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CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS

QUARTERLY PROGRESS REPORT APRIL - JUNE 1982

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QUARTERLY PROGRESS REPORT APRIL - JUNE 1982

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SUMMARY

During this report period radiation damage measurements were initiated on strong base anion exchange resins (IRN-78) and mixed bed resins (IRN-150). H_2 gas generation rates for the fully-swollen anion resin are substantially greater than for the cation resin IRN-77. Initial data yield a G value of ~0.5. Again, oxygen is quickly scavenged from the atmosphere over irradiated anion resins. After a dose of ~2×10^8 rad, the anion resins release significant amounts of free standing liquid. This liquid is basic and does not promote mild steel corrosion in OH^- form resin.

Additional analysis of the decomposition products of irradiated IRN-77 resin supports the identification of sulfuric acid formed by radiolytic scission of the functional group as the acidic species in solution, and indicates that, in H^+ form resin, mild steel corrosion might be simply modeled by sulfuric acid attack. In the corrosion process, corrosion products and acidic species can evidently be transported a distance of at least several centimeters within the bed.

Initial experiments indicate that when heavily irradiated resins are solidified in concrete, the resulting forms are at least as durable as those containing similar amounts of unirradiated resin. Arrangements have been made to obtain samples of epoxy coating materials and high-density polyethylene for studies on container materials. These should be available early next quarter.

Electron irradiations of IRN-77 resin were begun during this quarter. Initial gas generation data, at dose rates of ~5×10^7 rad/h, provide evidence for a dose rate effect. In contrast, gas generation yields obtained during gamma irradiation at ~8×10^6 rad/h agree well with those obtained earlier at lower dose rates. These latter measurements indicate that the radiation-induced decomposition of IRN-77 resin in a sealed environment is not noticeably influenced by atmospheric nitrogen or oxygen initially present.

CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS
QUARTERLY PROGRESS REPORT, APRIL-JUNE 1982

1. INTRODUCTION

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

1.1 Background and Program Objectives

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

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

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

2.1 Monitoring Efforts on Epicor-II Liner Characterization

An Epicor-II liner used in decontamination of water in the TMI-II auxiliary building has been characterized at Battelle Columbus Laboratories. This liner (PF-16) contains organic and inorganic ion exchange media. Results will be reviewed as they become available.

The possibility of BNL obtaining portions of existing core samples is being determined at BCL and EG and G (INEL). DOE personnel also indicated that characterization of an Epicor-II liner containing only organic resin will be carried out. Part of this task formally includes providing field samples for BNL. Arrangements are presently being made. It is anticipated that these samples will be available late in the fiscal year.

2.2 Availability of Resins from Reactor Sites

Personnel at the Hatch reactor site have not responded to our written inquiry. In May, EG and G (INEL) personnel engaged in monitoring resin solidification processes at reactor sites visited our laboratory. They indicated that it should be possible to provide BNL with samples of reactor resins from the Brunswick Plant. This possibility is being explored - it is anticipated, however, that these resins would be relatively low activity level.

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

Long-term (> 6 months) irradiation of the various forms of IRN-77 resin at dose rates of approximately 4×10^6 rad/h and 10^5 rad/h are continuing. In addition, sealed tube irradiations of IRN-78 resin and IRN-150 resin were carried out. Results of these experiments, and additional characterization of IRN-77 resins, will be described below.

3.1 Sample Preparation and Irradiation Procedures

The results presented here refer to samples of resin prepared and gamma irradiated in sealed Pyrex tubes, according to procedures described previously (Swyler and Dayal, 1982, Section 3.1). The moisture content for the resin was determined both by oven drying, as described previously, and by thermogravimetric analysis (TGA).* The IRN-78 resin was used in two forms: the as-delivered (OH^-) form and the Cl^- form, produced by batch contacting 500 g of OH^- form resin with 5 L of 1M NaCl solution. Prior to irradiation the samples were rinsed with deionized water and then drip dried in a vacuum funnel. Subsequently, the moisture contents were determined to be 67% for the OH^- form and 48% for the Cl^- form. For the OH^- form, samples were prepared with and without mild steel corrosion coupons. IRN-150 resin, which is a mixture of IRN-77 and IRN-78 resin, was used in the as-delivered (H^+OH^-) form. The moisture content after rinsing and drying was determined to be 57%. Again samples of the IRN-150 resin were prepared with and without mild steel corrosion coupons.

3.2 Gas Generation in IRN-78 Resin

Both the pressure and the composition of the gases generated (or taken up) during the irradiation of the different forms of IRN-78 resin were measured. The experimental techniques have been described previously (Swyler and Dayal, Section 3.2). Curves of radiolytic gas pressure vs. irradiation time are shown in Figure 3.1 for a dose rate of 1.5×10^6 rad/h. Gas generation rates do not depend sensitively on the resin form (OH^- vs Cl^-) or the presence of corrosion coupons. The total gas generation rate is about five times that observed with IRN-77 cation resin, in the absence of corrosion.

*Perkin-Elmer Model TGS-2.

