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CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS

QUARTERLY PROGRESS REPORT
APRIL-SEPTEMBER 1981

MASTER

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APRIL-SEPTEMBER 1981

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ABSTRACT

A research program is under way to systematically characterize the type of radwastes which may be generated in cleanup procedures following off-normal reactor operations. Specifically, the program is presently investigating how the properties of wastes containing ion-exchange media may be modified by heavy doses of irradiation from sorbed radionuclides. Special effort is being devoted toward quantifying the effects of factors such as radiation dose rate, chemical loading on the ion exchangers, moisture content and composition of external media, etc., which may influence the relation between laboratory test results and field performance.

Initial irradiation damage measurements have been carried out on organic cation resin IRN-77 in both hydrogen and sodium forms. Gamma irradiation of both of these materials produces water soluble acidic decomposition products; the acid product yields depend on the chemical loading and are lower for the sodium form. Corrosion weight loss on mild steel coupons contacted with moist resins is increased by irradiation. In dry resins, corrosion is greatly reduced, if not eliminated, although radiation damage to the resins still occurs. Initial corrosion rate data during irradiation have been obtained for moist hydrogen form resins at approximately 10^6 rad/h. These indicate a decrease in the corrosion rate as the irradiation proceeds. In the hydrogen form resin, acid product yields are consistent with sulfuric acid formation by irradiation-induced degradation of the functional group; in the sodium form, it is not clear whether the functional group is more durable or whether self-buffering is occurring. In certain aspects, the damage produced by fast electrons and by gamma rays appears to be equivalent. Field survey data indicate that the present results are relevant to loadings achieved in normal operating procedures.

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CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS PROGRESS REPORT, APRIL-SEPTEMBER 1981

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 first progress report issued under this contract. Subsequent reports will be issued on a quarterly schedule. In this section, background information is provided which is intended to define the scope and objectives of the program. The various tasks within the program are described to provide initial context for evaluating the progress that is reported in subsequent sections.

1.1 Background and Program Objectives

Organic ion exchange resins continue to be an important and critical factor in efforts to clean liquid radwaste. It is realized, however, that degradation processes, which occur with high total doses of ionizing radiation ($>10^8$ rad), are in general not understood, and that little data relevant to certain resin types are available.⁽¹⁾ In a recent review by Swyler, Barletta, and Davis,⁽²⁾ the current status of radiation damage, pertinent to the short-term storage of ion exchange media waste generated at Three Mile Island, Unit-II (TMI-II) is presented. This work, conducted at Georgia Tech,⁽³⁾ Penn State,⁽⁴⁾ and BNL has been chosen to typify those resins and environments employed in the EPICOR-II demineralizer system. Other observations of gas generation and limited observations on the effects of absorbed radiation on the physical appearance of resins have been documented.⁽⁵⁻⁷⁾ Less effort has been expended to detail or explain structural or chemical changes occurring during irradiation. Similarly, the correlation between resin degradation and environmental concerns, e.g., corrosion, leaching, etc., requires clarification.

The objective of this program is to develop a data base applicable to NRC licensing considerations for the storage and disposal of unique radioactive wastes. As unique wastes, the program specifically considers organic and inorganic ion exchange media subjected to high internal irradiation doses as a result of heavy radionuclide loadings. Typical of such wastes are the resins and zeolites either employed or contemplated for use in water decontamination procedures at TMI-II as mentioned above. Previous experience has indicated that in such materials, internal irradiation can produce degradation effects of potential consequence in regard to licensing considerations. Briefly, the properties of the wastes may undergo a more or less continuous evolution as the irradiation dose builds up, both during storage and following incorporation of the wastes in an ultimate disposal form. This program is aimed at generating information which will permit characterization of the anticipated properties of unique waste products under field conditions. This involves four separate phases. First, a scoping study to determine the manner in which material properties of engineering interest might be altered by irradiation

effects, second, an examination and delineation of those factors which govern the relationship between laboratory evaluations and field performance; third, a phenomenological/mechanistic description of the important radiation effects that may be anticipated for several generic materials under field conditions; and fourth, a specification of the type of tests which would adequately assess the radiation durability of a particular ion exchange waste product in a given licensing application.

1.2 Organization of the Project

The project is organized as five 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 Tasks 3 and 4, irradiation effects on inorganic ion exchange media and on solidified forms containing ion exchange media are to be characterized. Task 5 will assess issues specifically dealing with the development of test procedures for assessing the significance of radiation effects on the use, storage and disposal of ion exchange media under field conditions. Progress in these various activities is described below.

2. CHARACTERIZATION OF FIELD EXPERIENCE WITH HEAVILY LOADED ION EXCHANGE MEDIA (K. J. Swyler and P. Piciulo)

Brookhaven National Laboratory, under separate contract to NRC (FIN A-3159-1), is conducting a survey concerning the use of organic and inorganic ion exchange media at nuclear power plants. In the present program, this survey is being reviewed to identify industry's experience regarding ion exchange resins which have received high doses of beta-gamma radiation. Thus far, one facility has been identified that evidently generates resins loaded to approximately 100 Ci/ft³. Attempts will be made to obtain samples of this material for characterization in our laboratory.

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3. PARAMETRIC STUDY OF RADIATION-INDUCED DEGRADATION OF ORGANIC ION EXCHANGE MEDIA (J. Adams, C. Dodge, W. Becker, and W. Tremel)

During the report period, efforts were concentrated on scoping measurements to identify key factors governing the radiation-induced degradation of organic ion exchange media. Specifically, measurements were carried out to examine the effect of moisture content, resin loading, and radiation dose rate on the radiation induced degradation of Amberlite IRN-77 ion exchange resin.*

IRN-77 is a strong acid cation exchanger widely used in the nuclear industry. It incorporates sulfonic ($-SO_3^-$) exchange groups on a backbone of styrene-divinyl benzene copolymer. The divinyl benzene provides crosslinking in direct relation to its amount present; for IRN-77, this is about 8%. Both the backbone and the exchange group of IRN-77 are typical of a wide class of materials used in the nuclear industry. In addition, there is some radiation damage information previously available on this material,^(2,5,6) and IRN-77 is also the reference material used in resin-cement solidification experiments under another NRC sponsored program in our laboratory. Consequently, IRN-77 has been adopted as a generic strong acid cation exchange for use in our program. Subsequently, other materials will be identified for study as generic representatives of other common classes of ion exchangers. Thus far, investigations have been almost entirely restricted to IRN-77 resin. Other types have been selected for future study.

