IRN-77 (H <sup>+</sup> )	1.37109	5.3	9.4		9.4	7.7	0.01	4.2	0.08	0.35	2.2
(3)	IRN-77 (H+)	8.0x.08	15.0			b	5.9	0.06	11.6	0.15	.58	1.9
(4)	IRN-77 (H <sup>+</sup> )	7.2x108		15.2		14.9	4.6	0.06	0.47	0.14	0.58	1.1
(5)	IRN-77 (H+)	8.0x108	14.7			***	7.1	0.04	11.1	0.1.	0.05	2.4
(6)	IRN-77 (11*)	9.8×108	14.7			-	4.5	0.02	11.1	0.13	0.17	2.0
(7)	IRN-77 (11+)	9.6×108		15.7		15.2	7.9	***		-	0.50	1.9
(8)	IRN-77 (11*)	9.9×10 <sup>8</sup>	6.2	2.4	5.1d	2.4	8.5	***	4.9	0.05	0.67	3.9
(9)	IRN-78 (OHT)	4.2×108		4.0	13.5	3.9	13.5				0.23	
(10)	IRN-77 (H <sup>+</sup> )	5.5x108		1.2	17	1.3	6.7	0.01	0.01		0.31	1.3

#### Radiolytic Gas Generation for Resins Irradiated in Various Atmospheres

"All samples contained 12 g of fully swollen reain except (6), which contained 6 g. The gas was not sampled prior to irradiation. Post-irradiation nitrogen analysis indicates air was accidently introduced in measurements 1 and 8. C--- lot detected; pressure <0.01 psi. dThe oxygen added to this sample was  $18_{02}$ .  $C^{18}_{02}$  was not detected.  $12C_{16}_{018}$  was present at a partial pressure of 0.3 psi;  $12C_{18}_{018}$  was present at a partial presure of 0.07 psi.

The data do not indicate any pronounced variation in hydrogen generation in H+ form resin with atmospheric composition. G-values for H2 generation in an inert He environment are 0.10+.02; for irradiation in an atmosphere originally containing air,  $G(H_2) = 0.12^{4}.02$ . For samples irradiated in excess oxygen,  $G(H_2) = 0.12$  for an initial oxygen pressure (air plus added oxygen) of 6 psi and  $G(H_2) = 0.17$  for an initial oxygen pressure of 17 psi. This latter value, however, refers to a measurement at lower radiation dose rate (measurement 10). One environmental effect 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 irradiaton under oxygen. The maximum free liquid loss was ~.04 mL/g.

CO<sub>2</sub> is found when samples are irradiated in the absence of oxygen (measurements 4 and 7), although CO<sub>2</sub> levels are somewhat greater for samples irradiated under exic conditions. CO<sub>2</sub> formation was studied by isotope doping techniques. In this measurement the initial ratio of  ${}^{18}O_2$  to  ${}^{16}O_2$  in the atmosphere was about 4:1. Following irradiation, the ratio of  ${}^{18}O_2$  to  ${}^{16}O_2$  was  ${}^{-1:10}$ ;  ${}^{18}O_2$  was not detected, and the ratio of  ${}^{16}O_1{}^{18}$  to  ${}^{16}O_2$  was l:10. This indicates that most of the oxygen present in the CO and CO<sub>2</sub> generated probably comes from decomposition of water within the resin on the resin itself rather than from the atmosphere (see Section 3.2.1-3.2.3).

For samples irradiated in an oxygen atmosphere, the total pressure vs time curves can be interpreted as a decrease in gas pressure due to oxygen uptake and a linear increase due to radiolytic gas generation. An example is shown below. The straight line is least squares fitted to the linear portion of the curve (Figure 3.15).



Figure 3.15 Gas pressure over H<sup>+</sup> IRN-77 resin during irradiation at  $8\times10^6$  rad/h. The sample originally contained 6.4 psi of  $0_2$ .

The straight line is then extrapolated to the origin and subtracted from the data. The resulting difference curve (Figure 3.16a) represents the pressure decrease due to radiolytic oxygen uptake corrected for an assumed linear gas generation which occurs simultaneously. The linear hypothesis is tupported by the fact that the pressure defined by the intercept of the fitted straight line ( $P_I$ , Figure 3.15) corresponds almost exactly to the total pressure of stable gases (He, N<sub>2</sub>, Ar) determined after the irradiation. Semilogrithmic plot of the difference curve, (Figure 3.16b) which we take to represent the partial pressure of oxygen in the system, indicate that the oxygen scavenging follows a first order rate equation:

 $\frac{d[0_2]}{dD} = K[0_2]$ (3.2)

Where [02] = amount of oxygen in the gas phase over the irradiated resin sample,

D = radiation dose, in rad.



Figure 3.16 Linear (a) and semilogrithmic (b) plots of the difference between the data and the fitted straight line in Figure 3.14.

For the experimental conditions of measurement 8, K = 6.4 x  $10^{-8}$  rad<sup>-1</sup>, corresponding to an uptake of 90% of the available oxygen by 12 g of resin after a dose of ~3.0 x  $10^7$  rad. The maximum oxygen uptake observed in these experiments was ~3.01 x  $10^{-3}$  moles, (measurement No. 10) at a dose of 3 x  $10^7$  rad in 12 g of resin. There are approximately  $3x10^{-1}$  moles of carbon (and 3 x  $10^{-2}$  moles of  $-SO_3H$ ) in 12 g of fully swollen resin. If the oxygen scavenging involves only attack at the carbon atoms, a maximum -1% of the available carbon atoms are oxidized by atmospheric oxygen in measurement No. 10. In fully swollen resins, some oxidation can also occur in the absence of atmospheric oxygen, as indicated by the  $CO_2$  data. Mohoric and Kramer (1968) have also observed  $CO_2$  evolution for resin samples irradiated in evacuated vessels. The ratio of H<sub>2</sub> to  $CO_2$  in their experiments (~4:1) is roughly similar to that in the present experiments. Extensive oxidation might contribute to agglomeration of resins irradiated in open systems.<sup>6</sup> In all experiments described in this report, no agglomeration was evident for any resins irradiated in a sealed environment.

Analysis of results for the 6-g sample suggests that the rate constant K is roughly proportional to resin mass. K may increase at lower radiation dose rates, accounting for the oxygen scavenging at low doses observed at 4 x  $10^4$  rad/h (Table 3.13). The mechanism of oxygen scavenging has not been established; several possibilities exist and are described in the polymer radiation literature (c.f., Gillen and Clough, 1981).

## 3.2 Irradiation Effects on Resin Solidification and Leaching

# 3.2.1 Solidification of Irradiated Resins

Scoping experiments were carried out on the solidification of irradiated resins. The object was to determine how resin irradiation affected the process latitude for solidification in Portland cement. Resin-cement formulations for the study were derived from previous work in BNL's radwaste and container research program, in which process latitude for unirradiated resin solidification was specifically investigated (Manaktala and Weiss, 1980). Four formulations with increasing waste-to-cement ratios were selected (Table 3.21). For the lower waste/cement + water values (formulations 1 and 2) satisfactory forms can be made from unirradiated resin. For higher ratios formulation 3 with unirradiated resin was found to crack upon immersion in deionized water (Weiss and Morcos, 1981); formulation 4 with uni-radiated resin did not consistently produce a freestanding product (Manaktala and Weiss, 1980).

A number of small cylindrical (2-in. diameter x 4-in. long) resincement forms were cast from irradiated (9 x  $10^8$  rad) and unirradiated IRN-77 resin in the sodium form. Following curing in the casting mold for 28 days at room temperature, the samples were socked for 28 days in deionized water at

"Recent experiments on samples irradiated in an open atmosphere support this assertion.

room temperature. Those samples which did not crack during the soak were then compression tested to determine the compressive strength. The general procedures have been described elsewhere (Manaktala and Weiss, 1980; Weiss and Morcos, 1981). For the irradiated resins, a moisture loss of about 5% during irradiation was compensated for by adding deionized water to bring the resin moisture content up to  $\sim$ 53% before mixing. Test conditions and results to date are shown in Table 3.21.

#### Table 3.21

Waste/ Cement +Water	Swollen Resin (g)	Water (g)	Portland Cement (g)	Resin Condition	Compressive Strength (psi)
	( 13.8	55.0	137.5	RA )	1
0.07	1 :		:	R I	2.7 x 10-
	, 27.5	55.0	137.5	NRb )	
	( -			NR	$(2.1 \pm 0.4) \times 10$
	1 .	-		NR )	
0.14	< · ·			R )	the second second
	1 .	-		R	(2.2 <u>+</u> 0.5) x 1
	( -			R J	
	1 48 9	48.9	122.5	NR )	FC
	10.2	*		NR	F
0.29	) .			NR	F
0143	) .			R	
	1 .			R	1.5 x 103
	· ·		•	R	
	1 44 0	18 0	122.5	R )	
0.00	) 00.0	40.9	-	R	$1.1 \times 10^{3}$
0.34	1 -	*	×	R 1	
	Waste/ Cement +Water 0.07 0.14 0.29	Waste/ Swollen Cement Resin +Water (g) 0.07 { 13.8 - 0.14 { . 0.14 .	Waste/       Swollen         Cement       Resin       Water         +Water       (g)       (g)         0.07       13.8       55.0         0.14       27.5       55.0         0.14       -       -         0.29       48.9       48.9         -       -       -         0.29       66.0       48.9	Waste/       Swollen       Portland         Cement       Resin       Water       Cement         +Water       (g)       (g)       (g)         0.07 $13.8$ 55.0       137.5         0.07 $27.5$ 55.0       137.5         0.14 $27.5$ 55.0       137.5         0.14 $27.5$ 55.0       137.5         0.29 $48.9$ 48.9       122.5         0.29 $66.0$ $48.9$ 122.5	Waste/       Swollen       Portland         Cement       Resin       Water       Cement       Resin         +Water       (g)       (g)       (g)       Condition         0.07       13.8       55.0       137.5       RA         -       -       R       R         -       -       R       R         0.07       27.5       55.0       137.5       NR b         0.14       27.5       55.0       137.5       NR b         -       -       -       R       R         0.14       48.9       122.5       NR b       NR b         -       -       -       R       R         0.29       48.9       122.5       NR b       NR b         -       -       R       R       R         -       -       -       R       R         -       -       -       R       R         -       -       -       R       R         -       -       -       R       R         -       -       -       -       R         -       -       -       R       R

# Compression Test Data on Resin-Cement Waste Forms

cr \* Sample cracked during 28-day immersion.

For formulation 3 in Table 3.21, the forms containing unirradiated resin failed, while those containing irradiated resin did not. Formulation 4 containing irradiated resin remained intact on soaking and exhibited reasonable compressive strength. In previous work, formulation 4 failed when unirradiated resins were used. Consequently, for irradiated resin, solidification is possible at increased waste-to-cement ratios.

The compressive strength of the samples decreases systematically with increasing waste-to-cement ratios. For formulation 2 where forms with both irradiated and unirradiated resins remained intact during the 28-day soak, the compressive strength of two types of sample did not differ significantly. The

forms containing irradiated resin (upper, Figure 3.17) appear darker and more porous than those made with unirradiated resin (lower, Figure 3.17). Comparative leach studies were carried out to compare leach rates for samples containing irradiated and unirradiated resin.



Figure 3.17 Resin-cement forms made with irradiated (upper) and unirradiated (lower) resin after soaking for 28 days in deionized water.