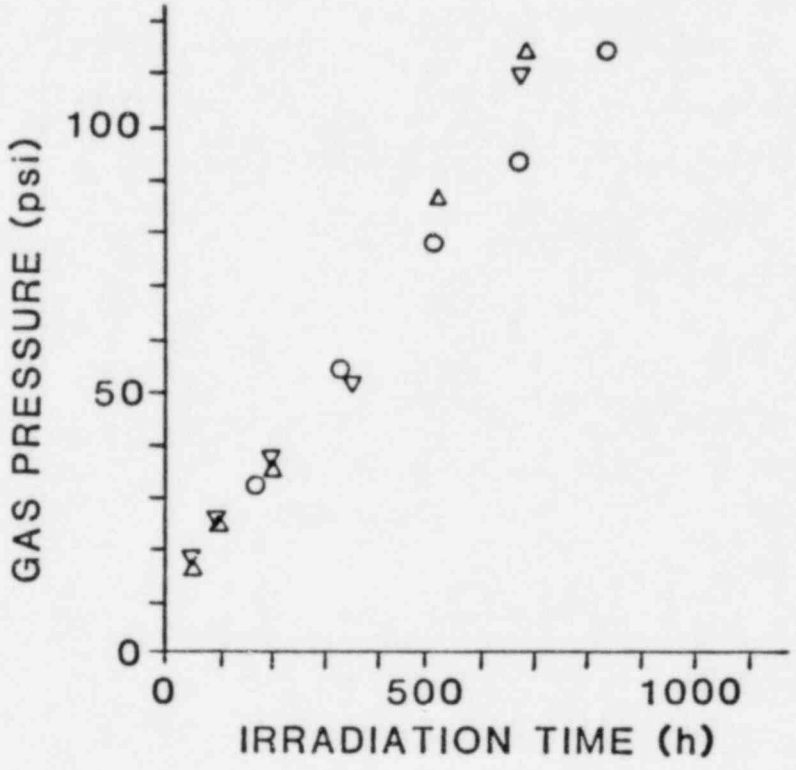

Figure 3.1 Gas pressure over IRN-78 resin vs irradiation time at 1.58×10^6 rad/h. O = Cl^- form, Δ = OH^- form, ∇ = OH^- form with corrosion coupon.

The partial pressures of the various gases found in the atmosphere over irradiated IRN-77 H^+ resin have been calculated from the observed total pressure and compositional analysis. The partial pressures are shown in Table 3.1 for different irradiation times.

Table 3.1

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

Sample Form	Irradiation Time (h)	Pressure (psi)							
		H_2	CO	CO_2	N_2	O_2	Ar	CH_4	$(CH_3)_3N$
Cl^-	672	56	0.32	10	11	0.04	0.14	1.10	ND
"	840	68	0.39	12	11	0.13	0.14	1.42	ND
OH^-	50	4	0.20	ND	11	0.004	0.15	0.11	1.1
"	504	73	ND	ND	11	0.03	0.15	1.13	0.36
OH^- with coupon	50	4	0.04	ND	12	0.01	0.16	0.09	1.00
"	100	11	0.11	ND	13	0.65	0.16	0.24	1.1
"	200	24	ND	ND	11	ND	0.13	0.48	1.2
"	360	40	0.14	ND	9	0.21	0.11	0.07	0.49

ND = None detected.

Hydrogen is the major radiolytic gas generated for all the resin forms. The generation rate is apparently about 30% greater for the OH^- form resin. There is no evidence of additional hydrogen generation due to corrosion. In all cases, atmospheric oxygen is scavenged.

For Cl^- form resin, CO_2 is produced with an apparent H_2:CO_2 ratio of about 5.5:1. Methane formation is also observed. CO_2 is not evident in the atmosphere over OH^- 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 3.1. 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 through 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 heavy and soluble. Here, the possibility for stratification in the sampling apparatus exists. The possibility of stratification is being checked by drawing successive gas samples from certain 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 mixed in the sampling process. Trimethyamine is either inhomogeneously mixed, in a "heavy fraction", or possibly maintained at a certain vapor pressure over an aqueous solution.

Experiments were also 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.

3.3 Formation of Soluble Radiolysis Products in IRN-78 Resin

pH analysis and other measurements are being carried out on liquid contacting the various forms of IRN-78 resin. As indicated earlier, for irradiation doses approaching 3×10^8 rad the resins lose their ability to retain water, and a free liquid phase becomes evident. In later analysis, this free liquid was removed by centrifuging and separately analyzed. The remaining resin was then contacted with deionized water, in the ratio 2 g to 10 mL, and the supernate analyzed as in previous measurements.

Preliminary results are shown in Table 3.2. For OH^- form resin, a relatively low ($\sim 8 \times 10^7$ rad) dose increases the pH by about 1.5 or 2 units. Subsequently, and unlike the case for cation resin, the freshly measured pH remains relatively stable at about 10.5 as the irradiation proceeds. For resin in the Cl^- form, the pH remains nearly neutral, while the concentration of chloride in solution increases with irradiation dose. The maximum Cl^- yield indicated corresponds to ~0.9 meq/g of dry resin. This is approximately 20% of the total exchange capacity. For several of the OH^- form samples, the supernatant pH was remeasured after aging for 9-12 weeks in polyethylene vials. In general, this aging produced a pH decrease in the supernate of irradiated resins, and a pH increase for unirradiated control samples.