The particular features of radiation-induced degradation which were examined in work carried out during this report period include, (1) formation of acidic species; (2) corrosion of mild steel contacted with resin; (3) physical changes in the resin (agglomeration), and (4) nature of the degradation products. As mentioned earlier, these features are being examined as a function of resin moisture content, resin chemical loading, and radiation dose rate. Progress and results to date are described below.

3.1 Scoping Studies of the Effect of Radiation Dose on Acidic Product Formation

Earlier pH measurements were carried out on IRN-77 resin which had been subjected to different doses of gamma and electron irradiation. The IRN-77 resin was used in both hydrogen and sodium form. The hydrogen form was obtained from the manufacturer. In this material, all the exchange sites are occupied by hydrogen ions. The moisture content of the as-delivered material is approximately 50% by weight. Some of this hydrogen form material was converted to sodium form by a series of sequential rinses with a NaCl-NaOH solution and deionized water. The procedure is standard in our laboratory and is described in greater detail elsewhere.⁽⁸⁾ Subsequent to sodium exchange, which was terminated when the deionized water rinses showed a pH >6, the material was dewatered to a moisture content of approximately 50%.

*Rhom and Haas, Philadelphia, PA.

For gamma irradiations, 10 g-samples of IRN-77 resin in H^+ and Na^+ forms were weighed into Pyrex test tubes. These tubes were 12.5 mm inside diameter and 120 mm high; the resin filled the tube to a height of approximately 100 mm. The tubes were then plugged with glass wool, which did not produce an air-tight seal, permitting both moisture and radiolytic gases to escape. The loaded tubes were then exposed to ^{60}Co gamma radiation in an air environment at a dose rate of approximately 4×10^6 rad/h. The irradiation temperature was measured by a thermocouple emplaced in one such tube; the temperature at the center of the tube was $25^\circ C$.

Following removal of the sample tubes from the irradiation facility, two grams of resin were removed from each tube and mixed with 10 mL of deionized water in a glass bottle. The pH of the supernate was then determined with a glass electrode.

pH data obtained in this manner are shown in Table 3.1 for the sodium and hydrogen forms of IRN-77 resin irradiated to various total doses. The table also gives data for "C" resin, which is a proprietary ion exchange resin supplied by a commercial vendor of decontamination systems. Interest in the "C" resin stemmed from its possible use in decontamination procedures at Three Mile Island, Unit-II. (See Reference 9 for a more extensive description of experimental technical assistance tasks carried out at BNL in support of TMI cleanup operations.)

Table 3.1
Hydrogen Ion Concentration (as pH) of Water in Contact With
Irradiated Ion Exchange Resins

Dose (rad)	pH ^a			
	C-66%	C-66% (Na^+) ^b	IRN-77 (H^+)	IRN-77 (Na^+)
0	4.4	7.0	3.5	6.8
10^7 (γ)	2.6	---	2.5	4.7
1.25×10^7 (e^-)	---	---	2.5	---
3×10^7 (γ)	2.0	---	2.0	3.6
4.6×10^7 (e^-)	---	---	2.0	---
10^8 (γ)	1.6	3.0	1.5	2.9
3×10^8 (γ)	1.1	---	1.0	2.1
10^9 (γ)	0.9	---	0.6	1.3

^aMeasured in supernate of a mixture of 2 g of resin and 10 mL of deionized water.

^bTitrated to pH 7 with NaOH prior to irradiation.

The data indicate a steady decrease in pH with increasing radiation dose. A "yield" for this radiation damage process can be defined as $-\Delta\text{pH}/\Delta\log\phi$, where ϕ is the radiation dose. Initial analysis along these lines suggests that, in the hydrogen form of IRN-77, the concentration of hydrogen ion $[\text{H}^+]$ in solution increases approximately linearly with irradiation dose:

$$[\text{H}^+] = 3.3 \times 10^{-10} \phi \text{ (hydrogen form)} \quad (3.1)$$

with ϕ in rad and $[\text{H}^+]$ in moles/liter. If one assumes that all the hydrogen in solution results from degradation of exchange sites, the number of degraded sites (N) per unit resin mass is given by

$$N = 1.6 \times 10^{-9} \phi \text{ (hydrogen form)} \quad (3.2)$$

with N in meq/g. For the sodium form resin, the pH yield is lower for a given radiation dose, over the region indicated. Also, the apparent concentration of damaged species does not increase linearly with radiation dose. The H^+ concentration in this case is given (approximately) by

$$[\text{H}^+] = 1.8 \times 10^{-15} \times \phi^{3/2} \text{ (sodium form)} \quad (3.3)$$

or, per gram of resin

$$N = 9 \times 10^{-15} \phi^{3/2} \text{ (sodium form)} \quad (3.4)$$

Intuitively, the lower pH yield for the sodium form of the resins is not surprising, since the material is initially less acidic than the hydrogen form. More importantly, however, these initial data suggest that, insofar as formation of acid products is concerned, the functional dependence on radiation dose (and, consequently, the mechanism) may depend on resin loading.

Expressions such as 3.1 and 3.3 can be differentiated with respect to to give yields or G-values for acid product formation. Similarly, the validity of the assumptions leading to Equations 3.2 and 3.4 can be checked by examining the correlation between acid product formation and loss of exchange capacity.^(5,6) Prior to such detailed considerations, however, the validity and generality of this very preliminary analysis must be carefully examined. Future work will consider how well such yields provide an unambiguous measure of radiation damage⁽⁶⁾; the initial results are encouraging.