# 3.2.2 Leaching Behavior of Forms Containing Irradiated Resins

In order to evaluate the effect of resin irradiation on radionuclide retention, leach tests were carried out on solidified forms made with irradiated and unirradiated resin. The forms were cast from IRN-77 resin (Na<sup>+</sup> form), water and type I Portland cement. The formulation used was 27.5 g resin to 55.0 g water to 137.5 g Portland cement. (Formulation 2 in Table 3.21). This formulation is identical that used in "scale-up" leaching studies in our laboratory (Dayal, et al. 1983). The resin contained <sup>1,37</sup>Cs and <sup>85</sup>Sr as radiotracers. For forms incorporating irradiated resin, the spiked resin was irradiated to 9 x  $10^8$  rad before solidification.

The irradiated and unirradiated resins were cast into 2-in.-diameter x 2-in.-high cylindrical forms and leached in deionized water according to the modified IAEA procedure described elsewhere (Barletta et al., 1981; Morcos et al., 1982). Results for the cumulative fractional cesium release as a function of leaching time are shown in Figures 3.18 and 3.19.



Figure 3.18 Cumulative fractional cesium release from 2 in. x 2 in. resin-cement composite made with unirradiated resin. V/S = volume-to-surface ratio = 0.85 cm. • = data for similar forms from "scale-up" study of Dayal et al. (1983).



Figure 3.19 Cumulative fractional cesium release from 2 in. x 2 in. resin-cement composite made with resin exposed to  $9 \times 10^8$  rad. V/S = 0.85 cm.

For unirradiated resin, the data are in reasonable agreement with previous measurements in our laboratory (Weiss and Morcos, 1981; Dayal et al., 1983). The data indicate an increased leachability in forms containing the irradiated resin. The C.F.R. for these forms after 24 days of leaching is roughly twice as great as that for the control forms. This difference may reflect an increase in initial release due to the loss of Cs retention capability in the irradiated resin beads. The increased porosity evident in the forms cast from irradiated resin (Figure 3.17) might also enhance the Cs release.

Similar observations on irradiated resin-cement composites have been reported by other workers. Barletta et al. (1981) have found that irradiations did not degrade the solidification properties of D-mix, a proprietary material claimed to be typical of resins used in the Epicor-II system. Heavy irradiation of this material (10<sup>9</sup> rad) prior to solidification resulted in increased Cs leachability. Neilson and Colombo (1982) have reported that irradiation of resin-cement composites following solidification can improve resistance to cracking upon immersion in water, as in Section 3.2.1.

# 3.2.3 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 oven 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 3.22. A dramatic decrease in swelling pressure is evident for high radiation dose levels, although the beads did not shrink significantly under irradiation (c.f., Figure 3.14).

# Table 3.22

Ir: I	radiation Dose (rad)	Irradiation Environment	Sw	elling essure <sup>a</sup> psi
	0		335	+ 43
2.4	x 10 <sup>5</sup>	sealed	208	-
4.5	x 10 <sup>8</sup>	sealed	278	+ 60
1	x 10 <sup>9</sup>	sealed	21	+ 4
1	x 10 <sup>9</sup>	vented	8	<u>+</u> 3
	0		257	+ 4
1	x 10 <sup>5</sup>	sealed	218	+ 1
7.5	x 10 <sup>8</sup>	sealed	143	<del>+</del> 41
1	x 10 <sup>9</sup>	sealed	33	+ 1
1	x 10 <sup>9</sup>	vented	14	<del>+</del> 6
	2.4 4.5 1 1 7.5 1	Irradiation Dose (rad) 0 2.4 x 10 <sup>5</sup> 4.5 x 10 <sup>8</sup> 1 x 10 <sup>9</sup> 1 x 10 <sup>9</sup> 0 1 x 10 <sup>5</sup> 7.5 x 10 <sup>8</sup> 1 x 10 <sup>9</sup> 1 x 10 <sup>9</sup> 1 x 10 <sup>9</sup>	Irradiation Irradiation Dose Environment (rad) $\begin{array}{c} 0 &\\ 2.4 \times 10^5 & \text{sealed}\\ 4.5 \times 10^8 & \text{sealed}\\ 1 \times 10^9 & \text{sealed}\\ 1 \times 10^9 & \text{vented}\\ \end{array}$ $\begin{array}{c} 0 &\\ 1 \times 10^5 & \text{sealed}\\ 7.5 \times 10^8 & \text{sealed}\\ 1 \times 10^9 & \text{vented}\\ \end{array}$	Irradiation       Irradiation       Switched         Dose       Environment       Product         (rad)       1       1         0        335         2.4 x 10 <sup>5</sup> sealed       208         4.5 x 10 <sup>8</sup> sealed       278         1 x 10 <sup>9</sup> sealed       21         1 x 10 <sup>9</sup> vented       8         0        257         1 x 10 <sup>5</sup> sealed       218         7.5 x 10 <sup>8</sup> sealed       143         1 x 10 <sup>9</sup> sealed       33         1 x 10 <sup>9</sup> vented       34

Swelling Force Exerted by Irradiated IRN-77 Resin

Pressure exerted against a 0.5 in.-diam pistou upon rewetting the dried resin in a fixed volume.

The somewhat precipitous decrease in swelling force between  $\sim 7 \times 10^8$ and 1 x 10<sup>9</sup> rad may be due to somewhat different experimental conditions samples irradiated to 10<sup>9</sup> 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 0<sub>2</sub>) underwent a relatively greater degradation. It has been speculated that cracking of resin/cement forms upon immersion in water is due to swelling of the resin beads (c.f., Morcos and Weiss 1980). If this is the case, the increased waste loading latitude obtained for solidified forms with irradiated resins may be attributable to a decreased swelling force in the irradiated resin upon hydration.

# 3.3 Mechanistic Studies

Experiments were carried out investigating the mechanistic aspects of several effects described in Sections 3.1 and 3.2. Results of these experiments, and their interpretation are given in this section.

## 3.3.1 Radiolytic Degradation Mechanisms

Several physically distinct processes may act to produce overall radiolytic scission of the functional group. Proposed mechanisms fell into three classes, as described in the literature (Karpukhina et al., 1976; Hall and Streat, 1903; Tulupov et al., 1973; Ichikawa and Hagiwara, 1973). These are illustrated below for sulfonic acid cation resin.

 Direct radiolytic scission of the functional group, possibly followed by free radical hydrolysis:

 $ArSO_3^{"} \longrightarrow Ar' + SO_3^{-}$  (radiolytic scission) (3.3)

$$so_3 + \cdot H + OH^-$$
 (3.4a)

$$h_{20} + \cdot s_{03}^{-}$$
 (hydrolysis) (3.4b)

II. Attack on the functional group by aqueous radiolysis products:

 $H_{20} \longrightarrow H_{, \circ} OH_{, \circ} e^{-}aq, H_{2}, H_{2}O_{2} (water radiolysis) (3.5)$ 

possible subsequent processes: e.g.,

$$ArSO_3^- + H_2O_2 \rightarrow ArO^- + SO_3 + H_2O \text{ (peroxide attack)} \tag{3.5a}$$
$$ArSO_3^- + H \rightarrow ArH + SO_3^- \text{ (Hydrogen atom attack)} \tag{3.5b}$$

III. Formation of sulfones by redox reaction between functional groups;

 $ArSO_{3}H + ArSO_{3}H \longrightarrow ArSO_{2}Ar + 4_{2}SO_{4}$ (3.6)

Also, an important possibility is the back-reaction, such as

$$Ar' + SO_3 \rightarrow ArSO_3$$
 (recombination) (3.7)

which decreases the radiation damage yield. Finally, in I, II and III above, we have not included reactions between free radicals produced in functional group scission and free radicals resulting from water radiolysis. Such reactions commonly lead to a radiation dose-rate dependence, which is not observed.

It is of practical importance to distinguish between these mechanisms. For example, if Class II mechanisms predominate, radiolysis yields may be strongly dependent on external media and concentrations or radical scavengers, etc. This would affect the correspondence between laboratory results and field performance.

Also, the distinction between Class I and Class III process is of central importance in radiolytic acidity formation. The key question is whether additional hydrogen ion is produced in the oxidation of the SO3<sup>=</sup> group to SO4<sup>=</sup>, which is observed in solution. For Class (I) reactions, the oxidation could occur, for example, via

$$SO_2^{=} + H^{+} + H_2O_2 \rightarrow H_2O + HSO_4^{=}$$
 (3.8)

A number of agents might oxidize the sulfite ion in solution. In any event, for loadings other than H<sup>+</sup>, the bisulfate salt (e.g., NaHSO4) would then result. The bisulfate salt solution can of course be considered an acidic mixture of H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>. On the other hand, in a Class III process, redox considerations do not require that H<sup>+</sup> is produced in the oxidation of SO<sub>3</sub><sup>=</sup> to SO<sub>4</sub><sup>=</sup>. One functional group is oxidized and another simultaneously reduced. In this case, no acidity accompanies functional group scission for loadings other than H<sup>+</sup>. Only pure salts are produced and conversion from the H<sup>+</sup> form would completely protect the resin. In this Section, experiments are described which are aimed at distinguishing between the different mechanisms.

## 3.3.2 Role of Hydrogen Peroxide in Radiolytic Resin Decomposition

Measurements were conducted to determine the effect of hydrogen peroxide on radiolytic resin degradation (c.f., Moody and Thomas, 1972). The principal aim was to examine the role of aqueous radiolysis products in functional group scission. A second objective was to determine how well radiolysis effects can be represented by peroxide attack alone.

In an initial experiment, 5-g samples of H<sup>4</sup> form resin were contacted with 50-mL solutions of 10, 1,  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$  M H<sub>2</sub>O<sub>2</sub> in deionized water. As a control specimen, deionized water was also contacted with the resin. Samples were sealed with parafilm to prevent evaporation; physical changes in the resin were noted periodically.

Over a period of 44 days, the originally dark brown (caramel) colored resin was bleached to a pale yellow color with increasing H2O2 concentration (Figure 3.20). Little color difference was distinguishable between the  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ , and control specimens. This bleaching was the only evident physical change. No agglomeration of the resin, dissolution or fracturing was observed. The liquid remained colorless for all samples throughout the test period.



Figure 3.26 IRN-77 resin in various  $H_2O_2$  solutions (5.0 g resin/50.0-mL  $H_2O_2$  solution). Top (left to right): 10 M, 1 M, 1 x 10<sup>-1</sup> M, 1 x 10-2 M  $H_2O_2$ . Bottom (left to right): 1 x 10<sup>-3</sup> M, 1 x 10<sup>-4</sup> M, 1 x 10<sup>-5</sup> M  $H_2O_2$ , and deionized water only.

- 52 -

To further examine the effect of hydrogen peroxide attack on resin, a series of samples were made containing 5 g of hydrogen form resin and 20 mL of a serially diluted ACS grade 30.0% (8.8 M) hydrogen peroxide reagent. Peroxide solutions in the same molarity without resin were also made up as a check on autodegradation of the peroxide. The pH of these samples remained stable over an 18-day period. Resin-peroxide solution pH and sulfate contents were measured initially after make-up and two more times over a 45-day period. Separate samples were analyzed for each data point to avoid concentrating the solution by successive aliquot subtraction. Results are given in Table 3.23.