Table 3.2

Properties of Liquids Contacting Irradiated[a] IRN-78 Resin

Sample Type	Irradiation or Holding Time (h)	Liquid Yield (mL)	Liquid pH	Supernatant pH Fresh	Supernatant pH Aged 9-12 Weeks	Cl^- in Supernatant) (mg)
Cl^-	168	0.84	5.71	7.08		2.4×10^4
	336	1.20	6.42	6.75		3.3×10^4
	504	1.93	7.37	5.91		
	672	2.06	7.28	5.64		
	840	2.13	7.03	5.31		
Cl^-	168	<0.1	---	6.89		
Control	336	<0.1	---	6.17		53
	504	<0.1	---	5.13		
	672	<0.1	---	---		
	840	<0.1	---	6.24		
OH^-	50	NM	NM	10.35*	10.00	
	100	NM	NM	10.57*	9.40	
	200	NM	NM	11.01*	9.53	
	504	2.38	10.52	10.57		68
	672	2.49	10.35	10.69		
OH^-	50	<0.1	---	8.79	9.83	
Control	100	<0.1	---	8.59	9.85	
	200	<0.1	---	9.41	9.96	
	504	<0.1	---	7.38		<5
	672	<0.1	---			
OH^- With	50	NM	NM	10.33*	10.87	
Coupon	100	NM	NM	10.61*	9.71	
	200	~1	---	10.99	9.71	
	360	~2	---	10.03	9.60	
OH^- With	72	<0.1	---	8.90	9.65	
Coupon,	122	<0.1	---	9.12	9.81	
Control	222	<0.1	---	9.42	9.95	
	520	<0.1	---	7.30		

[a]All irradiations carried out at 1.58×10^6 rad/h.
Control - Unirradiated samples, stored for times indicated.
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.

Substantial amounts of free liquid are released by both Cl^- and OH^- form resins as the irradiation dose increases. In terms of pH, the liquid from the OH^- form resin is not very different from the supernate formed with centrifuged resins and deionized water. As the free liquid is released, the resin undergoes a considerable shrinkage. For OH^- form resins, the maximum yield of 2.49 mL per 6 g of swollen resin corresponds to a release of about 60% of the water originally present. This produces a shrinkage of ~40% in the resin.

3.4 Mild Steel Corrosion in OH^- Form IRN-78 Resin

Weight loss data for mild steel corrosion coupons contacted with OH^- resin during irradiation are given in Table 3.3. Data are also presented for coupons contacted with irradiated control samples and held for lengths of time equivalent to those in the irradiation experiments.

Table 3.3

Corrosion Weight Loss for Mild Steel Coupons
Contacted with IRN-78 OH^- Form Resin

Sample Type	Irradiation Time (h)	Total Contact Time (h)	Coupon Weight Loss	
			Percent	mg/cm^2
Irradiated	50	77	0.5	1.0
"	100	122	0.2	0.4
"	200	222	0.4	0.7
"	360	382	-0.13	-0.3
Control	0	72	0.4	0.7
"	0	122	0.3	0.5
"	0	222	0.6	1.1
"	0	520		

The coupons emerged from the resin shiny bright, without any visible evidence of corrosive attack. The weight loss data given above show no consistent trend, and the values given sensibly represent the detection limit. Consequently the present data show no evidence for (short-term) corrosion of mild steel contacted with irradiated IRN-78 resin in the OH^- form.

3.5 Preliminary Results on IRN-150 Resin

Experiments are under way to characterize radiolytic gas generation, corrosion, formation of decomposition products, etc., in IRN-150 mixed bed resin. This material is a mixture of IRN-77 (H^+) resin and IRN-78 (OH^-) resin. A major aim of this experiment is to determine how, if at all, radiation damage response of the composite material reflects the interactive behavior of the individual components, whose individual behavior has been characterized

previously; initial data suggest that, in terms of gas generation and mild steel corrosion, IRN-150 resin does represent an intermediate case between pure IRN-77 and pure IRN-78. These experiments are continuing.

3.6 Radiolytic Sulfate Ion Yields in H^+ Form IRN-77 Resin

Sulfate ion concentrations in the supernate of irradiated H^+ form IRN-77 resin have been determined. Irradiation conditions and experimental methods have been described previously (Swyler and Dayal, 1982). In Figure 3.2, sulfate yields are plotted vs irradiation dose at different dose rates. The results are essentially similar to those found previously for Na^+ form resin (Swyler and Dayal, 1982, Figure 3.3). "G" values for sulfate formation estimated from this data are ~0.4 near 10^9 rad and ~0.7 near 10^8 rad.