3.2 Effect of Moisture and Resin Loading on Resin Degradation and Corrosion

An experiment was carried out to determine the sensitivity of resin degradation and corrosion to moisture content. IRN-77 resins, prepared in the sodium and hydrogen forms as described earlier, were air dried at 40°C to different moisture contents. The drying was accomplished by virtue of a drying curve, prepared by measuring resin weight loss as a function of drying time. Drying in this manner does not result in extensive resin degradation; as shown by earlier measurements. The resin samples are next contacted with mild steel (ASTM 1020) corrosion coupons and then either irradiated with gamma-rays to a dose of 3×10^8 rad, or stored at room temperature without irradiation. In either case, the Pyrex glass sample tubes are plugged with cork stoppers to prevent loss of moisture. Following irradiation or storage, the corrosion coupons are removed and examined for weight loss. Corrosion scale is mechanically removed from the coupons with a toothbrush prior to weight loss determination. Two-gram resin samples are mixed with 10 mL of deionized water and the pH of the mixtures is determined. For the irradiated samples, these pH determinations are carried out for resins near the top of the sample tube (T), and for resins near the bottom (B), adjacent to the corrosion coupon. Results of these measurements are shown in Table 3.2.

The overall effects of resin loading and irradiation on pH illustrated in Table 3.2 are in reasonable accord with earlier data. The pH drops upon irradiation, and the effect is more pronounced in the hydrogen form resin. Quantitatively, at 3×10^8 rad the pH values in the present experiment (in which the irradiation was carried out in stoppered tubes) are somewhat higher than those observed for irradiation under vented conditions (Table 3.1). Possibly the corrosion process affects the overall pH (see Section 3.3). More importantly, however, the present data show significant effects of resin moisture content. Specifically,

- Without exception, corrosion of mild steel decreases in resins of lower moisture content. At the lowest moisture content, there was no obvious evidence of coupon corrosion in either the irradiated or unirradiated specimens.
- In all cases where corrosion was observed in the irradiated resins, there was a pronounced darkening of the resin adjacent to the metal coupon at the bottom of the sample tube. Under these conditions, water mixed with resin from the bottom of the tube was differently colored from that mixed with resin from the top of the same tube. The pH, however, is roughly the same for each mixture.
- Even at low moisture content, where corrosion was not observed, the resins are affected by irradiation. For both the Na^+ form and the H^+ form, the mixture pH is significantly decreased by irradiation.

These initial results clearly indicate the significance of moisture content as a variable affecting resin performance. The present results suggest that corrosion can be greatly reduced if the resins can be dried before

protracted storage. We intend to explore this possibility in the research program. Presently, it seems that moisture may be more important as a transport/electrolytic medium in corrosion than in producing irradiation-induced resin degradation directly. At this point, however, this assertion must be considered tentative. The pH values in Table 3.1 have not yet been corrected to account for the fact that the actual amount of resin in a 2-g-sample varies with moisture content. Similarly, the differences in contact time for corrosion between the various samples make quantitative comparisons tenuous. (The low initial pH values of the Na⁺ form are also a bit surprising.) Taken together, these data indicate the importance of moisture content as a parameter for further study in understanding resin performance under field conditions.

Table 3.2

Effect of Moisture Content on Irradiated and Unirradiated Resins

Resin Form	Percent Moisture	pH of D.I.W. Resin/Mixtures	Coupon Percent Weight Loss
<u>Unirradiated</u>			
H+	55	2.8, 3.2, 3.1	9, 5, 6
H+	27	3.3, 3.1	2, 4
H+	14	3.2, 3.3	0, 0
Na+	50	3.6, 3.5, 3.5	4, 4, 4
Na+	25	3.5, 3.4	1, 1
Na+	13	3.3, 3.5	0, 0
<u>3 x 10⁸ rad</u>			
H+	55	top 1.7, 1.6 bottom 1.5	20, 8
H+	27	top 1.5, 1.3 bottom 1.4, 1.4	4, 7
H+	14	top 1.6, 1.5 bottom 1.5, 1.5	0, 0
Na+	50	top 2.5, 2.3 bottom 2.8, 2.6	4, 5
Na+	25	top 2.3, 2.2 bottom 2.5, 2.4	2, 3
Na+	13	top 2.4, 2.4 bottom 2.4, 2.4	0, 0

Contact times for corrosion experiments:

Unirradiated samples: 190 h

Irradiated samples:

50-55% moisture: 78 h unirradiated + 75 h irradiated.

25-27% moisture: 75 h unirradiated + 75 h irradiated.

13-14% moisture: 6 h unirradiated + 75 h irradiated.

The liquids obtained in these pH measurements exhibit a pronounced coloration. These are presently being chemically and spectroscopically analyzed to identify the decomposition products present. Initial results of these studies are described in Section 3.4.

3.3 Effect of Radiation Dose Rate on Resin Degradation and Radiation Corrosion

For resin wastes generated in the auxiliary building cleanup activities at TMI, total gamma doses of up to approximately 10^9 rad per liner have been predicted over a 10-year storage period.⁽²⁾ While there remains some question as to the equivalence of internal versus external radiation sources, external source irradiation is the method of choice for experimentation, as most significant radiation effects are easily achieved, while problems regarding contamination can be avoided. Experiments are under way to determine the relationship between the corrosion rate of a mild steel (1018) in contact with a strongly acidic cation resin (Amberlite IRN-77) and the rate of external gamma irradiation to which this system is exposed. Gamma fluxes of 10^4 , 10^5 , and 10^6 rad/h are being employed to irradiate samples to a total dose of 10^8 , 10^9 , and 10^{10} rad, respectively. Chemical and structural changes are monitored as a function of absorbed dose.

As-received IRN-77 resin was backwashed for 20 min. with deionized water, stored under water for four days, and then vacuum filtered for 5 min. to remove excess surface water. A 55 weight percent water content was determined, in agreement with the as-received moisture content. Samples of 1018 steel* were rolled to 0.020 in. thickness and cut to a size of 1.76 in. long and 0.25 in. wide. The coupons included a butt-weld at the center. The coupons were then cleaned and stored in acetone until ready for use. Immediately before insertion into the resin, the coupons were weighed to four significant digits. Forty-eight samples of coupons in contact with 4.00 g of resin were prepared in 1/2-in.-diam by 3-in.-long glass test tubes. These tubes were sealed with cork stoppers to prevent spillage and moisture loss, then tapped several times to ensure packing of the resin beads about the coupons.