#### Table 3.23

(H <sub>2</sub> O <sub>2</sub> ) <sup>a</sup> Moles/L 0 8.8x10 <sup>-6</sup>		pH			(SO4") Moles/L		S Mol	04" Yield es/g Resin	
	Day 1	Day 22	Day 45	Day 1	Day 22	Day 45	Day 1	Day 22	Day 45
0 8.8x10 <sup>-6</sup> 8.8x10 <sup>-5</sup> 8.8x10 <sup>-4</sup> 8.8x10 <sup>-3</sup> 8.8x10 <sup>-2</sup> 8.8x10 <sup>-1</sup> 8.8	3.4 3.6 3.4 3.4 3.4 3.4 3.5 2.5	3.4 3.3 3.1 2.9 2.7 2.7 2.7 1.7	3.1 3.2 3.0 2.7 2.5 2.4 2.6 1.5	3.8x10 <sup>-5</sup> 4.1x10 <sup>-5</sup> 4.0x10 <sup>-5</sup> 3.7x10 <sup>-5</sup> 5.4x10 <sup>-5</sup> 6.1x10 <sup>-5</sup> 7.4x10 <sup>-5</sup> 2.5x10 <sup>-4</sup>	5.7x10 <sup>-5</sup> 5.0x10 <sup>-5</sup> 6.3x10 <sup>-5</sup> 1.2x10 <sup>-4</sup> 3.3x10 <sup>-4</sup> 4.8x10 <sup>-4</sup> 3.9x10 <sup>-4</sup> 1.5x10 <sup>-3</sup>	$\begin{array}{c} 8.0 \times 10^{-7} \\ 5.4 \times 10^{-5} \\ 1.1 \times 10^{-4} \\ 1.5 \times 10^{-4} \\ 5.1 \times 10^{-4} \\ 7.5 \times 10^{-4} \\ 7.8 \times 10^{-4} \\ 2.9 \times 10^{-3} \end{array}$	1.5x10 <sup>-7</sup> 1.6x10 <sup>-7</sup> 1.5x10 <sup>-7</sup> 1.5x10 <sup>-7</sup> 2.2x10 <sup>+7</sup> 2.4x10 <sup>-7</sup> 3.0x10 <sup>-7</sup> 1.0x10 <sup>-6</sup>	2.3x10 <sup>-7</sup> 2.0x10 <sup>-7</sup> 2.5x10 <sup>-7</sup> 4.8x10 <sup>-7</sup> 1.3x10 <sup>-6</sup> 1.9x10 <sup>-6</sup> 1.6x10 <sup>-6</sup> 6.0x10 <sup>-6</sup>	3.2x10-7 2.7x10-7 4.4x10-7 6.0x10-7 2.0x10-6 3.0x10-6 3.1x10-6 1.2x10-5

pH and Sulfate Content of Peroxide-Resin Solutions

Peroxide reacts with the resin to form acidic species and free sulfate. The pH values for the greates:  $H_2O_2$  concentrations (~10 molar) approach these found in heavily irradiated samples. The correlation between  $SO_4^{=}$  ion concentration and pH, however, is quite different from that found in the supernate irradiated samples. Free  $SO_4^{=}$  concentrations and sulfate ion yields are more than an order of magnitude lower than those found in irradiated samples at equivalent pH (Figure 3.3). Unlike the case for irradiation, the acidity produced by peroxide contact cannot be accounted for by sulfuric acid formation. The acidity may be due instead to an organic acid such as to benzene sulfonic acid or its derivatives (Wiley and Reich, 1968).

Results for irradiated mixtures of resin and hydrogen peroxide solutions are shown in Table 3.24. In this experiment, resin-peroxide samples were either held as control samples, or irradiated for 10- and 20-day periods after preparation. The trends for unirradiated control samples are generally similar to those in Table 3.23.

For the irradiated samples in Table 3.24, pH decreases and  $S04^{=}$  increases with increasing irradiation time; the pH and  $S04^{=}$  yields are sensibly independent of H<sub>2</sub>O<sub>2</sub> concentration. The SO4<sup>=</sup> yields per gram of swollen resin irradiated in the perioxide solutions are comparable to those found for resins irradiated in the swollen form at corresponding doses. The

- 53 -

pH values are comparable to those found earlier for resins irradiated in deionized water (allowing for the difference in resin-water ratios). Accordingly, in the present experiments, any effect of added H202 on decomposition of the functional group is overwhelmed by the irradiation effects. Also, samples irradiated in contact with peroxide showed a gross physical degradation which was not observed in a sealed environment, or for samples irradiated in the absence of peroxide (Figure 3.21).

#### Table 3.24

Irradiation Dose Rate	Supernatant Initial (H2O2)	p	54	(S) (30	04") les/L)	SO4 (moles)	Yield (r cesin)
(rad/h)	(woles/L)	day 10	day 20	day 10	day 20	day 10	day 20
0	0	3.8	3.2	$2.4 \times 10^{-5}$	5.3 x 10 <sup>-4</sup>	4.3 x 10 <sup>-8</sup>	8.8 x 10 <sup>-7</sup>
0	8 x 10-3	3.0	N.M.	2.3 × 10^{-4}	3.7 x 10 <sup>-4</sup>	4.0 x 10 <sup>-7</sup>	6.1 x 10 <sup>-7</sup>
0	8.8	2.8	2.5	5.1 × 10^{-4}	1.1 x 10 <sup>-3</sup>	8.7 x 10 <sup>-7</sup>	1.9 x 10 <sup>-6</sup>
1.5 x 10 <sup>6</sup>	0	0.83	0.66	0.18	0.32	$3.0 \times 10^{-4}$	5.5 x 10 <sup>-3</sup>
1.5 x 10 <sup>6</sup>	8 x 10 <sup>-3</sup>	0.92	0.64	0.15	0.31	2.5 × 10^{-4}	5.0 x 10 <sup>-3</sup>
1.5 x 10 <sup>6</sup>	8.8	0.85	<0.6	0.18	0.31	3.0 × 10^{-4}	5.0 x 10 <sup>-3</sup>

pli and Sulfate Content of Irradiated and Unirradiated Keuin-Peroxide Solutionsa

Solution = 5 mL of H2O2 solution contacted with 3-g fully-swollen IRN-77 resin and then held as control samples or irradiated for the times indicated.

aN.M. . not measured.



Figure 3.21 IRN-77 resin irradiated in H<sub>2</sub>O<sub>2</sub> solutions. Left: resin +8 M H<sub>2</sub>O<sub>2</sub>; center - resin +.008 M H<sub>2</sub>O<sub>2</sub>; right - resin + deionized water.

We conclude that, during irradiation, hydrogen peroxide formation is not a rate-limiting step in radiolytic attack on the functional group. Hydrogen peroxide apparently 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 largely attributed to formation of soluble organic acids released in attack on the resin backbone.

# 3.3.3 Role of Ion-Exchange Processes in Release of Soluble Species.

In a Class I mechanism, one expects decomposition products such as NaHSO<sub>4</sub>, containing sodium and sulfate ions in a 1:1 ratio. The data do not fit this simple picture; however, ion-exchange processes must also be considered. In the sodium form resin for example, the primary acidic decomposition product, sodium hydrogen sulfate, could be converted to the sodium sulfate by hydrogen-sodium exchange at an undamaged functional site on the sodium form resin:

(3.9)

 $NaHSO_4 \rightarrow Na^+ + H^+ + SO_4^=$ 

H<sup>+</sup> + ArSO<sub>3</sub>Na --- ArSO<sub>3</sub>H + Na<sup>+</sup>

This could account for the protective effect, relative to radiolycic acid product formation, observed with  $Na^+$  form resin (Section 3.3).

To determine if this mechanism is plausible, measurements first were carried out to investigate the ability of Na<sup>+</sup> form resin to take up H<sup>+</sup> from NaHSO4 solution. In 2-g samples of IRN-77 resin in the sodium form were added to 10-mL solutions of sodium bisulfate in various molarities. The pH of the solution was measured with a glass electrode before and after the resin addition, allowing time for the system to equilibrate.

Under the present conditions, acidity can in fact be considerably reduced by ion-exchange processes (Table 3.25). Titration measurements on irradiated resin samples (Table 3.26) also indicate that at pH 2.8 more than 50% of the H<sup>+</sup> is contained in the resin. A weaker acid is also present in solution and ~2% of the sites in unirradiated resin were in H<sup>+</sup> form. The residual H<sup>+</sup> would not contribute significantly to pH changes upon irradiation in the present experiments.

Much of the sulfate release and acidity may evidently be attributed to NaHSO4 formation and subsequent ion exchange. However, the cumulative correspondence is not complete. At equivalent pH, more sulfate is present in the supernate over irradiated samples than in pure resin/bisulfate solutions. Some of this sulfate may be generated in a process not involving NaHSO4 formation.

- 55 -
#### Table 3.25

NaHSO4 Solution Molarity <sup>a</sup>	0.0	0.001	0.005	0.01	0.05	0.1
Solution pH	5.6	2.9	2.7	2.0	1.7	1.4
Solution + Resin pH	5.0	3.1	3.4	2.3	2.0	1.6

#### pH Elevation of NaHSO4 Solutions (10 mL) by Sodium Form IRN-77 Resin (2 g)

<sup>a</sup>All molarities are approximate.

#### Table 3.26

				meg H+/g Re	sin
Radiation	Supernatea		Superr	nate	Resin
(rad)	Fresh	Agedb	Calculated <sup>c</sup>	Titrated	Titrated
0	5.00	4.00	.005	0.037	0.05
$4.7 \times 10^{7}$	4.10	4.18	.003	0.009	0.06
$1.0 \times 10^{8}$	3.65	3.83	.007	0.020	0.10
$1.7 \times 10^{9}$	2.75	2.82	.083	0.160	0.19

Titration Data for Irradiated Na<sup>+</sup> Form Resin

a2-g resin in 100-mL deionized water. <sup>b</sup>Stored for six months. <sup>c</sup>Calculated from pH data.

#### 3.3.4 Exchange Capacity of Irradiated Sulfuric Acid Resin

In Class I or II processes, exchange capacity decreases by one equivalent for each mole of SO4<sup>=</sup> produced. For Class III processes, exchange capacity decreases by two equivalents per mole of SO4<sup>=</sup>. Exchange capacity measurements were carried out on irradiated fully swollen IRN-77 resins; data are given in Table 3.27. These data are plotted vs sulfate yields in the supernate of the irradiated resins (Section 3.1.1) in Figure 3.23. Hypothetical exchange capacity vs supernate sulfate yield curves for the different processes are also shown.

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Ta	D	A	- 5	21	
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Resin Type	Irradiation Dose Rate rad/h	Irradiation Dose (rad)	% Moisture	Total Exchange Capacity (meq/g dry resin)	
H <sup>+</sup> with	0	0	54.6	5.83	-
coupon	0	0	56.7	5.94	
	$4 \times 10^{4}$	2.0x107	56.2	5.57	
	4 x10 <sup>4</sup>	4.1x10 <sup>7</sup>	54.2	5.69	
	1 x10 <sup>5</sup>	5.6x10 <sup>7</sup>	55.2	5.58	
	1 x10 <sup>5</sup>	1.1x10 <sup>8</sup>	55.3	5.60	
	1.6x10 <sup>6</sup>	8.0x10 <sup>8</sup>	57.1	5.46	
	1.6x10 <sup>6</sup>	1.6x10 <sup>9</sup>	55.0	4.85	
Na <sup>+</sup> with	0	0	55.2	5.53	
coupon	0	0	54.5	5.46	
	4 x10 <sup>4</sup>	1.9x10 <sup>7</sup>	55.6	5.57	
	4 x10 <sup>4</sup>	3.9x10 <sup>7</sup>	55.0	5.56	
	1 x10 <sup>5</sup>	4.8x107	55.0	5.46	
	1 x10 <sup>5</sup>	9.9x107	55.2	5.42	
	1.6x10 <sup>6</sup>	8.0x108	55.4	4.93	
	1,6x10 <sup>6</sup>	1.6x10 <sup>9</sup>	51.8	4.45	
Na+	0	0	55.4	5.49	
	0	0	55.0	5.50	
	4 x104	2.2x107	55.5	5.67	
	4 x10 <sup>4</sup>	4.2x107	55.6	5.42	
	1 x10 <sup>5</sup>	5.5x107	57.8	5.66	
	1 x10 <sup>5</sup>	8.8x107	56.5	5.56	
	1.6x106	9.1x108	56.0	5,47	
	1,6x10 <sup>6</sup>	1.7x109	52.2	4.90	

Exchange Capacity of Irradiated<sup>a</sup> IRN-77 Resins

<sup>a</sup>All irradiations carried out in Pyrex tubes as described in Swyler and Weiss (1981). "With coupon" indicates contact with mild steel corrosion coupons during irradiation.