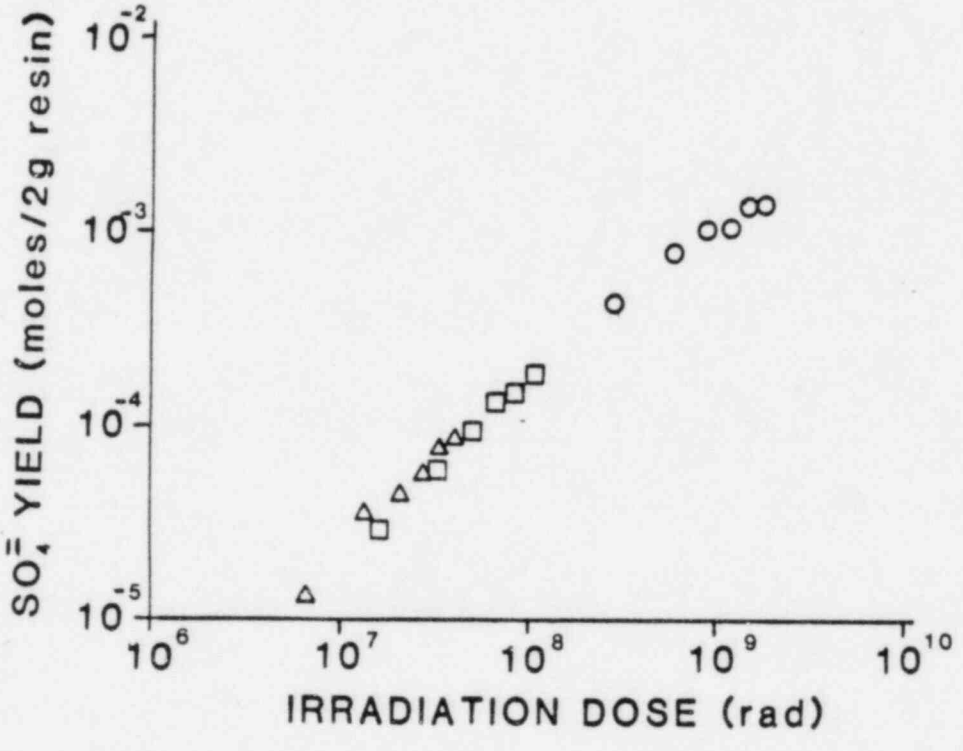

Figure 3.2 Soluble sulfate generation vs irradiation dose for IRN-77 H^+ form resin (2 g) without corrosion coupons. Dose rates (rad/h): o -1.7×10^6; □- 1×10^5; Δ - 4×10^4.

These data support the earlier conclusion that the radiolytic attack on the functional group is not sensitive to pH conditions, or to sodium vs hydrogen loading. A similar behavior has been reported for Dowex-50 resin by Kazanjian and Harrell (1974) irradiated under somewhat different conditions. As in the sodium form resins, G values for $SO_4^=$ formation appear to decrease with increasing radiation dose. We cannot entirely rule out the possibility that this represents a radiation dose-rate effect until more long-term data become available. Other workers, however, have also observed or postulated relationships in which radiation damage yields in sulfonic acid ion exchange media decrease with increasing radiation dose (c.f., Utley, 1959).

3.7 Correlation of Sulfate and pH Values in the Supernate of IRN-77 Resin

We have continued to investigate the correlation between the acidity and sulfate within the supernate of irradiated resins. Figure 3.3 shows a plot of pH vs total $SO_4^=$ levels* in the supernate of H^+ form IRN-77 resin. A theoretical curve calculated for the dissociation of H_2SO_4 is also shown. In accord with previous observations, the data agree reasonably well with the anticipated behavior of H_2SO_4. A similar plot for Na^+ form IRN-77 resin is shown in Figure 3.4. A calculated curve for the dissociation of $NaHSO_4$ is also given. In agreement with earlier observations, the experimental pH is at least one unit greater than would be expected on the basis of $NaHSO_4$ formation.

*This assumes a homogeneous distribution of $SO_4^=$ in 10 mL of liquid phase, both within and outside the resin.

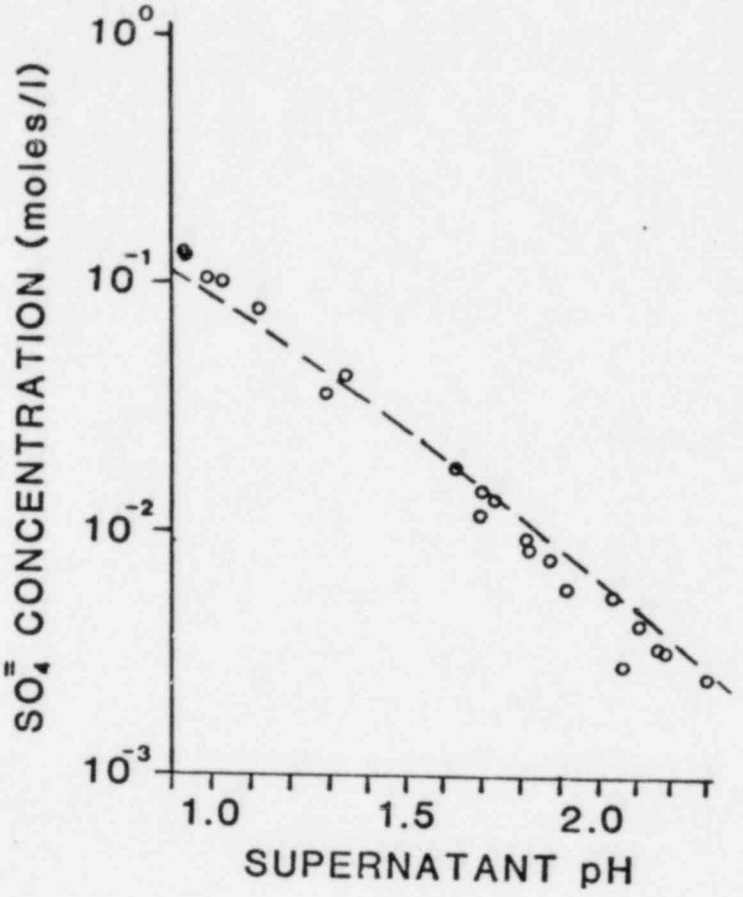

Figure 3.3 $SO_4^=$ ion levels vs pH in the supernate of IRN-77 H^+ form resin, subjected to various irradiation doses. The dashed line indicates the behavior expected for the dissociation of H_2SO_4.