Irradiation was performed at BNL's gamma irradiation facility. The shielding water of the pool is kept constant at 10°C. However, during irradiation, samples are warmed to roughly room temperature. Twelve of the 48 samples were irradiated at a dose rate of approximately 1×10^6 rad/h, 12 at approximately 1×10^5 rad/h, and 12 at approximately 1×10^4 rad/h. Twelve samples were stored at room temperature as controls. For the first two sets of samples, a total dose of approximately 1×10^9 rad/h has been (or will be) attained in 49 and 347 days, respectively. For the 10^4 rad/h samples, a total dose of approximately 1×10^8 rad will be attained (402 days). As of this time, the samples have been irradiated a total of approximately 48 days. One sample from each group is being withdrawn at a time

*Sanyu Cold Finished Steel Co., LTD., Hiracata City, Osaka, Japan.

corresponding to 1/12th of the calculated total irradiation time (approx. 4, 29, and 34 days for 10^6 , 10^5 , and 10^4 rad/h irradiations, respectively). A control sample is removed every 31 days. Thus far, 11 of the 12 samples irradiated at 10^6 rad/h have been examined, and two each of the 10^4 and 10^5 rad/hr and control samples have been withdrawn.

Upon removal from the resin, the coupon is photographed in the corroded state, followed by removal of the corrosion layer by 3-4 min. vigorous stirring in Clarke's solution.* The coupon is then rinsed with acetone, reweighed, and a photograph of the cleaned sample taken. Two grams of the irradiated resin are withdrawn from the test tube and placed in contact with 10 mL of deionized water. After approximately one day, the pH of the solution is determined.

In Figures 3.1 and 3.2 are shown plots of weight loss of the corrosion coupons and pH of the irradiated resin/water solutions as a function of irradiation times for samples irradiated at a dose rate of approximately 1×10^6 rad/h. Weight loss was calculated as the percent of the initial weight after the coupon was cleaned in Clarke's solution. Samples irradiated at approximately 1×10^4 rad/h, had weight losses of 30.8 and 44.6% and pH's of 3.22 and 3.35 after 34 and 68 days, respectively. After 29 and 58 days, samples irradiated at approximately 1×10^5 rad/h had weight losses of 27.6 and 26.9% and pH's of 2.57 and 2.98, respectively. Unirradiated control samples had weight losses of 24.4 and 20.0% and pH's of 4.07 and 3.04 after 31 and 63 days.

Several noteworthy observations were made during this time interval. First, as irradiated resin is added to deionized water, the solution becomes colored. The bonds of any agglomerated resin beads are quickly broken and the adhesive layer dissolved. The color and optical density of the resulting solution is dependent on the chemistry and thickness of the actual layer being dissolved from the resin bead surface. Those resins subjected to a low total dose appear to produce pale yellow or orange colored solutions. Those subjected to larger total doses seem to generally produce solutions of brown tones. Although one would expect the intensity of these colors to increase as total dose increases, such is not the case. Those samples irradiated to a total dose of approximately 5×10^8 rad appear much darker in color than those with a dose of approximately 1×10^9 rad. These samples have been photographed and are shown in Figure 3.3(A) and 3.3(B).

A second observation was that the physical appearance of the corrosion coupons (for the 10^6 irradiated specimens) changed during the irradiation period. Coupons withdrawn during the first 10 days of the test appeared as normally air-oxidized steel surfaces, i.e., rusty red with local pitting and severe corrosion adjacent to those spots where individual resin beads actually contacted the steel surface. An example of this is shown in Figure 3.4 in

*Standard Recommended Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, ANS/ASTM 61-72.

Figure 3.1 Weight loss vs. irradiation time for 1018 steel coupons contacted with irradiated IRN-77 resin.

Figure 3.2 pH of deionized water (10 mL) contacted with irradiated IRN-77 resin (2 g) as a function of resin irradiation time. The resins were contacted with mild steel coupons.

Figure 3.3(A) Solutions of deionized water (10 mL) and irradiated IRN-77 resin (2 g). The resin was irradiated at approximately 10^6 rad/h over the times indicated.

Figure 3.3(B) Solutions of deionized water (10 mL) and irradiated IRN-77 resin. The resin (2 g) was irradiated at approximately 10^6 rad/h over the times indicated.

Figure 3.4 1018 steel corrosion coupons contacted with IRN-77 resin and irradiated for 8 days.
Top: Before cleaning. Bottom: After cleaning.

both the corroded condition and in the cleaned condition. This particular specimen was irradiated at approximately 1×10^6 rad/h for 8 days. From the 16th through the 24th days, the coupons no longer appeared red colored, but rather had a black, seemingly moist, coating on the coupon. Documentation of this is shown in Figure 3.5 in the corroded and in the cleaned condition. This sample was irradiated for 16 days. Finally, after about the 28th day, corrosion coupons once again appeared orange-red in color, though the transition to this condition was gradual. A sample irradiated for 41 days is shown in Figure 3.6, in the corroded and cleaned state. As a point of interest, a pristine uncorroded coupon was photographed in its initial state and again after 4 minutes immersed in Clarke's solution (Figure 3.7). Note that attack of the base metal is minimal. From the photographs in Figures 3.4, 3.5, and 3.6, for the cleaned coupons it is evident that the fabrication processes (e.g., rolling, welding, etc.) have an input as to the mode of corrosive attack. The rather deep and obvious transverse pattern is likely a result of preferential attack at grain boundaries, elongated in that direction by the rolling process.

The last observation made was, that control samples, though all prepared and stored in the same manner, appear drastically different in appearance after about one month. As shown in Figure 3.8, the resin in some samples has become uniformly dark, some has become striated (light on the top, dark on bottom), while still others remain essentially unchanged. In each case where the dark resin appears, the resin volume is significantly compacted. Close inspection of the samples shows that the cork/glass interface is stained for those samples containing dark resin while this interface is unchanged for the others. For the latter, this cork seal is suspected of allowing water vapor and/or gaseous products of the corrosion process to escape. It is possible that the entrapment of these gases and moisture causes an interaction with the steel coupon which discolors the resin.