Certain factors affect the sensitivity of the exchange capacity and the moisture content determinations. When irradiated resins are weighed out and then rinsed with water, weight loss due to dissolution or liquid loss of the resin can be up to 20% of the total resin weight. When a capacity determination is done, it only reflects the exchange capacity of the remaining insoluble resin. The sulfate yield data, however, refer to sulfate release per gram of both soluble and insoluble resin components. Weight change due to loss of  $S04^{=}$  ion in the rinsing process are accounted for in the hypothetical

curve. However, extensive dissolution of the resin backbone could skew the curve. Finally, the hypothetical curve involves two assumptions: first, that any weakly acidic (e.g., phenolic) groups formed by irradiation did not contribute significantly to the measured exchange capacity, and second that the supernatant sulfate levels provide an absolute measure of the total free sulfate produced by scission at the time the exchange capacity was determined. With this caveat, the data in Figure 3.22 suggest that Class III reactions do not play a major role in functional group scission for the fully swollen resins. The data also clearly indicate that the irradiated resin retains sufficient exchange capacity to be potentially effective in uptake of radiolytic  $H^+$ .



Figure 3.22 Cation exchange capacity vs soluble sulfate supernate yields for irradiated IRN-77 resin. Solid line: Hypothetical curve assuming l mmol of SO4<sup>=</sup> represents a decrease in total exchange capacity of l meq. (class I or II process), dashed line: hypothetical curve assuming l mmol of SO4<sup>=</sup> represents a decrease in total exchange capacity of 2 meq (class III process).

#### 4. CONCLUSIONS AND SUMMARY

At this point, it is possible to qualitatively interpret certain features of the experimental results. Conclusions are discussed in Sections 4.1 and 4.2. The practical consequences of this work are summarized in Section 4.3.

#### 4.1 Radiolytic Attack on the Resin Functional Group

• For fully swollen sulfonic acid resin, scission of the functional group may be largely due to direct radiolysis (Class I mechanism). With the possible exception of H atom, it does not appear that aqueous radiolysis products play a dominant role in initiating radiolytic scission of the fully swollen resin (Class II mechanism).

The radiolytic attack on the functional group cannot be modeled by Class (II) reactions involving hydrogen peroxide produced in aqueous radiolysis (Section 3.3). From the present data it is not possible to rule out Class (II) reactions involving aqueous radiolysis products other than H<sub>2</sub>O<sub>2</sub>. However,

(1) The lack of pH dependence (Section 3) argues against a significant role for e<sup>-</sup>aq, since the hydrated electron would be scavenged by the reaction

H30+ + e aq -+ H + H20

(4.1)

(2) The process of thermal desulfonation of aromatic compounds involves electrophilic attack by a proton (Morrison and Boyd, 1960). The lack of a pH dependence in radiolytic desulfonation suggests that this process is not analogous to thermal attack. A similar conclusion has been reached by Tulupov et al. (1972).

(3) Experiments with specific scavengers for H· and OH· have not been carried out. In the mixed bed with NaCl loadings, fractional sulfate yields are apparently not significantly affected by Cl<sup>-</sup> ion present in the free liquid. Since Cl<sup>-</sup> is a scavanger for OH; this suggests that OH· is not directly involved in functional group attack.

(4) Ichikawa and Hagiwara (1973) conclude that the sulfonic acid group is attacked by H atom produced in water radiolysis (reaction 3.6b Class II mechanism). The protective effect of Fe<sup>+++</sup> loading is attributed to the H atom scavenging reaction

(4.2)

In our experiments, however, (Table 3.4) there is no indication that Fe<sup>+++</sup> is reduced to Fe<sup>++</sup> in solution, with an attendant pH decrease. On the other hand, Karpukima et al. (1976) attribute the low temperature radiolytic formation of 'SO3<sup>-</sup> to dissociative electron capture, and assign the protective effect of Fe<sup>+++</sup> to electron scavenging. This mechanism does not require that the hydrated electron be produced in aqueous radiolysis.

A distinction between scission (Class I,II) and cross-linking (Class III) reactions is possible on the basis of the proportionality between sulfate release and loss of exchange capacity. In Class (III) reactions, two functional groups are destroyed for each molecule of H<sub>2</sub>SO<sub>4</sub> produced. This behavior is not supported with our exchange capacity data (Section 3.3) or by the work of Kazanjian and Horrell (1974). This argues in favor of scission (Class I,II) reaction predominating over cross-linking (Class III) in the fully swollen resin. An important feature of the Class I reaction is that it is evidently not very sensitive to the composition of external media or irradiation dose rate.

• Radiolytic scission of the sulfonic acid group initially shows roughly linear dependence on radiation dose, and may be limited by back-reactions at high radiation damage levels. The present data cannot distinguish whether this mechanism involves first order or second order kinetics:

For fully swollen H<sup>+</sup> and Na<sup>+</sup> form sulfonic acid resin, sulfate yields in the supernate at first increase in a roughly linear manner with increasing irradiation dose. For higher doses (>5 x  $10^8$  rad), the sulfate yield begins to level off and approach a limiting or a saturation value. The departure from linearity occurs at a point where the supernatant sulfate yield corresponds to scission of about 15% of the available exchange sites. The limiting supernatant sulfate yields correspond to scission of about 33% of the available exchange sites.

For fully swollen resin, the G-values for sulfate release to the supernate are in reasonable agreement with those of other workers (Kazanjian and Horrell, 1974) or similar systems. This corresponence further suggests that there are not gross disparities between sulfate yields obtained by rinsing and by measuring the supernate. As a first approximation, however, one might expect limiting values of sulfate release to approach 100% of the available exchange sites in the resin. The lower value (~33%) of limiting release inferred from the present measurements may result from two causes:

First, at higher concentrations or radiation doses, some sulfate may be bound in the resin, possibly due to irradiation induced sites having anion functionality. While rinsing/aging experiments have not yet ruled out this possibility, initial analysis does not indicate that significant amounts of sulfate are bound in the resin.

Second, the resin structure is affected by radiation in such a way as to retard the scission of the functional group. A "cage effect" has been proposed in the Russian literature in which, in more compact resins, recombination effects and back reactions are promoted and G values decrease. This is in keeping with the observation of decreased radiation damage in resins with a greater degree of chemical cross-linking (Gangwer et al., 1977). Radiation may also cause cross-linking. Indeed, in Class (III) mechanisms, cross-links are formed in the process of functional group scission. Consequently the saturation value of sulfate release may reflect the cross-linking density at which further scission of the functional group is effectively retarded by recombination reactions. Most kinetic studies on radiation damage in sulfonic acid resin refer to the decrease in exchange capacity (E) with radiation dose. Early studies (Egorov and Novokov, 1966) assumed a first order dependence of exchange capacity on radiation dose (D):

$$\frac{dE}{dD} = -k_1 E \tag{4.3}$$

For somewhat different radiation conditions, Tulupov and co-workers have concluded that the loss of sulfonic acid group exchange capacity is due to combination of Class (I) and cross-linking Class (III) reactions; the loss of exchange capacity is governed by second-order kinetics (Tulupov and Butaev, 1980):

$$\frac{dE}{dD} = -k_2 E^2 \tag{4.4}$$

Assuming the sulfate release to be directly proportional to the decrease in exchange capacity gives

$$S = S_{\infty} (1 - e^{-k_1 D})$$
 (4.5)

for the first order process, and for the second order process,

 $S = S_{\infty} \left( \frac{k_2 DE_0}{k_2 DE_0 + 1} \right)$ (4.6)

In the expression,  $E_0$  is the initial exchange capacity, S the sulfate release, and  $S_\infty$  the limiting value for sulfate release. We have fitted both first order and second order expressions to the sulfate release data. The present data do not extend to high enough doses to clearly discriminate between first and second order processes. The fits indicate that below a dose of ~ $20^9$  rad, this distinction is not pronounced. The sulfate release is prestically linear with doses up to ~ $5x10^8$  rad.

• For dry sulfonic acid resins, the principal mechanism for radiolytic seission of the functional group may be cross-link formation (Class III mechanisms).

Since swelling decreases with moisture content, one would expect any "cage effect" promoting back reactions to become more important as the resin is dried. If water were completely absent, Class (II) reactions cannot take place; water could not stabilize the products of Class (I) reactions against back-reactions. The sulfate yield is thus reduced, in agreement with experiment. Cross-linking (Class III) reactions, however, could still occur. When irradiated oven-dry resin is contacted with deionized water,  $SO_4^{=}$  ion is released. An attractive feature of Class (III) reactions is that the production of  $SO_4^{=}$  is directly accounted for. without requiring environmental interactions to oxidize 'SO<sub>3</sub><sup>=</sup>. However, for resin loadings other than H<sup>+</sup>, Class (III) reactions, if they occur, would be expected to produce only pure salts (e.g., Na<sub>2</sub>SO<sub>4</sub>). A definite pH decrease was in fact observed for irradiated oven-dry resins in the Na<sup>+</sup> form. Still, we believe with the Russian workers (Tupulov and Butaev, 1980) that Class (III) reactions become more favored at low moisture content.

• The acidity of sulfonic acid resin (other than H<sup>+</sup> form) cannot be simply modeled either by direct scission (Class I) processes, or by scission/ cross-linking (Class III) processes. Acidity of irradiated resins may be significantly reduced by ion-exchange processes following functional group scission.

As pointed out in Section 3.3, the distinction between Class (I) and Class (III) is of central importance in radiolytic acidity formation. At present, an unambiguous choice between the two alternatives is not possible both mechanisms may contribute to some degree. For example, in fully swollen Na<sup>+</sup> form resin, the radioytic acidity is low for a Class (I) reaction and too high for a Class (III) reaction. For fully swollen resin, we believe that the acidity data can best be explained by an ion-exchange processes following a direct radiolytic scission. However, it remains possible that Class (III) processes could make some contribution, particularly if some acidity in fully swollen resin results either from a small amount of residual H<sup>+</sup> on the resin or soluble organic acids.<sup>\*</sup>

• In agreement with a general trend (c.f., Gangwer et al., 1977) anion resins are simply less radiation resistant than cation resins of similar backbone structure. Trimethylamine may be a significant decomposition product:

Ahmed et al. (1966) concluded that, in aqueous resin slurries, Class (I) and Class (II) mechanisms make roughly equal contribution to radiolytic scission of the quaternary ammonium functional group. The Class (I) mechanisms in hydroxide form resin is thought to be a Hoffman type reaction producing trimethylamine:

 $Ar-CH_2 - N(CH_3)_3^+ OH^- \longrightarrow Ar-CH_2OH + N(CH_3)_3$  (4.5)

The Class (II) reaction is believed to involve attack by the hydrated electron; again the end product is trimethylamine.

In our experiments, trimethylamine is observed in the gas phase for irradiated OHT form anion resins. For resins in the ClT form, and for HOH and NaCl form mixed bed resin, trimethylamine was not observed as a gas. This may reflect either a change in decomposition mechanism or, more probably, pH dependent solubility effects. The irradiated OHT form resin is quite basic, while the ClT, HOH and NaCl forms are acidic.