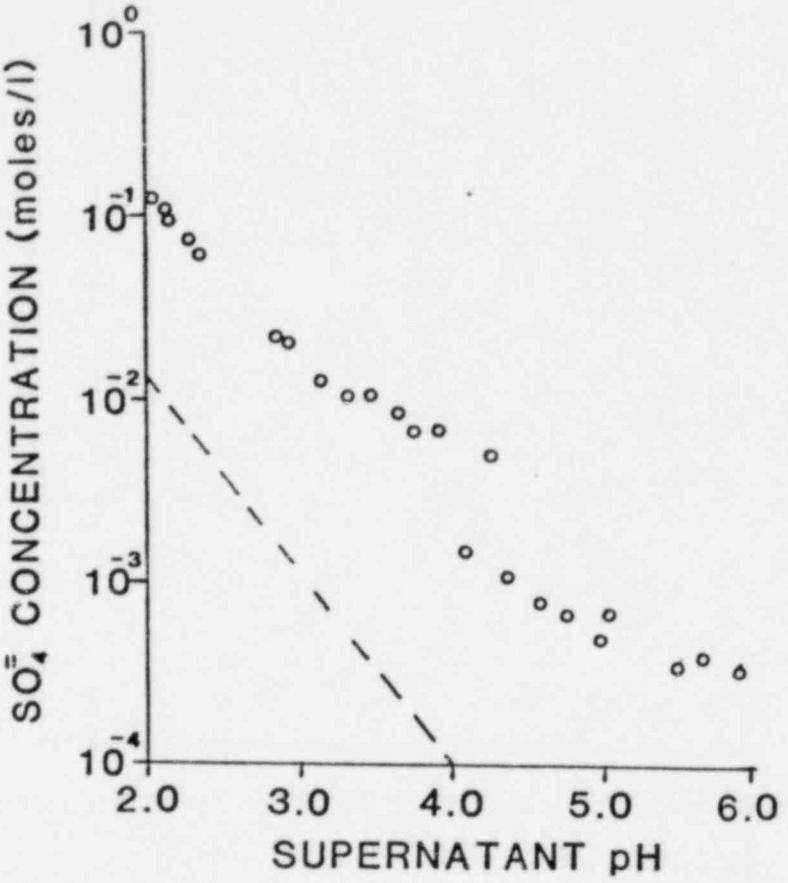

Figure 3.4 $SO_4^=$ ion levels vs pH in the supernate of IRN-77 Na^+ form resin subjected to various irradiation doses. The dashed line indicates the behavior anticipated for the dissociation of $NaHSO_4$.

The supernates of several samples of irradiated H^+ form resin were also 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 $2x10^7$ rad to 100% at 10^9 rad (Table 3.4). These results confirm the earlier assertion that 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.

Table 3.4

Fraction of Sulfuric Acid in the Supernate of Irradiated H^+ Form IRN-77 Resin vs Irradiation Dose

Irradiation Dose (rad)	Sulfuric Acid (Percent)
2×10^7	66
3.9×10^7	85
8.0×10^8	104
1.6×10^9	100

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

4.1 Solidification of Irradiated Resins

A number of small cylindrical (2-in. diameter x 4-in. long) resin-cement forms have been cast from irradiated (9 x 10^8 rad) and unirradiated IRN-77 resin in the sodium form. Following curing in air for 28 days at room temperature, the samples were soaked for 28 days in deionized water at 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 ~53% before mixing. Test conditions and results to date are shown in Table 4.1.

Table 4.1

Compression Test Data on Resin-Cement Waste Forms

Formulation	Resin (g)	Water (g)	Portland Cement (g)	Resin Condition	Compressive Strength (psi)
1	27.5	55.0	137.5	NR	2400
	"	"	"	NR	2173
	"	"	"	NR	1630
	"	"	"	R	2174
	"	"	"	R	1812
	"	"	"	R	2717
2	48.9	48.9	122.5	NR	F
	"	"	"	NR	F
	"	"	"	NR	F
	"	"	"	R	1467
	"	"	"	R	1463
	"	"	"	R	1463
3	66.0	48.9	122.5	R	1101
	"	"	"	R	1105
	"	"	"	R	1101
4	13.75	55.0	137.5	R	2717
	"	"	"	R	2717
	"	"	"	R	2717

R = Resin irradiated prior to solidification.
NR = Unirradiated resin.
F = Sample cracked during 28 day immersion.

Thus far, cement forms made with heavily irradiated resin do not appear any less durable than those incorporating unirradiated resins. In fact, the trend seems the converse: for formulation (2) in Table 4.1, the forms containing unirradiated resin failed, while those containing irradiated resin did not. Formulation (3) containing irradiated resin remained intact on soaking and exhibited reasonable compression strength. In previous work, this formulation has been found to fail when unirradiated resins are used.

For formulation (1) where forms with both irradiated and unirradiated resins remained intact during the 28-day soak, the two types of sample differ visually. The forms containing irradiated resin (upper, Figure 4.1) appear darker and more porous than those made with pristine resin (lower, Figure 4.1). Comparative leach studies are under way to compare leach rates for samples containing irradiated and unirradiated resin.