Continued on Page 22

Figure 3.5 1018 steel corrosion coupons contacted with IRN-77 resin and irradiated for 16 days.
Top: Before cleaning. Bottom: After cleaning.

Figure 3.6 1018 steel corrosion coupons contacted with IRN-77 resin and irradiated for 41 days.
Top: Before cleaning. Bottom: After cleaning.

Figure 3.7 1018 mild steel coupon before (top) and after (bottom) 4-minute immersion in Clarke's solution.

Figure 3.8 IRN-77 resin samples, contacted with steel corrosion coupons, and stored for one month.

3.4 Analysis of Resin Decomposition Products

As indicated earlier, acidic products and color changes are observed in aqueous solutions contacting irradiated resins. Experiments are currently under way to characterize the decomposition species in solution. Techniques include UV, visible, and IR spectroscopy, and several methods of sulfate analysis. Initially, these techniques have been applied to the liquids generated in the moisture content experiment described in Section 3.2. Results to date are described below.

3.4.1 Ultraviolet Absorption Spectra of Liquids in Contact With Resins

Ultraviolet spectra were taken on the supernatant of both the irradiated and unirradiated forms of IRN-77 cation exchange resins generated in the moisture content experiment (Section 3.2). Representative spectra for both the hydrogen and sodium forms show a broad structured band in the ultraviolet. This band is weakly evident in liquids contacting unirradiated resin, and is substantially increased by irradiation.

Several early trends are evident in the initial UV data. The strength of the absorption depends upon resin loading (H^+ or Na^+) moisture content, and corrosion mechanisms. For unirradiated samples, the absorption is much stronger for the sodium form. Upon irradiation, the absorption increases in the hydrogen form, but this increase is less pronounced in "B" resin samples adjacent to corrosion coupons. The exception is for the 18B sample (12% moisture) where no corrosion occurred.

The same general trends are observed for the sodium form. Taken together, these results suggest that at least one species contributing to the absorption is either generated more efficiently in resins of low moisture content, or is taken up in a corrosion-associated process. For the hydrogen form resin, UV absorption increases as pH drops. For the sodium form of the resins, however, there is as yet no clear correlation between solution pH and absorption strength in the UV.

3.4.2 Sulfate in Liquids Contacting Resins

A study to determine the acid species present in the irradiated samples was done using a Dionex Model 10 ion chromatograph (IC) with an anion exchange column. A sample of the supernatant above the irradiated resins in the hydrogen form shows sulfate concentrations of 10^{-1} M (see Tables 3.3 and 3.4). This result was correlated with another method based on an automated methyl thymol blue (MTB) procedure and the results agree to within 20% with the IC giving higher values. Scoping work on all samples in the hydrogen form using the MTB method shows a correlation between sulfate levels and pH.

The qualitative equivalence between pH and sulfate concentration has been investigated. In the analytic techniques described above, sulfate ion ($SO_4^{=}$), and bisulfate ion (HSO_4^-) will be detected as sulfate. In the actual solution, the ratio of sulfate to bisulfate will vary with pH.

Table 3.3

Sulfate Analysis of Liquids Contacting Irradiated Hydrogen Form Resin

Percent Moisture	Sample	Dose (rad)	Moles/L $\text{SO}_4^{2-} + \text{HSO}_4^-$	pH	Moles/L Na ⁺
55	10	3×10^8	4.0×10^{-2}	1.2	$< 2 \times 10^1$
	11 T		4.2×10^{-2}	1.1	
	11 B		4.1×10^{-2}	1.3	
	22	0	1.9×10^{-4}	2.4	
	30		1.5×10^{-4}	2.5	
	31		2.7×10^{-4}	2.5	
27	14 T	3×10^8	5.5×10^{-2}	1.2	
	14 B		6.2×10^{-2}	1.2	
	15 T		9.3×10^{-2}	1.1	
	15 B	0	5.0×10^{-2}	1.3	
	24		1.6×10^{-4}	2.6	
	34		4.1×10^{-4}	2.4	
14	18 T	3×10^8	6.8×10^{-2}	1.1	
	18 B		8.6×10^{-2}	1.1	
	19 T		9.8×10^{-2}	1.1	
	19 B	0	1.3×10^{-1}	1.0	
	26		3.5×10^{-4}	2.3	
	36		1.2×10^{-3}	2.0	

^aIn the analytical technique, HSO_4^- is converted to SO_4^{2-} .

^bThe pH values are recorded approximately 3 months after those reported in Table 3.2.

Table 3.4

Sulfate Analysis of Liquids Contacting Irradiated Sodium Form Resin

Percent Moisture	Sample	Dose (rad)	Moles/L $\text{SO}_4^{2-} + \text{HSO}_4^-$	pH	Moles/L Na^+
50	12 T	3×10^8	4.1×10^{-2}	2.0	1.4×10^{-1}
	12 B		3.5×10^{-2}	2.2	8.90×10^{-2}
	13 T		3.6×10^{-2}	2.0	1.15×10^{-1}
	13 B		3.6×10^{-2}	2.1	1.06×10^{-1}
	32	0	8.6×10^{-4}	3.2	7.00×10^{-3}
	33		6.2×10^{-4}	3.3	6.10×10^{-3}
25	23		7.3×10^{-4}	3.3	8.70×10^{-3}
	16 T	3×10^8	5.3×10^{-2}	2.0	---
	16 B		4.4×10^{-2}	2.3	8.90×10^{-2}
	17 T		3.3×10^{-2}	2.1	1.18×10^{-1}
	17 B		2.9×10^{-2}	2.2	1.03×10^{-1}
	25	0	1.1×10^{-3}	3.1	8.7×10^{-3}
13	35		8.2×10^{-4}	3.1	7.0×10^{-3}
	20 T	3×10^8	3.4×10^{-2}	2.1	1.18×10^{-1}
	20 B		4.6×10^{-2}	2.1	---
	21 T		4.8×10^{-2}	---	---
	21 B		3.1×10^{-2}	2.2	1.22×10^{-1}
	27	0	2.6×10^{-3}	2.7	1.9×10^{-2}
	37		1.9×10^{-3}	2.7	2.4×10^{-2}

^aIn the analytical technique, HSO_4^- is converted to SO_4^{2-} .