Trimethylamine forms trimethlyammonium ion in aqueous media; if trimethylamine is a major product of functional group decomposition, hydration

"Benzene sulfonic acid has not been detected in U.V. spectra of the supernate solutions. of the following amine reaction 4.5 may largely account for the basicity of irradiated OHT form resin. The irradiated CLT form resin does not form strongly basic solutions. For this material, if trimethylamine is in fact a primary decomposition product, basic species produced in the hydration of the amine are apparently balanced by formation of an acidic species in the functional group scission:

ArCH2-N(CH3)3<sup>+</sup> C1<sup>-</sup> + H20 ----

 $ArCH_2OH + N(CH_3)_3 + H^+ + C1^-$ 

The result of Eq. 4.6 would be a solution of trimethylammonium chloride.

• In mixed bed systems, the acidity produced in the decomposition of the cation component is not balanced by basic species produced in the anion resin:

In NaCl form mixed bed resin, acidity is expected, since the Na<sup>+</sup> form yields acidic species, while the Cl<sup>-</sup> form does not produce strong bases (reaction 4.6). For the HOH form resin, partial neutralization of the acidic species occurs, in comparison to pH yields from the H<sup>+</sup> form resin alone. However, in either case, it does not appear that the low pH conditions in the mixed bed system have protected the anion resin against loss of functionality. Since the low pH conditions in the mixed bed did not protect the anion resin, the role of e<sup>-</sup>aq in functional group scission (Ahmed et al., 1966) may be questionable.

• For mixed bed resins, earlier work (Baumann, 1966) has indicated that the release of acidic species may be prevented by an exchange process on the OH<sup>-</sup> form anion resin, e.g.,

2Ar · CH<sub>2</sub> · N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> OH<sup>-</sup> + H<sub>2</sub>SO<sub>4</sub> ----

 $2Ar \cdot CH_2 \cdot N(CH_3)_3^+ SO_4^= + 2H_2O$ 

In the present experiments, this mechanism is not completely effective in reducing acidity, possibly due to loss of functionality in the anion resin.

In the HOH and NaCl form resin, ion balance data indicate the existence of another positively charged species in solution. This species could be trimethylammonium ion or other ammonium forms produced in the decomposition of the anion resin. The pH for the HOH form would then reflect the equilibrium between a weak base (e.g.,  $HN(CH_3)_3^+ + OH^-$ ) and a strong acid ( $H_2SO_4$ ). For the NaCl form resin, the rapid sodium release (Figure 3.8) is noteworthy. In this case, counterion release may be promoted by decomposition of the anion resin; ammonium ions produced in this decomposition could convert the sodium form cation resin to the ammonium form. This mechanism might promote the release of other cations also.

(4.6)

(4.7)

• The yield of free liquid from the anion resin is increased when the resin is incorporated in a mixed bed. Baumann (1966) has also reported that shrinkage in the cation resin is greater when the resin is irradiated in a mixed bed than in single component form. This shrinkage is probaly analogous to the liquid release observed in our experiments. Several possible mechanisms could account for this effect.

#### 4.2 Radiolytic Gas Generation

• In sulforic acid resin G(H<sub>2</sub>) values for hydrogen generation in fullyswollen resins are somewhat lower than expected on the basis of pore water radiolysis:

 $G(H_2)$  for pure water is ~0.45 (Draganic and Draganic, 1971). For a resin containing 50% moisture, one would expect  $G(H_2) = 0.23$  from water radiolysis alone, exclusive of resin-water interactions. For H<sup>+</sup> form resin,  $G(H_2)$  is ~0.13 and does not vary with radiation dose rate. However, in agreement with other studies (McFarland, 1981), hydrogen pressure increases linearly with radiation dose to considerable values (>30 psi) without saturation. In resin-water systems, some process must acavenge species (e.g., OH) which back-react with H<sub>2</sub> to limit saturation pressures in pure water radiolysis, some mechanisms must act to reduce the G-value. In tritrated water experiments, Mohorcic et al. (1974) have found that H atom is taken up by fully swollen Dowex resin with a G-value of C.52. If some of this hydrogen uptake involves reactions with H produced in aqueous radiolysis,  $G(H_2)$  would be reduced.

 For anion resins, in keeping with previous results, G(H<sub>2</sub>) is substantially greater than in cation resins:

The G-value for OH<sup>-</sup> resin is significantly larger than for Cl<sup>-</sup> resin. Since the relative G-values for hydrogen generation are not affected when cation and anion components are mixed, (Section 3) the reason for the different H<sub>2</sub> yield in Cl<sup>-</sup> and OH<sup>-</sup> form resin is not clear. Since the G-values in each case are greater than those expected for pure water radiolysis, decomposition of the functional group may contribute to the gas generation.

For all irradiated resins atmospheric oxygen is quickly scavenged, apparently by a first order kinetic process:

The rate constant for this process is such that, for a closed system, explosive mixtures of oxygen and radiolytic hydrogen were not produced. For irradiation in an open system, as much as 1% of the available carbon atoms may be attacked or oxidized at a dose of  $\sim 3 \times 10^7$  rad. Damage at this level or greater might affect agglomeration behavior.\* Oxidation, indicated by CO<sub>2</sub> generation, may also occur in closed systems involving oxygen present in the

<sup>\*</sup>Recent results on samples unirradiated in open systems indicate that this is in fact the case.

resin or pore water. Free oxygen could also affect the redox reactions involved in attack on the functional group and the stability of the  $SO_3^{=}$  ion (possibly reducing acidity in Class (I) mechanisms - see Section 4.1) - extensive data are not available.

#### 4.3 Practical Consequences of Radiation Damage to Organic Ion-Exchange Resins

The practical implications of the results presented in this report may be summarized as follows.

- For radiation doses in excess of ~10<sup>8</sup> rad, extensive attack occurs on the functional group of polystyrene-divinylbenzene sulfonic acid cation resin. The practical consequences of this effect are:
  - (a) Generation of strongly acidic conditions (pH<2) in aqueous solutions of irradiated resins, leading to a potentially corrosive environment.
  - (b) Release of sulfate ion and/or SO<sub>2</sub> gas. Sulfate ion may interact with solidification agents while SO<sub>2</sub> is a corrosive gas in moist environment.
  - (c) Loss of ion-exchange capacity, with the accompanying release of exchangable counterions including radionuclides.
- For doses up to  $\sim 5 \times 10^8$  rad, each 10 megarads of absorbed dose produces  $\sim 8 \times 10^{-6}$  moles of sulfate ion in the supernate per gram of fully swollen sulfonic acid resin. For H<sup>+</sup> form resin the sulfate ion forms almost pure sulfuric acid. For resin in other forms, the sulfate is present as a mixture of sulfuric acid and sulfate salts of the counterion. For radiation doses up to  $\sim 5 \times 10^8$  rad, attack on the functional group can be roughly modeled as linear with radiation dose which is consistent with either first or second order kinetics.
- In fully swollen sulfouic acid resin sulfate ion is most probably produced by direct radiolytic scission of the functional group, and subsequent hydrolysis of the radical products. This process is not highly dependent on pH environment and resin loading. There is no evidence for a catalytic effect of iron on radiolytic decomposition of the functional group. Iron in fact, decreases sulfate yields. Finally, the yield for radiolytic scission of the functional group does not depend on radiation dose rate. This insensitivity to environmental parameters makes the sulfate yield a convenient measure of radiation durability for regulatory considerations and simplifies the application of laboratory data to field performance. In particular, the present results indicate that, in a sealed environment, accelerated testing at high radiation dose rates is a valid procedure.

- In the field the amount of acidity which results from a given sulfate yield will depend on the resin loading. The acidity will be reduced first by a protective ion-exchange effect in which H<sup>+</sup> ion is exchanged for cation at undamaged resin sites. Second, some of the sulfate may be produced by a mechanism in which H<sup>+</sup> ion is not generated in the oxidation of -SO3<sup>-</sup> to SO4<sup>-</sup>. In this case, the oxygen may come from the decomposition of an adjacent functional group (in a cross-linking reaction), or from the atmosphere, rather than from the pore water. To the extent that this second process operates, conversion of the resin from the H<sup>+</sup> form would protect the resin against radiolytic sulfuric acid formation, unless substantial residual H<sup>+</sup> remains in the resin after conversion. In any event, the acidity is substantially reduced for loadings other than H<sup>+</sup>. The acidity however is by no means eliminated.
- Acidity and radiolytic attack can be reduced (but not eliminated) by drying the sulfonic acid resin. Reducing the moisture content from 50 to 5% decreases radiolytic sulfate yields by 75%. For dry resins irradiated in a closed environment, a probable radiolytic reaction is 2ArSO<sub>3</sub>—Ar-SO<sub>2</sub>-Ar + SO<sub>4</sub><sup>=</sup> with the formation of a sulfone cross-link -- one functional group is oxidized and the other reduced.
- For doses in excess of ~3 x 10<sup>8</sup> rad, radiolytic acidity formation
  was not prevented by using IRN-77/78 resins in mixed bed form (at a
  cation/anion capacity ratio of 1:1). At these doses the cation resin
  loses its capacity to exchange ON<sup>-</sup> for anions (sulfate) released in
  the degradation of the cation resin. The weakly basic species produced in the radiolytic degradation of the anion functional group does
  not neutralize the strong acids released from the cation resin.
- In several ways, the anion component in a mixed bed system may be a drawback from the viewpoint of radiation stability:
  - (a) The anion component does not protect the cation component from radiation, or conversely.
  - (b) The radiolytic hydrogen yield from the anion component is several times greater than for the cation component.
  - (c) Decomposition products from the anion resin may tend to convert the undamaged cation resin into an ammonium form, by ion-exchange processes, promoting the release of radioactive cations. The extent to which this process occurs would depend on the relative selectivity of the different ions. For sulfonic acid resin, the selectivity of sodium is lower than that for ammonium, and the selectivity of cesium is greater.
  - (d) Most importantly, the irradiated cation resin releases substantial amounts of free liquid. Indeed, release of this

liquid is promoted when the resin is incorporated in mixed bed form. This liquid can serve as a transport medium for radionuclides or corrosive species released from the cation resin.

For organic resin wastes, current NRC guidelines limit the integrated dose to  $10^8$  rad under storage or burial conditions. Extrapolating to  $10^8$  rad, the free liquid released from NaCl form resin is about 14% by volume. This is more than 20 times the amount presently considered initially acceptable in a high-integrity container at burial.

The present experiments refer almost entirely to irradiations in a closed system. Under these conditions, hydrogen is the principal radiolytic gas produced. For the fully swollen cation resin, hydrogen generation most probably involves the radiolysis of incorporated water. Yields (~1.2 x 10<sup>-6</sup> moles H<sub>2</sub> per g resin for a dose of 10 Mrad) are somewhat lower than the scaled values for pure radiolysis water. However, unlike the case for pure water, considerable hydrogen pressures (several atmospheres) can be achieved without saturation.

At  $10^8$  rad, an unvented cation resin container with a void volume of 33% would experience a hydrogen overpressure of ~0.5 atmospheres. For anion resin, the H<sub>2</sub> overpressure would be of the order 1.5 to 2.5 atmospheres. For the cation resin, radiolytic hydrogen yields are not strongly dependent on radiation dose rate; this supports the validity of accelerated testing. Hydrogen yields can be substantially reduced in field operations by drying the resin.

- Oxygen gas is removed from the environment of irradiated resins by an efficient radiolytic oxidation process. This occurs for both cation and anion resins in both dry and fully swollen form. In a sealed environment this process quickly depletes atmospheric oxygen initially present, and will prevent the formation of combustible mixtures of hydrogen and radiolytic oxygen. The oxygen scavanging occurs by a first order kinetic process. The rate constant for this process is such that a dose of 10 Mrad to 1 g of remin will take up ~20% of the available oxygen, in the absence of saturation effects. For samples irradiated in a sealed environment, agglomeration of the resin was not observed. This result, and observations on samples irradiated in excess oxygen indicates that radiolytic resin agglomeration may partly involve extensive radiolytic oxidation. Oxidation will be reduced in a sealed environment.
- At this point heavy irradiation appears to enhance, rather than degrade the solidification properties of sulfonic acid resin. The Cs leachability of resin cement forms may increase when the resin is irradiated prior to solidification. This may be due either to a change in effective diffusivity of Cs in the form, due to incorporated sulfates for example, or to loss of resin functionality.