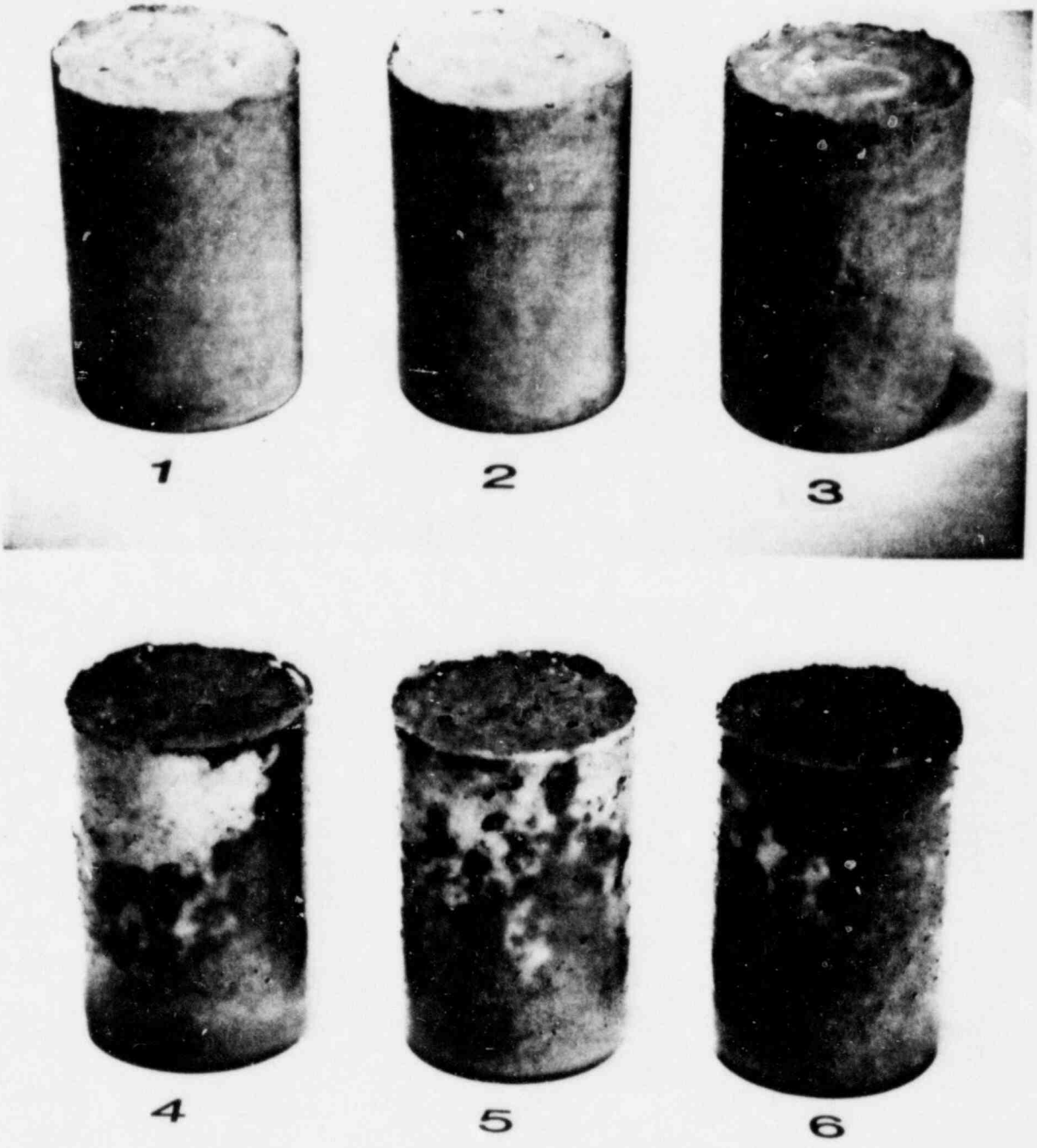

Fig. 4.1 Resin-cement forms made with irradiated (upper) and unirradiated (lower) resin after soaking for 28 days in deionized water.

4.2 Irradiation Effects on Container Materials

During this report period arrangements were made to obtain samples of epoxy rust-resistant coatings of the type proposed for high-integrity container designs. Informational needs in this area were discussed with EG and G (INEL) personnel involved in the design of a high integrity container for spent Epicor-II resin disposal. Scoping studies on these materials, and on high-density polyethylene should begin next quarter. These measurements will explicitly consider radiation dose-rate effects.

5. MECHANISTIC STUDIES AND DEVELOPMENT OF TEST PROCEDURES

Experiments described in this section are carried out with two objectives. The first is to characterize or determine the mechanisms which lead to the evolution and degradation of ion exchange waste properties of interest in storage and disposal. The second objective is to employ the results of these experiments to define test procedures which will realistically relate laboratory evaluations to field performance.

5.1 Corrosion Studies

Experiments to investigate the mechanism of mild steel corrosion in IRN-77 resin continued during this report period. "Column" experiments to measure the transport of corrosion products and corrosive species within a resin bed have been described previously (Swyler and Dayal, 1982). These measurements are continuing. Observation to date include the following:

- Pitting corrosion of the type observed with irradiated IRN-77 resin can in fact be reproduced by "loading" unirradiated resins with sulfuric acid. The loading is done by contacting the resin with sulfuric acid and then centrifuging the free liquid off. Several columns of Na^+ and H^+ form resin at different pH were prepared and contacted with corrosion coupon discs placed at the top of the column. As in the case of coupons contacted with irradiated resins, a "front" of discolored resin moved down the column from the corroding specimens as contact time increased. This coloring clearly indicates the presence of corrosion products. While the "front" is not always sharply defined, the distance the front travelled down the column was estimated visually as a function of contact time. Over the 10-day duration of the experiment, rates of travel ranged from roughly 1 mm per day for the H^+ form resin loaded to low pH, to ~0.2 mm per day or less for as-delivered Na^+ form resin. In the latter case rates of travel evidently decrease with increasing contact time. Within the individual colums, the pH of the resin in the upper and lower halves does not differ substantially. In fact, the upper portion, which is in contact with the corrosion coupon, is generally somewhat more acidic. Since the effect of corrosion is to elevate the overall pH, the lack of a pronounced pH gradient within the tube suggests that, with the resin, transport processes are operative over a distance of at least several centimeters. Analysis of these results is continuing, and similar experiments are under way with irradiated resins.