^bThe pH values are recorded approximately 3 months after those reported in Table 3.2

Using known sulfuric acid dissociation constants, the ratio of sulfate to bisulfate in the reaction

was calculated as function of pH. Then, a curve of $[\text{HSO}_4^-] + [\text{SO}_4^{2-}]$ vs pH was constructed for this reaction and compared with the sulfate and pH data in Tables 3.3 and 3.4. This comparison leads to the following conclusions.

1. For solutions of irradiated resins in the hydrogen form, the pH and sulfate content are in quantitative agreement with reaction (3.5); the acidity can be attributed to sulfuric acid formation. There is no need to invoke presence of other species such as SO_3^{2-} .

2. For solutions of unirradiated hydrogen form resin, the pH is lower than would be anticipated on the basis of sulfuric acid solution. Apparently, other acidic species are present. Locally low pH conditions may be produced within or near the resins by equilibrium dissociation of hydrogen ion from the exchange sites. This acidity would presumably be detected in measurements contacting the resins, but not in aliquots withdrawn from above the sample (see Section 4.1).
3. For both the irradiated and unirradiated resin in the sodium form, the solutions show more total sulphur than can be attributed to sulfuric acid at the measured pH. In the irradiated samples, the solution sulfate concentrations approach those in irradiated hydrogen form resins (approx. 5×10^{-2} M). The pH, however, is almost one full unit higher. This would indicate that, in terms of total formation of soluble sulfonates by radiation damage at the exchange sites, both hydrogen and sodium form respond similarly. In the sodium form, however, the acid yield is lower since roughly 90% of the sulfonates are evidently present in a salt (presumably of sodium) or as a less acidic species than H_2SO_4 .

Initial comparison indicates some correlation between absorption peak intensity and sulfate concentration. For example, the increased absorption observed in unirradiated sodium form samples (in comparison to hydrogen form) is generally reflected in an increased sulfate concentration. This correlation will be examined further in subsequent measurements.

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4. DEVELOPMENT OF TEST METHODS (J. Adams, C. Dodge, and W. Tremel)

During this report period, measurements were carried out addressing two issues in radiation test development. One effort considers the equivalence of radiation and chemically induced degradation of organic resins. Specifically, the role of peroxides, which are common radiolysis products, on resin degradation is being studied.⁽¹⁰⁾ In a second experiment, the equivalence of gamma and electron irradiation on resin degradation is under investigation. This must be understood to ensure that the beta component of the irradiations produced by internal beta decay is adequately accounted for in test simulations. Activities in these areas are described below.

4.1 Effect of Peroxides on Resin Degradation

A preliminary experiment was conducted to determine the effect of hydrogen peroxide on IRN-77 resin degradation. In this experiment, IRN-77 cation exchange resin was backwashed 15 minutes with deionized water then vacuum filtered 5 minutes to removed excess surface water. Eight 5.00-g samples of this resin were weighed and placed in individual Pyrex beakers. Solutions of 10, 1, 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5} M H_2O_2 in deionized water were prepared and 50.0 mL of each solution was contacted with the resin samples prepared above. A control solution of deionized water was also contacted with the resin. All samples were sealed with parafilm to prevent evaporation. Observations of physical changes in the resin were noted periodically, and pH's of the various solutions were determined after 10, 18, 23, and 44 days.

No physical changes other than bleaching of the resin were noted. The majority of these color changes occurred within the first week after contact with the peroxide solutions. As shown in Figure 4.1, the originally dark brown (caramel) colored resin was increasingly bleached to a pale yellow color with increasing H_2O_2 concentration. Little color difference was distinguishable between the 10^{-3} , 10^{-4} , 10^{-5} , and control specimens. No agglomeration of the resin occurred, nor was dissolution, fracturing, or other comminution of the resin observed. The liquid remained colorless for all samples throughout the test period.

pH of the liquid as a function of time is shown in Table 4.1. This was measured using a Corning calomel combination electrode with a digital Corning (Model 125) meter. pH was measured with the electrode tip just contacting the surface of the resin. It was noted that when the electrode was immersed beneath the resin layer, pH dropped to <0.5 for each sample. When pH of the liquid above the resin was measured, a value of 2-5 was obtained. In each case, pH showed a decreasing trend with time, leveling off or increasing slightly after 23 days.

Figure 4.1 IRN-77 resin in various H₂O₂ solutions (5.0 g resin/50.0 mL H₂O₂ solution). Top (left to right): 10 M, 1 M, 0.1 M, 1 x 10⁻² M H₂O₂. Bottom (left to right): 1 x 10⁻³ M, 1 x 10⁻⁴ M, 1 x 10⁻⁵ M H₂O₂, and deionized water only.

Table 4.1

pH of IRN-77 Contacting Hydrogen Peroxide^a

	Days in Contact With Peroxide			
	10	18	23	44
10	.5	.4	.3	.3
1	.9	1.0	.7	.7
.1	1.3	1.0	.8	.8
.01	1.4	1.2	1.1	1.1
.001	1.6	1.3	0.9	1.0
.0001	1.7	1.5	1.0	1.3
.00001	1.7	1.4	1.2	1.4
Control	1.6	1.5	1.1	1.3

^aMeasurements taken with pH electrode just contacting resin surface.

A second experiment was conducted to examine the effect of hydrogen peroxide attack on pH in greater detail, and to isolate and effects due to auto degradation of the peroxide. A series of samples were made up in 250-mL-erlenmeyer flasks each containing 20 g of resin in the "as delivered" hydrogen form. To each flask was added 100 mL of a serially diluted ACS grade 30.0% (8.8 M) hydrogen peroxide reagent from Fisher Scientific Company. The contents were then swirled and stoppered. Control samples without resin were also made up as a check on auto degradation of the peroxide. In contrast to earlier measurements, where the electrode contacted the resin, pH measurements were made on 10-mL aliquots withdrawn from each sample and measured on a Beckman Model 4500 pH meter using a Beckman combination glass electrode No. 71124. Analyses were made initially after make up and three more times over an 18-day period. The results are presented in Table 4.2.