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- 71 -

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41

## WATER TREATMENT IN NUCLEAR POWER PLANTS

#### G. P. Simon

## TABLE OF CONTENTS

1.	Introduction
п.	Radioactive Decay
III.	The Role of Ion Exchangers in a Nuclear Power Plant
IV.	Breakdown Products and Ion Exchangers
Refer	ences

## I. INTRODUCTION

Nuclear reactors create large quantities of potentially harmful radioactive nuclides. It is the general concern of reactor technologists to achieve some useful objective from the controlled fission process while at the same time rendering harmless the radioactivity produced. The primary coolant and moderator water in contact with the nuclear core acts as a vehicle of transport for the radionuclides produced in the core and reactor vessel surfaces to areas outside the reactor vessel and ultimately to the environment.

Radionuclides are produced by the alteration of the atomic nucleus followed by the emission from the altered or excited nucleus of energetic elementary particles or photons. The radioactivity, or decay, is usually designated by the elementary particles emitted. Table 1 is a list of these emissions and elementary particles of interest in reactor coolant technology including those involved in basic nuclear reactions.

These emissions are all basically harmful to biological living systems. The hazards may arise from the radioactivity acting either externally or internally. The relative hazard is dependent upon the emission, its chemical nature, and the decay rate of the radionuclide under consideration.

## II. RADIOACTIVE DECAY

Radioactive decay is characteristic of a wide range of both naturally occurring and synthesized radionuclides. Decay rate is a unique property of each nuclide. This characteristic change can be described mathematically as follows:

Ion Exchange for Pollution Control

Radioactive Emissions and Nuclear Particles'

ABLI

Emission	Charge	Mass no.	Synabol	Energy range (MeV)	
Positron	1+	~0	β+	up to 4-5	
Beta	1-	~0	β+	0.015-15	
Neutron	0	1	n	up to 12	
Alpha	2+	4	a	1.5-11.7	
Gamma	0	0	y	0.01-7	
Proton	1+	1	p-	_	
Deuteron	1+	2	D		
Triton	1+	3	Т	-	

 $\eta = \eta_0 e^{-\lambda t}$ 

(1)

where  $\eta_{\bullet} =$  number of radionuclide atoms present at time zero,  $\eta =$  number of radionuclide atoms present at any time,  $\lambda =$  characteristic decay constant, and t = time.

For all but very special circumstances and then only to a minor degree,  $\lambda$  is independent of temperature, pressure, and chemical state. The time  $(t_{1/2})$  required for an initial number  $(\eta_{\circ})$  of radioactive atoms to decay to half its value is defined as the "half-life" and is expressed by:

	0.693	
177 -	<u>λ</u>	(2)

The characteristic half-lives of the known nuclides extend over a wide range, from fractions of a millisecond to up to 10<sup>18</sup> years. The decay rate, or half-life, is an important factor in considering any waste treatment process, since the products being treated may involve both high-energy emission with a short half-life and low-energy emission with a relatively high persistence or long half-life.

Radioactivity is generally expressed as the rate of disintegration without regard to the type of emissions involved. The standard unit is a curie, and is defined as the quantity of radionuclide in which the number of disintegrations per second is  $3.7 \times 10^{10}$ ; the weight, in grams M<sub>ci</sub>, of one curie of a single radionuclide is given by

$$M_{Ci} = 6.15 \times 10^{-14} \frac{M}{\lambda}$$
 (3)

where M is the gram molecular weight and  $\lambda$  is the decay constant expressed in reciprocal seconds. Table 2 gives a comparison of the curie weight of some commonly encountered radionuclides in primary coolant water from pressurized and boiling water reactors; an indication of the source of the radionuclide of interest is also included in this table.

The energy of radionuclide decay is, by the law of conservation of momentum, distributed between the emitted particle and the daughter nuclide. This distribution is dependent on the mass relationships between the radionuclide and the emitted particle. In beta decay, a high proportion of the energy is emitted with the particle. In alpha decay, a somewhat high proportion of the energy is retained by the daughter radionuclide due to the relatively large mass of the alpha particle. The energy distribution differences between beta and alpha decay are illustrated in Figure 1. This figure also shows the great variety available for energy release as the radionuclide approaches a stable ground state. In assessing the relative significance and treatment process to con-

.

## Half-life and Mass Relationship of Radionuclides'

R

adionuclide	Source	Half life	Mass (g/C
"Ni	Structural	8 × 10° years	13.1
"c	Make-up water	5600 years	6.22
""Cs	Fuel leak	33 years	1.26 × 10-1
* Sr	Fuel leak	28 years	7.03 × 10 <sup>-3</sup>
° Co	Structural	5.27 years	8.8 × 10-+
"Fe	Structural	2.94 years	4.5×10→
"Fe	Structural	45 days	2.03 × 10-*
" Cs	Fuel leak	2.3 years	8.6×10-4
Ru	Fuel leak	1.0 years	2.95 × 10-4
"Ce	Fuel leak	282 years	3.1 × 10-4
"Co	Structural	71 days	3.14 × 10-4
<sup>11</sup> Cr	Structural	21.8 days	1.08 × 10 <sup>-4</sup>
Rb	Fuel leak	19.5 days	1 28 × 10-*
He Ba	Fuel leak	12.8 days	1.37 × 10-4
	Foel leak	8.14 days	8.15×10*
°Y	Fuel leak	61 hr	1.75 × 10-4
140 La	Fuel leak	40 hr	1.78 × 10**
"La	Fuel leak	40 hr	1.78×10 <sup>-+</sup>
Ma Na	Make-up water	15.1 hr	1.15 × 10-7
"a	Make-up water	4.4 × 10 <sup>s</sup> years	44.1
"S	Make-up water	87.1 days	2.34 × 10-4
"Cu	Structural	12.8 hr	2.61 × 10-'
Mn 25	Structural	2.6 hr	4.59 × 10-*
", N	Make-up water	7.4 sec	1.04 × 10-11
<sup>39</sup> Sr	Fuel leak	53 days	3.61 × 10-1
"F	Water	110 min	1.05 × 10-4
",N	Water	10 min	6.92 × 10-*
Mn 23	Structural	313 days	1.29 × 10-4
1 1	Fuel leak	21 hr	8.93 × 10 <sup>-1</sup>
<sup>133</sup> 1	Fuel leak	6.7 hr	2.88×10**
"Zr	Structural	65 days	4.72×10**
w w	Structural	130 days	1.8×10*
w	Structural	24 days	3.44 × 10-4

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FIGURE 2. Trilinear chart of nuclides. (From Sullivan, W. H., *Trilinear Chart of Nuclides*, Oak Ridge National Laboratory, J.S. Government Printing Office, Washington, D.C., 1954, 83. With permission.)

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trol a radionuclide, it is essential to review the decay scheme and evaluate its impact on the environment and the treatment process being used.

The chemical changes associated with radionuclide decay are readily seen on a chart of nuclides arranged according to constant number of neutrons (Z) and constant mass number (A). An excellent reference chart of this type is the Trilinear Chart of Nuclides, available from the Government Printing Office.<sup>3</sup> Figure 2 is a key to types of radioactive transformation available from this chart.

In the production of electric power by nuclear means, the predominant reactor system currently in use is 'he pressurized water reactor (PWR). In these systems, the heat is extracted from the core with water under high pressure, so as to keep the system below the nucleate boiling point. The water still under pressure is circulated in a closed loop through a steam generator back to the reactor core. In most systems of this type, a small percentage of the total flow is continuously demineralized and returned to the main stream. This by-pass purification is used to maintain the quality of the coolant water; in addition, it helps control the radioactivity levels formed in the water from corrosion and abrasion of internal surfaces wetted by the rapidly recirculating primary coolant. Radionuclides formed from corrosion products and other sources are shown in Table 3 for a typical FWR power plant.

The radionuclide distributions given in Table 3 will vary with the nature of the reactor structural materials, fuel cladding, chemicals added for corrosion control, water

#### TABLE 3

Typical Radionuclides in Coolant of a Pressurized Water Nuclear Power Plant<sup>4</sup>

		Activity	level,
		steady	state
Nuclide	Half-life	(µCi/	m1)
"N	7.3 sec		100
"N	4.1 sec		800
**K	7.7 min		× 10-1
"Ar	1.8 hr	4	× 10-2
"F	1.9 hr	4	× 10-2
54Mn	2.6 hr	5	× 10-3
"Cu	12.8 hr	3	× 10-4
24Na	15 hr	1	× 10-1
WWW	24 hr	3	× 10-
**Fe	45 days	1.1	× 10-*
"Ta	111 days	0.6	× 10-4
⊷Co	5.3 days	2.5	× 10-





purity, type of reactor, and neutron flux. The radioactivity level is also influenced by the ratio between the primary coolant volume and the purification flowrate. In this respect, there are differences between PWR and boiling water reactor (BWR) power plants, as indicated by Figures 3 and 4.

# III. THE ROLE OF ION EXCHANGERS IN A NUCLEAR POWER PLANT

Ion-exchange materials are used extensively in the nuclear power industry for the following (Figures 3 and 4):<sup>3-6</sup>



FIGURE 4. Liquid stream treatment system for typical BWR. (From Lin, K. H., 79th Natl. Meeting, American Institute of Chemical Engineers, Houston, March 1975. With permission.)

- 1. Preparation of make-up water
- 2. Treatment of condensate
- 3. Purification of primary coolant
- 4. Maintenance of spent fuel storage pools
- 5. Treatment of low-level radioactive wastes
  - a. High-purity, low chemical content
  - b. Chemical wastes, lab drains, and laundry wastes

Some typical specifications for these various applications of pure and ultrapure water are given in Tables 4 and 5.

In each case, the form of the ion-exchange materials used will depend to a great extent on the desired result. In addition, concepts concerning the equipment required to achieve an end result are continually changing in the nuclear power industry. We will try to review these changes and their relative significance in the following sections.

#### A. Make-Up Water

In the preparation of make-up water, it is desirable and necessary to produce a water quality as close as possible to that which is required by the circulating system under consideration.<sup>1</sup> When this is accomplished, then changes due to chemical excursions are minimized and smooth operation results.

In most light water nuclear plants in service, the make-up water requirements are usually satisfied with a small volume output system. This is understandable, since the circulating stream contains radioactivity and is therefore constructed with a high degree of integrity with respect to leakage. In addition, in the case of BWR plants, the steam is not withdrawn for processing. All the steam leaving the reactor is returned as

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Ion Exchange for Pollution Control

#### TABLE 4

## Typical Reactor Water Requirements

		Reactor type		
	PWR Primary coolant	BWR		
Process stream		Generator	Condensate	
Component				
H, (cc/kg)*	15-35	none	none	
Dissolved O <sub>1</sub> (ppm)	≤0.01	≤0.01	10-30	
Halogens (ppm)	≤0.1	≤0.1	50.05	
Total dissolved salts (ppm)	≤1.0	≤1.0	≤0.05	
Normal pH (77°F)	9.5-10.5	7.0-7.5	7.0-7.5	
' STP				

#### TABLE 5

Typical Auxiliary Water Requirements Common to Both PWR and BWR Systems

	Make-up	Smant fuel	Wastewater	
Component	water	storage	Reuse	Discharge
Halogens (ppm) Dissolved O <sub>1</sub> (ppm)	≪0.1 ≪0.1	n.a.* n.a.	≤5 n.a.	n.a.
TDS (ppm) Color (APHA* units)	≤0.05 n.a.	n.a. 0—5	€0.5 0	n.a.
Turbidity (APHA units) pH (77°F)	n.a. Footnote c	0-5	0-5	<100 <100
Activity level (µCi/1) Silica (nom as SiQ-)	n.a.	≤100	≤100	7.0—7.5 ≤10
Conductivity	<1.0	Ξ.	_	2

Not applicable.