- A correlation between hydrogen generation and mild steel corrosion in IRN-77 H^+ resin indicates that, on the average, roughly one mole of H_2 is produced for every mole of Fe consumed in corrosion. This relationship appears relatively insensitive to radiation dose or dose rate (Figure 5.1) for corrosion in a sealed environment. This behavior is consistent with sulfuric acid attack at low pH (Mathur and Vasudevan, 1982). Interestingly, Figure 5.1 also suggests that, even

in samples irradiated at high dose rates, all the hydrogen generation can be accounted for by corrosion. However, a substantial rate of hydrogen generation has been observed in samples of IRN-77 H^+ and Na^+ form resin without corrosion coupon, as indicated earlier (Swyler and Weiss, 1981; Swyler and Dayal, 1982).

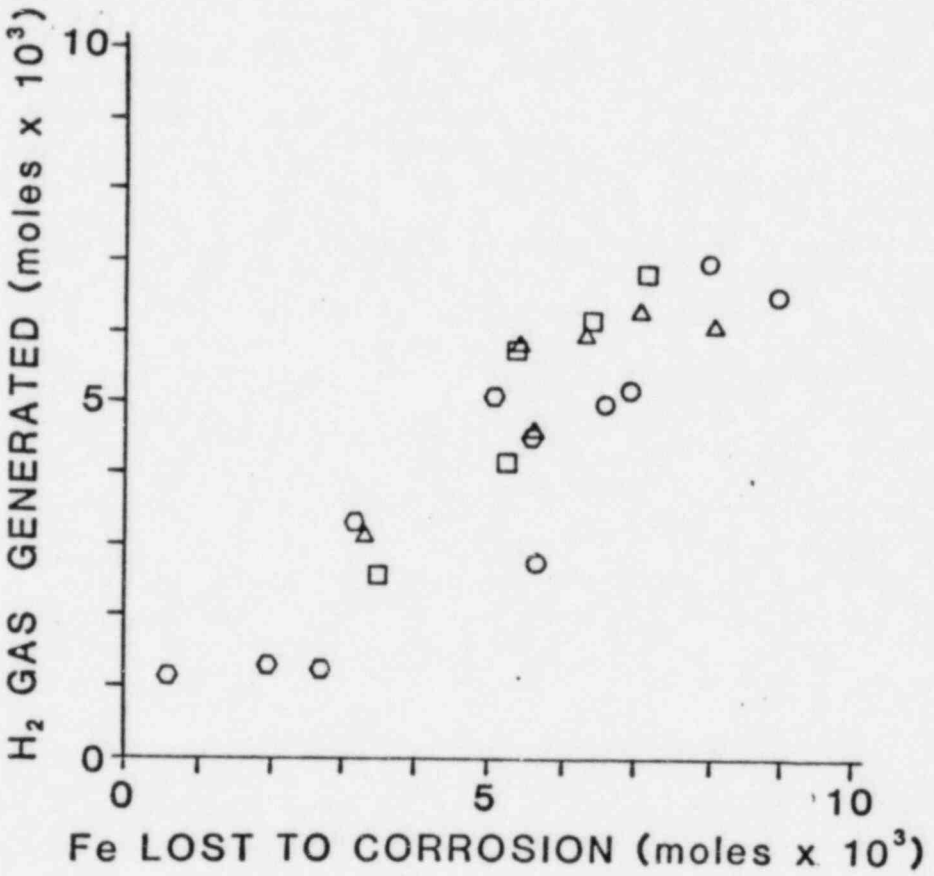

Figure 5.1 Hydrogen gas yields vs corrosion weight loss in mild steel coupon contacted with H^+ form IRN-77 resin; radiation dose rates (rad/h): 0 = 1.7×10^6; □ = 1×10^5; △ = 4×10^4; ⬡ = unirradiated.

5.2 Other Experiments

- A series of samples of IRN-77 resin in the H^+ form resin have been gamma irradiated in sealed vessels equipped with a pressure transducer. The resin was used in the fully swollen form (~52% moisture) and the irradiations were carried out at ~8×10^6 rad/h. The irradiation were carried out in atmospheres of air, helium and oxygen-18. G-values for H_2 generation generally agree with those reported earlier for irradiation in Pyrex tubes at lower dose rates. Further, the values do not depend sensitively on sample mass or irradiation atmosphere. For samples irradiated in an oxygen atmosphere, the pressure vs time curves can be accurately decomposed into a decrease due to oxygen uptake and a linear increase dose to radiolytic gas generation (Figure 5.2). This technique, coupled with $O_2{}^{18}$ tracer method, is being used to examine oxidation processes in the resin and the correlation between O_2 uptake and CO_2 generation.

- Initial electron irradiations of IRN-77 resin were carried out during this report period. Samples were irradiated with 2 MeV electrons at dose rates of ~5×10^7 rad/h, at temperatures of ~40°C. Under these conditions, pressure continued to increase over the resin samples for several days after the irradiations were terminated. This effect has not been observed in samples following gamma irradiation and may indicate the presence of intermediate stages in the decomposition process which becomes rate limiting only at high dose rates.