The control samples show virtually no pH change, indicating the peroxides were sensibly stable over the entire period of the analysis (the 8.8×10^{-6} M sample does show some pH increase). The resin plus water samples are moderately acidic, pH = 3.40, indicating that there are water soluble acidic components in the samples that dissolve immediately and do not change during the course of the experiment. The resin plus peroxide samples show a consistent downward trend indicating that either the water soluble contaminant in the resin is breaking down, or that the resin itself is breaking down, or that both processes are taking place. The change in color of the resin from a dark brown to a light yellow in the more concentrated peroxide solutions is an indication that resin attack is occurring. It is also noted that the 8.8×10^{-1} M down to the 8.8×10^{-4} peroxide solutions are almost identical in their pH change, approximately 0.65 units, whereas the 8.8 M solution shows a much more dramatic pH change, 1.79 units, suggesting a different mechanism of

attack on the sample. However, these results can only be considered semi-quantitative because as aliquots are withdrawn, enrichment of the supernatant is taking place giving lower values than would be found in a constant volume solution. A future experiment to eliminate this effect will consist of making quadruplicates at each peroxide concentration and withdrawing the aliquot only once at each time.

Table 4.2
pH of Peroxide-Resin Solutions

Sample ^a	pH			
	Day 1	Day 6	Day 11	Day 18
DI H ₂ O	5.6	5.7	5.6	5.6
H ₂ O + resin	3.4	3.4	3.4	3.4
H ₂ O + resin	3.4	3.4	3.4	3.4
8x10 ⁻⁶ M H ₂ O ₂ /H ₂ O	5.6	5.8	5.9	5.9
8.8x10 ⁻⁵ M H ₂ O ₂ /H ₂ O	5.6	5.5	5.6	5.6
8.8x10 ⁻⁴ M H ₂ O ₂ /H ₂ O	5.6	5.5	5.6	5.6
8.8x10 ⁻³ M H ₂ O ₂ /H ₂ O	5.6	5.6	5.6	5.6
8.8x10 ⁻² M H ₂ O ₂ /H ₂ O	5.6	5.5	5.5	5.5
8.8x10 ⁻¹ M H ₂ O ₂ /H ₂ O	5.5	5.5	5.5	5.5
8.8x10 ⁰ M H ₂ O ₂ /H ₂ O	4.0	4.0	4.0	4.0
8.8x10 ⁻⁶ M H ₂ O ₂ /H ₂ O + resin	3.4	3.4	3.4	3.4
8.8x10 ⁻⁵ M H ₂ O ₂ /H ₂ O + resin	3.4	3.3	3.2	3.1
8.8x10 ⁻⁴ M H ₂ O ₂ /H ₂ O + resin	3.4	3.2	3.0	2.8
8.8x10 ⁻³ M H ₂ O ₂ /H ₂ O + resin	3.4	3.1	2.9	2.7
8.8x10 ⁻² M H ₂ O ₂ /H ₂ O + resin	3.4	3.1	2.9	2.7
8.8x10 ⁻¹ M H ₂ O ₂ /H ₂ O + resin	3.3	3.0	2.9	2.7
8.8 M H ₂ O ₂ /H ₂ O + resin	2.6	2.0	1.8	1.6

^aSamples made from 20 g of IRN-77 resin plus 100 mL of peroxide solution.

These experiments indicate that acidic species are formed by an interaction between hydrogen peroxide and IRN-77 resin. As noted earlier, acidic species are also produced by irradiation. However, other effects (formation of colored liquids, agglomeration, darkening of the resins, etc.) observed under irradiation are not produced by hydrogen peroxide attack in deionized water. Consequently, it does not appear that the radiation-induced decomposition of IRN-77 resin can be simulated by hydrogen peroxide attack in the absence of irradiation or other chemical species. Another interesting observation in these measurements is the substantial difference in pH between measurements made on the supernate above the resins (Table 4.1) and on aliquots withdrawn from this supernate (Table 4.2). Evidently, in some cases homogeneous pH conditions are not achieved in aqueous solutions. This effect depends sensitively on the solubility and dissociation constant of the various acidic species present. For irradiated resins, the available evidence (see Section 3) indicates that the important anions are sulfate or bisulfate, which are homogeneously distributed. The anions present in the low pH resin-peroxide mixtures have not yet been identified. Possibly, these involve (high molecular weight) species which are only partly soluble.

4.2 Electron Irradiation Studies

To examine the equivalence of gamma-ray and electron irradiation in producing resin decomposition, samples of IRN-77 resin are being irradiated with fast electrons. The irradiations are carried out at BNL's Dynamitron Accelerator. Samples of as-delivered IRN-77 resin in the hydrogen form are placed in thin walled sample chambers constructed from 304 stainless steel. The sample chambers are rectangular, (2.5 cm x 2.5 cm x 0.5 cm) and all joints are welded. Irradiations are carried out by placing the sample chamber, containing the resin sample, with its large cross section perpendicular to the electron beam axis. The electron beam impinges on the sample cell through thin windows in the accelerator vacuum beam line.

Operating at 2 MeV, the incident electrons are sufficiently energetic to produce a roughly uniform energy deposition along the thin (0.5 cm) dimension of the sample. The electron beam is magnetically steered (rastered) over the large face of the sample cell to produce a uniform irradiation, and the total beam current is monitored by means of a faraday cup. The maximum dose rate is limited by beam heating effects. Sample temperature during irradiation is monitored by a thermocouple penetrating into the resin, and air cooling of the sample chamber is accomplished with muffin fans. For electron beam currents of about 3 μ a, a sample temperature of $\leq 40^\circ\text{C}$ can be easily maintained. The effective dose rate under this condition is calculated to be approximately 10^8 rad/h.

The irradiations can be carried out under either vented or sealed conditions. In the latter configuration, pressure developed within the cell can be continuously monitored with a strain gauge pressure transducer, both during and after irradiation. Following irradiation, the resin is removed from the sample cell for subsequent characterization. For irradiation in sealed cells, gas samples may be withdrawn for mass spectrographic analysis.

pH data obtained for electron irradiated IRN-77 resins vs. calculated absorbed dose are shown in Table 3.1. These are the entries denoted by (e⁻). The table indicates that the pH values are in good agreement with those obtained following gamma irradiation. In Figure 4.2, a curve of pressure vs. irradiation time is shown for IRN-77 resin electron irradiated in a sealed cell at 40°C. The dose rate is approximately 10⁸ rad/h. The initial pressure rise is due to heating of the sample cell from 25 to 40°C; the subsequent pressure decrease indicated could reflect gas uptake.⁽⁹⁾ For longer times, the pressure increases linearly with irradiation dose until the beam is interrupted. When the beam is restored, the pressure buildup proceeds as before.