American Public Health Association.

Make-up water pH is adjusted for the reactor system being designed.

treated condensate so that the circulating water inventory remains relatively constant. A make-up water treatment system which might apply is shown in Figure 5.

## B. Condensate Treatment

In the usual case, the condensate will contain only very small amounts of ionic contaminants that result from steam carryover, minor amounts of corrosion products i om the turbine or condenser surfaces or condenser leaks.' Condensate treatment therefore is necessary for the removal of these constituents so that they are not returned to the core vessel to become activated and concentrated.' In general the steam will carry over appreciable amounts of NH<sub>3</sub> (if used in the system), which is beneficial and helps reduce the corrosion rate especially at various heat-exchanger surfaces. Figures 6, 7, and 8 indicate some different points of application for condensate treatment from those shown in Figure 4.







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FIGURE 6. Big Rock BWR plant direct cycle system.

Ion Exchange for Pollution Control



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FIGURE 8. Dual cycle BWR system with superheat.

Comparison of Advantages and Disadvantages of Condensate Treatment Systems

Treatment sy	stem	Advantages	Disadvantages
Conventional mixed- bed polisher		Low pressure drop	Higb capital cost
		Good reserve in event of condenser leak	Somewhat limited by flowrate
		Low leakage levels Relatively low oper- ating costs	
Powdered in change materia	on-ex-	Low capital cost	High pressure drop
		Not flowrate limited	No reserve capacity
		Good filter effi-	High leakage rate
		Low volume of waste disposal	Relatively high op- erating cost
		High rate of reaction	Not good if TDS > 500 ppb

In most plants, conventional ion-exchange mixed beds are used in large vessels (50 ft<sup>3</sup> or more), while in others, small amounts of powdered,<sup>10</sup> or microfine beads of ionexchange materials are used in small equipment (Volume I, Chapter 6). There are advantages and disadvantages for each system, as shown in Table 6.

There are plants with both condensate treatment systems in use at the same time. It would appear that it will be some time before the industry is certain that one system has a technical advantage over the other.

## C. Primary Coolant Purification

### 1. NH,-OH Systems

Primary coolant purification is used in both the PWR and BWR systems." In the PWR plant, the process is carried out as shown in Figure 3 using an appropriate H-OH or salt form mixed bed on a side-stream loop. In the BWR application, it has become common practice to take the water for coolant purification at some point near the core, since it is at this point that the highest concentration of activated corrision products exists. Also, in BWR plants, the ion-exchange mixed bed starts out in the fully regenerated (H-OH) form and is slowly converted to the ammonium (NH<sub>4</sub>-OH) form while removing both particulate and soluble corrosion products.

An example of the performance of an NH<sub>4</sub>-OH mixed bed in service on primary coolant for a PWR system is given in Tables 7 and 8 and shown in Figures 9 and 10. The data given here separate the exchangeable soluble corrosion products from the filterable insoluble corrosion products, often called "crud." The data indicate that an equivalent 100 full power hours utilizes only the first third of the ion exchanger for the removal of the species of interest.

Table 9 summarizes the reactor problem areas. In both systems the coolant purification system is used to reduce the coolant radioactivity level after shutdown in order to facilitate maintenance. An indication of how the coolant purification demineralizer helps to reduce the radiation levels in a PWR system is shown in Figure 11. It is evident from the data shown that the radiation levels found 15 hr after shutdown are signifiIon Exchange for Pollution Control

#### TABLE 7

Performance of an NH.-OH Mixed Bed in Service

on a Primary Coolant of a PWR system14

Rudiation levels fter 1700 hr full ower operation (mR/hr)	Calculated for 15 hr decay (inR/ hr)*	Actually observed (mR/hr)
9000	8901	6
6000	5934	3
3000	2967	1
1000	988	3
550	554	3
400	205	0.4
150	148	0.3
100	08.9	5
15	14.8	0.6

\* Assuming that corrosion products have the following distribution after 1700 full power hours (Nuclide, % of reading):\*\*Co, 7;\*\*Fe, 1; \*\*Mn, 1;\*\*Mn, 73;\*\*Fe, 18.

#### TABLE 8

Distribution of Soluble Corrosion Products on an NH<sub>4</sub>-OH After an Equivalent of 100 Full Power Hours of Operation<sup>11</sup>

Sample vol as	15.25	Ionic cone meq/ml of mixed bed					
% of bed depth	NH.	Fe**	Cr3+	Nia	Co2+	Mn <sup>2+</sup>	Total
0-25 25-52 52-75 75-100	0.21 0.41 0.50 0.54 0.715	0.18 0.12 0.066 0.035 C. 100 Distributio	0.175 0.048 0.019 0.012 C.c. 4	0.015 0.010 0.008 0.006 0.006	0.007 0.005 0.004 0.003 0.005	0.003 0.003 0.003 0.004 0.004	0.590 0.596 0.600 0.600

Products (Crud) on an NH4-OH Mixed Bed after 100 equivalent Full Power Hours of Operation

Sample vol as	Metal oxides (mg/
o or ocu depth	ml of resin)
0-10	- 1
10-20	325
20-30	265
30-40	290
40-50	115
50 60	26
50-00	15
80-70	10
70	8
8090	9
95-100	10
	1
	151,3 2



FIGURE 9. Distribution of soluble corrosion products in an NH.-OH mixed bed. (From Simon, G. P., Abrams, C. M., and Lindsay, W. T., Jr., WAPD-TM-215, Bettis Atomic Power Laboratory, Pittsburgh, July 1960. With permission.)





#### TABLE 9

#### Reactor Coolant Problem Areas

1 Cladintegrity		
2. Clad corrosion	<ol> <li>Corrosion and wear</li> <li>Activity transport</li> </ol>	<ol> <li>Water preparation</li> <li>Poison prep, storage and removal</li> </ol>
3. Fission product release	3. Contamination	<ol> <li>Gaseous activity removal</li> </ol>
<ol> <li>Core deposits</li> <li>Chemical control</li> <li>Radiolysis of coolant</li> <li>Control-rod wear</li> </ol>	<ol> <li>Coolant purification</li> <li>pH control</li> <li>Poison control</li> <li>Decontamination</li> </ol>	4. Conc of active wastes
<ol> <li>Clad integrity</li> <li>Clad corrosion</li> <li>Fission prod. release</li> <li>Core deposits</li> <li>Radiolysis of coolant</li> <li>Control-rod wear</li> </ol>	<ol> <li>Corrosion and wear</li> <li>Activity transport</li> <li>Contamination</li> <li>Coolant purification</li> <li>Decontamination</li> <li>Turbine contamination</li> <li>Feed water purity</li> <li>Condensate treatment</li> </ol>	<ol> <li>Water preparation</li> <li>Gaseous activity</li> <li>Recombination of gases</li> <li>Conc. of active wastes</li> </ol>
	After 1700 full power hours	
	<ul> <li>3. Fission product release</li> <li>4. Core deposits</li> <li>5. Chemical control</li> <li>6. Radiolysis of coolant</li> <li>7. Control-rod wear</li> <li>1. Clad integrity</li> <li>2. Clad corrosion</li> <li>3. Fission prod. release</li> <li>4. Core deposits</li> <li>5. Radiolysis of coolant</li> <li>6. Control-rod wear</li> </ul>	<ul> <li>3. Fission product release</li> <li>4. Core deposits</li> <li>5. Chemical control</li> <li>6. Radiolysis of coolant</li> <li>7. Control-rod wear</li> <li>1. Clad integrity</li> <li>2. Clad corrosion</li> <li>3. Fission prod. release</li> <li>4. Coolant purification</li> <li>5. Poison control</li> <li>7. Decontamination</li> <li>1. Corrosion and wear</li> <li>2. Activity transport</li> <li>3. Contamination</li> <li>4. Coolant purification</li> <li>5. Radiolysis of coolant</li> <li>6. Control-rod wear</li> <li>6. Control-rod wear</li> <li>7. Control-rod wear</li> <li>8. Radiolysis of coolant</li> <li>6. Control-rod wear</li> <li>9. Contamination</li> <li>9. Contamination</li> <li>9. Contamination</li> <li>9. Decontamination</li> <li>9. Decon</li></ul>



FIGURE 11 Shippingport BWR boiler chamber radiation levels. All readings in milliroentgens per hour. (From Petro, W. M., Bettis Tech Review WAPD-BT12, April 1959. With permission.)

cantly lower than what would be expected from normal decay, assuming some ideal distribution of <sup>59</sup>Fe, <sup>60</sup>Co, <sup>58</sup>Mn, etc. The lower radiation levels found are primarily due to the fact that the primary system  $NH_4$ —OH mixed bed was in operation during the 15 hr cooldown period after 1700 hr of full power operation.<sup>11</sup> It is also clearly indicated that radiation levels near the operating mixed beds do not decrease to the same extent for the 15 hr period of interest.

2. Deborating System

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In PWR systems, it has become common practice to use boron as a means of con-

#### Ion Exchange for Pollution Control



trolling core activity and local variations in core reactivity. This effect has been called boric acid "shim" control, and as the term implies, it involves very small changes in neutron flow levels. The use of boron in PWR coolants brings about the following advantages:

- 1. Fewer and less expensive central rods can be used
- Simplified core design can be used.
- 3. A more uniform power distribution is achieved in the core.
- 4. A greater fuel loading can be used to achieve an extended core life.

Control rods are still necessary to keep up with and control those rapid changes due to power demands. Boron "shim" control, however, is used to advantage during startup when the coolant water density is decreasing as the system goes from ambient to operating temperature. During core life, the amount of samarium and xenon poisons in the fuel increases, and proportional decreases of boron concentration are necessary to maintain uniform operations.

Deborating anion-exchange materials are used during start-up to reduce initially high boron concentrations ( $\approx$  3000 ppm as B) to operating levels ( $\approx$  1800 ppm as B) and reduce continually the boron concentration as the fuel depletion and poisoning changes take place during the lifetime of the core.

The removal of borated "shim" from the primary coolant system of land-based nuclear power plants must be carefully controlled. Large quantities of boron, with or without radioactivity, are undesirable contaminants for the environment. Therefore, it has become general practice to treat any and all solutions containing boron for final complete and safe disposal. As indicated in Figure 6, this is accomplished by using a deborating strong-base, type I anion exchanger and recycling the boron-free water back to the primary coolant systems. In addition, the ion exchanger regenerants containing boron and the more concentrated boron solutions encountered during start-up are evaporated to provide a concentrate for final disposal.

#### 3. BWR Entrainment from Steam Generator

At low pressures and moderate temperatures, solute volatility is a minor source of transport compared to the physical carryover or entrainment.

The potential, therefore, exists in the superheater for accelerated attack by chloride solutions; it is also important to maintain chloride ion concentrations at low levels. To prevent the development of concentrated solutions, it would be necessary to maintain all surfaces at 590°F at all times. Then droplets carried in the steam without being deposited would dry out and the salt volatilize into the steam whenever the bulk concentration is less than the minimum solubility for the condition, in the superheater.

Caustic solutions, with the exception of LiOH, will not dry out. These solutions are aggressive to almost any ordinary material of construction used in the superheater. Therefore, free caustic in the steam generator source should be avoided at all times.