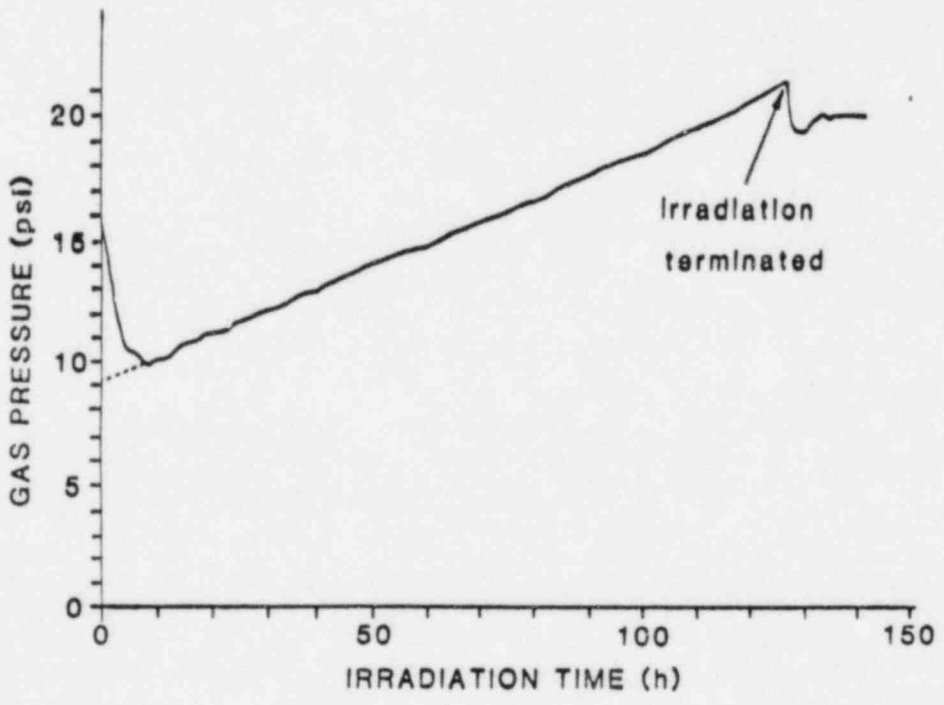

Figure 5.2 Gas pressure over H^+ IRN-77 resin during irradiation at 8×10^6 rad/h. The sample originally contained 9 psi of $O_2{}^{18}$.

6. DISCUSSIONS AND CONCLUSIONS

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

Initial characterization of radiation damage in IRN-78 anion resin has been carried out. Damage formation is substantially greater than in IRN-77 resin.

The relatively low radiation durability of anion resins has been recognized for some time (c.f., Gangwer, Goldstein, and Pillay, 1977). In the present case, gas generation rates are ~5 times greater for anion resin, as compared to cation resin with a chemically similar backbone. Moreover, the anion resin shrinks significantly, releasing substiantial amounts of free liquid, at relatively low total doses.

The practical implications of this behavior are evident. In mixed bed or layered systems, the anion component may dominate the gas generation and release large amounts of free liquid. Free liquid may increase transport properties and corrosive behavior within the bed. To the extent that the liquid is basic, however, this liquid may tend to neutralize the acidic species produced in the degradation of cation resins, thereby retarding corrosion. The balance between these competing effects can be determined by studying the behavior of mixed bed (IRN-150) resin which has been irradiated. These experiments are under way.

In mechanistic terms, the presence of trimethylamine in the vapor phase over OH^- form resins indicates that radiation damage ultimately involves removal of the intact functional group by scission of the C-N bond. [For the sulfonic acid group in IRN-77 resin this is evidently not the case since SO_2 is produced in the gas phase by irradiation of dry resins (c.f., Gangwer, Goldstein, and Pillay, 1977).] Consequently, it presently appears that the solution properties (i.e., pH changes, etc.) may be understood in terms of aqueous solutions of trimethyl amine (Ahmed, Clay, and Hall, 1966; Kazanjian and Herrell, 1975).

The differences between the radiation damage response of IRN-77 and IRN-78 resin may reflect differences either in the functional groups or in crosslinking; the moisture content and backbone are largely similar. Since one of the major differences is in hydrogen generation, the correspondence between hydrogen generation and loss of functionality is presently being examined. Changes in swelling behavior and moisture retention are commonly attributed to radiation-induced crosslinking in the backbone. The present comparison between IRN-77 and IRN-78 resins, however, suggests that the irradiation-induced swelling decrease in IRN-78 resin may involve attack on the functional group as well.

Solidified cement forms containing irradiated resins appear at least as durable as those made with unirradiated resins.

This trend is in accord with earlier observations (Barletta, Swyler, Chen, and Davis, 1981).

It has been speculated that increased wasteform durability may result from radiation-induced decreases in the resin swelling capacity. The tendency for irradiated cation resin to crack upon water addition has been noted previously. The loss in swelling capacity may involve either increased cross-linking (Rohm and Haas, 1967) or (presumably) attack on the functional groups.

Both the solution chemistry and the corrosive behavior of H^+ form IRN-77 resin are consistent with radiolytic formation of sulfuric acid.

This result may lead to a predictive capability for total corrosion. Present results suggest that corrosive behavior will be limited in an exponential manner by consumption of acidic species, but that these species can be transported over some distance during corrosion in a bed of fully-swollen resin. For IRN-77 resin the sodium form, acidity generation and corrosive attack cannot be simply modeled in terms of sodium hydrogen sulfate formation.

For both resin forms, fundamental radiolytic attack on the functional group, as evidenced by formation of sulfate ions, proceeds at roughly the same rate. Thus far, the attack on the functional group appears characteristic of an intrinsic process, which is not strongly influenced by environmental variables or radiation dose rate. Unlike the apparent case for the anion resin, additional radiochemical attack occurs on the functional group fragments in an aqueous environment. While the decomposition product of sulfonic acid resins irradiated in the dry state is SO_2 (Gangwer, Goldstein, and Pillay, 1977), the species in solution is oxidized to $SO_4^=$. The overall acidity for a given yield of $SO_4^=$ is determined by processes which are sensitive to the loading on the resin.

7. REFERENCES

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