#### 4. Turbine Deposits

In high-pressure and supercritical cycles in nuclear systems, problems arising from the transport of volatile solutes will be further complicated by the radioactivity of these volatile solutes. It is essential that this aspect of system operation be thoroughly reviewed before large-scale nuclear plants of this type are built. The transport and retention of iron, for example, will probably be less than 0.1 ppb. For a 1000 MWe plant, the steam flow will be of the order of 10 million lb/hr, or  $80 \times 10^{\circ}$  pounds per year. The iron transport will therefore be no less than 0.8 lb/year. This, together with other material, will be radioactive and will be a very real nuisance during turbine maintenance or repair.

#### D. Spent Fuel Storage Pools

The primary purpose of the ion-exchange materials used is to provide an optically clear water. This is necessary, since all the manipulations required for packaging spent fuel elements must be carried out underwater to keep radiation hazards to a minimum. In special cases, the H-OH form mixed bed is used to remove specific radioactive nuclides which find their way into the pool water from defective fuel elements and cladding failures. Relatively high concentrations of radionuclides may also occur in these facilities from mechanical operations carried out in the pool.

#### E. Waste Treatment

There are two techniques for recovering reactor wastewater.<sup>13</sup> In the first case, the wastewater is filtered, stored for the reduction of short-lived nuclides, and eventually demineralized and recycled. In order to provide the maximum decontamination factors, it has become common practice to employ H-OH form mixed beds in this application. In the second case, the wastewater is evaporated; normally, the evaporator condensate is polished with an H-OH mixed bed, and this treated water is also recycled back to the reactor make-up system.

Some typical decontamination factors that can be achieved with different ion-exchange treatment systems are shown in Table 10.<sup>5</sup>

The heaviest load for the waste disposal system occurs during plant shutdown for refueling. A typical rad waste system is shown in Figure 12. As indicated, plant letdown comes to the rad waste system through the primary purification demineralizer, and after flashing for the removal of radioactive gases, it is stored in one of three available large liquid waste hold-up tanks. Other hold-up storage facilities are available for reactor system drains, radiochemistry laboratory drains, decontamination drains, and building sumps. Evaporator bottoms and unrecoverable wastes are concentrated for final disposal.

In BWR systems, the full-flow condensate demineralizers are the main source of radioactive wastewater. A small amount or radioactivity is entrained irreversibly in the ion exchanger, but the bulk of the radioactivity is found in the spent regenerant chemicals or in the demineralizer backwash water.

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#### TABLE 10

Decontamination Factors Obtained Using Various Ion-exchange Systems\*

	Treatment system and source	Decontamination factor (average for system lifetime)		
Reactor system		1	Cs,Rb	All other solubles
PWR	Mixed bed (L'-BO," form)	10	2	10
	Cation bed (H' form)	1	10	100 (cations)
	Mixed bed (H*-OH' form)	100	2	100
	Anion bed (OH* form)	100	2	100 (anions)
BWR	Mixed bed (H'-OH' form)			
	Primary coolant	10	10	10
	Steam condensate	1000	10	1000
	Clean waste	100	10	100
	Dirty waste	100	2	100
	Cation bed (H* form) Dirty waste	1	10	100 (cations)
	Powder in any system	10	1	10



FIGURE 12. Typical rad waste system. (From Baumann, E. W., 147th Meeting Am. Chem. Soc., Philadelphia 1964. With permission.)

Except for materials with a high turbidity, equipment drainage and backwash water from condensate polishers are usually recoverable by filtration followed by ion exchange. This recovered wastewater is recycled back to condensate storage.

Regenerant chemicals are neutralized and evaporated. Solids or bottoms are sent to

packaging for eventual waste shipment. In isolated cases, evaporator bottoms have been discharged into the station circulating water which goes back to the environment.

With PWR plants, the primary means of handling waste streams is by evaporation. Condensate from the evaporator is recycled to the make-up system. Evaporator bottoms are combined with other plant waste solids and packaged for eventual shipping to a suitable disposal site.

#### F. Gaseous Products

Gaseous products from the flash tank are collected and stored to take advantage of the natural decay. After cryogenic purification, the gases are released in the stack.

Usually all holding tanks are duplicated so that a full tank of waste can be processed through two waste treatment ion exchangers in series and the effluent returned to an empty clean hold-up tank. Whenever the contents of the holding tank meet the minimum release specifications for the location, it is discharged through a fresh ion-exchanger bed to a final gas stripper and to monitoring tanks. From the monitoring tanks the processed waste is passed to the circulating water outfall where it is further diluted before reaching the environment. Whenever the content of a holding tank does not meet the minimum release requirements after the first ion-exchange treatment, it is reprocessed through a fresh mixed bed and returned to a clean liquid waste holding tank.

The rad waste ion-exchange treatment system usually consists of four 25-ft<sup>3</sup> mixed beds. The mixed beds consist of a strong-acid cation exchanger in the hydrogen form and an acrylic weak-base anion exchanger in the free-base form. The use of the weak-base insures the efficient removal of radioactive iodine. While rad waste deionizers are designed for flow rates up to 50 gal/min, they are usually found to be more efficient at flow rates of 15 to 20 gal/min.

It is common practice to pass the waste through the oldest mixed bed first so that this unit can be used as a filter for the removal of crud and particulate material. This process sequence protects the newly installed ion exchangers from becoming prematurely fouled.

Experience indicates that rad waste ion exchangers are required to process about 100,000 gal of contaminated water each month. Replacement appears to average about eight (25 ft<sup>2</sup>) charges per year. This indicates that each charge will handle about 150,000 gal of waste.

During that period when spent fuel shipments are made, there is an additional load on the rad waste system, since all the spent fuel cask decontamination solutions and flush water must be returned to a holding tank for processing.

A well-designed and properly operated rad waste system will normally release solutions to the environment which are less than the normal background radiation of the stream or river. Radiation from combined iodine and cesium radioisotopes will often be less than 10<sup>-\*</sup> microcuries/cc at the circulating water outfall.

#### IV. BREAKDOWN PRODUCTS AND ION EXCHANGERS

Studies covering radiolysis of ion-exchange resins as used in purification systems of reactors have been reported.<sup>14,15</sup> Kadioactive species, deposited from the coolant on ion-exchange resins, can cause decross-linking or can cause the release of soluble sulfonates or amines. These, on entering the high radioactive environment of the reactor, can also become radioactive. If these entities have ionic groups, they will be picked up by the ion exchangers. Proof of the existence of these by-products from ion-exchange resins is the fact that sulfur 35 and phosphorus 32 have been found in the reactor. The latter is due to the transformation of the decay of radioactive sulfur into phosphorus 32. CO,

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#### 60 Ion Exchange for Pollution Control

was also found, believed to be due to the oxidation of organic matter of mixed beds by radioactive deposits on the resins. The cation exchangers picked up 90% of the above radioactive species.

High radioactive dosages will cause damage to ion-exchange resins as evidenced by swelling and reduction in volume capacity. Although efficiency of the exchangers is reduced, the release of sulfur, nitrogen, and carbon species into the reactor is eliminated.

Most of the radioactive nuclides found in the coolant are removed by the cation exchanger as the species are mostly cations. Therefore, some plants use a cation exchanger followed by a mixed bed containing a much higher ratio of cation exchanger to anion exchanger.<sup>16</sup> More complete studies on the effect of radiation on ion exchangers can be found in Volume I, Chapter 5.

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# Ion Exchange for Pollution Control

## Volume II

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Dear Mr. McDaniel:

As you and Mr. Everett Wick requested in a conference call with me and Dr. M. G. Cowgill on this past June 22, we are sending you herewith by express delivery revisions to BNL's review of the topical report (TR) submitted by LN Technologies for their composite high-integrity container (HIC). We have made these revisions in response to NRC's comments on BNL's earlier LN Tech HIC TR review which we telefaxed to NRC on April 29. We have also incorporated additional comments by NRC (Comments 2.1 and 2.2 in your June 30, 1988 letter to me) with some minor modifications resulting from BNL's review of these comments.

We have enclosed the following items:

- "Draft Initial Comments on Topical Report for the LN Composite High Integrity Container (LN-87-005, Revision A, September 1987)." [This is the revised review referred to above.]
- "NRC's Question 2.2 in June 30 letter to K. McDaniel to B. Siskind," Memo to File from D. R. Mackenzie, dated July 11, 1988.
- "Irradiation-Induced Free Liquid Release from Ion-Exchange Resins," Memo to File from B. Siskind, dated July 11, 1988.
- 4. "Some Aspects of the Corrosion of Buried Stainless Steel Pipe at the Hanford Works," by R. F. Plott, HW-54341, 1948. [Requested in NRC Comment No. 1.1 in June 30 letter from K. McDaniel to B. Siskind; two copies.]

9907140141,880712 PDR WASTE WM-93 PDC Letter to Mr. Keith McDaniel July 12, 1988 Page 2

- 5. "A Study of the Effects of Cyclic Thermal Stresses on a Ductile Metal," by L. F. Coffin, Jr., Trans. ASME (Series A) 76, pp. 931-950 (1954). [Requested in NRC Comment No. 1.2 in June 30 letter. This is one of many possible references.]
- 6. "The Effects of Environment and Gamma Irradiation on the Mechanical Properties of High Density Polyethylene," by P. Sco et al., .JREG/CR-4607, March 1986. [Requested in NRC Comment No. 1.4 in June 30 letter. Copy of Figure 3.4 from this report also enclosed.]
- 7. "Low-Level Waste Package and Engineered Barrier Study," Quarterly Report, October-December 1987, by P. Soo et al., WM-3291-6, April 1988. [Requested in NRC Comment No. 1.5 in June 30 letter.]
- 8. "Irradiation Effects on the Storage and Disposal of Radwaste Containing Organic Ion-Exchange Media," Topical Report, by K. J. Swyler, et al., NUREG/CR-3383, October 1983. [Referenced in B. Siskind's enclosed Memo to File.]
- 9. G. P. Simon, "Water Treatment in Nuclear Power Plants," excerpted from 1979 CRC Press publication. [Referenced in B. Siskind's enclosed Memo to File.]

We are telefaxing you copies of the revised BNL review as well as the two enclosed memoranda to file in order to expedite the review process.

As the enclosed revised review notes in Comment No. 15, several of the references given by LN Technologies in the subject TR are incorrectly cited. My statement to you and Mr. Wick during this morning's telephone conversation that the BNL reviewers of the subject TR had not examined several of the references on irradiation effects on organic polymer materials which were cited in the TR was incorrect; the reviewers were able to obtain several of them, including the one on the effect of antioxidants, despite the incorrect citations. Such incorrect citations by the vendors result in additional effort for the TR review process.

In a conference call with you and Mr. Wick this past July 8, in connection with NRC Comment No. 2.1 on the LN Tech HIC TR, I said that I recalled some research work at BNL on radiolytic release of liquid from ion-exchange resins. My enclosed memorandum to file summarizes some of these results, which Dr. Karl Swyler reported in NUREG/CR-3383, published in October 1983. I am bringing this work to NRC's attention because of its potential implications for disposal of ion-exchange resins. Letter to Mr. Keith McDaniel July 12, 1988 Page 3

We have carried out the effort described herein under Task Order No. 7 of FIN A-3174. For further information about the enclosed materials, feel free to contact me, Dr. M. G. Cowgill (666-2082), Dr. D. R. MacKenzie (666-5373), or (when he returns from vacation next week) Dr. P. Soo (666-4094).

Sincerely,

Barry Sicknist

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Barry Siskind, Group Leader Nuclear Waste and Malarials Technology Division

BS/ts Enclosures

cc: (w/o enclosures) M. Cowgill D. MacKenzie

P. Soo