When the beam current (proportional to radiation dose rate) is reduced to half its value, the rate of gas generation (as measured by the curve slope) is also decreased by a factor of two. Since no changes (other than thermal effects) are produced when the beam is interrupted, and the gas generation rate appears to vary linearly with dose rate, these results suggest that the net amount of gas generated by a given irradiation dose will be independent of dose rate.

In the present measurement, under electron irradiation at approximately 10⁸ rad/h, we estimate a G value for gas formation of 0.4, where G is the number of molecules produced by an energy deposition of 100 eV. This value is generally commensurate with other determinations under gamma-irradiations at approximately 10⁶ rad/h.^(5,6,9) Thus far, the present results do not provide any evidence either for inequivalence of electrons and gamma rays (on a per unit dose basis) or for significant radiation dose rate effects on net gas and pH "yields."

Figure 4.2 Gas generation in IRN-77 resin during electron irradiation. Irradiation temperature = 40°C. Electron beam currents as indicated in μa .

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5. DISCUSSION AND SUMMARY

Results obtained during this report period hold a number of implications for future work. In practical terms, perhaps the most significant result is the absence of corrosion in mild steel coupons contacted with dried resins. The absence of corrosion in resins with low moisture content is almost certainly due to the absence of an aqueous electrolyte rather than any protective effect on the resins themselves. For example, initial pH data suggest that irradiation damage (as manifested by a formation of water soluble acidic decomposition products) takes place with an efficiency that is largely independent of moisture content.

This preliminary result argues against the notion that irradiation-induced resin decomposition can be attributed entirely to attack by peroxides formed radiolytically in the aqueous environment. Were this the case, one might expect reduced irradiation damage in resins of low moisture content. More direct evidence against the equivalence of radiation damage and peroxide attack is found by observing the effect of hydrogen peroxide on resin decomposition. Undoubtedly, one manifestation of radiation damage (i.e., formation of acidic species also occurs when resins are contacted with hydrogen peroxide or possibly other strong oxidants. However, other effects seen in irradiated resins such as darkening and agglomeration are not observed in peroxide solutions. In fact, hydrogen peroxide bleaches the resin. Consequently, it is clear that important features of radiation damage in IRN-77 resin cannot be simply reproduced by peroxide attack in deionized water in the absence of irradiation.

The distinction between bulk radiation damage to the resins and degradation produced by external radiolysis products is an important one. The external attack can be controlled to some extent by varying the environmental conditions; bulk damage would be an intrinsic property of the resins themselves. (An analogous situation exists in high-level waste management: the leaching behavior of a high-level waste form may be affected either by formation of radiolysis products in the leachant, or by irradiation damage to the waste form itself.) Thus far, the radiation induced degradation of IRN-77 resin appears to exhibit certain intrinsic features. The effect, measured as the formation of soluble sulfate ion by decomposition of the exchange group, does not seem to depend strongly on either resin moisture content or sodium vs hydrogen loading. The sodium form resin used in these preliminary experiments, however, is somewhat acidic. Additional measurements are planned using a carefully neutralized sodium form.

In the present experiments, the yield of sulfate may be expressed by a G-value or number of ions produced per 100 eV absorbed. The data in Tables 3.1, 3.3, and 3.4 lead to the following G-values for sulfate formation under gamma radiation in moist resins at approximately 10^6 rad/h (Table 5.1). There is some spread in G-values which may reflect variation in experimental conditions. For the most part, however, the analysis indicates that the yield of sulfate ion, as determined in the present experiments, appears to be a convenient measure of the basic radiation induced degradation processes in nuclear sulfonic resins.

Table 5.1

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

Data Source	Resin Form	G-Value
Table 3.1	H ⁺	0.79
Table 3.3	H ⁺	1.46
Table 3.4	Na ⁺	0.85

While the sulfate ion yield is not particularly sensitive to resin loading in the range employed thus far, the irradiation-induced pH decrease is quite different in sodium form and hydrogen form resins. For a given irradiation dose, the hydrogen form of IRN-77 resin becomes substantially more acidic than the sodium form. Moreover, the functional dependence of pH on radiation dose may be different for the two resin forms. For the hydrogen form, the irradiation-induced pH drop can be quantitatively accounted for by sulfuric acid formation. In the sodium form, the situation is somewhat different. Following irradiation to 3×10^8 rad, the hydrogen-ion concentration is only about one-tenth the sodium concentration; sodium ion, however, is presented at roughly twice the sulfate concentration. Assuming that all the sodium originates from the resin, as is almost certainly the case, this result suggests that some buffering action may be occurring in the irradiated sodium form resin.

Quite generally, attack on the $\text{-SO}_3\text{-Na}^+$ exchange group which produces soluble sulfur forms (SO_3^- , etc.) would be expected to liberate sodium ions in equal proportion. Presumably, the soluble sulfur is either oxidized to SO_4^- ion during irradiation or is converted to SO_4^- in the analytic process, since substantial SO_3^- has not been detected in the IC technique. In any event, one expects decomposition products such as NaHSO_4 , containing sodium and sulfur in a 1:1 ratio. At the indicated pH, dissociation of NaHSO_4 would produce $[\text{H}^+]$, $[\text{Na}^+]$, and $[\text{SO}_4^- + \text{HSO}_4^-]$ in the ratio 0.54:1:1. As indicated, the data do not fit this picture. The ratios are more nearly 0.1:2:1, suggesting that the principal species is Na_2SO_4 , which is substantially less acidic than NaHSO_4 . This might indicate either a loss of sulfur containing forms as gases. Alternately, self buffering might occur in the sodium form resin, in which the primary decomposition product, sodium hydrogen sulfate, is converted to the more benign sodium sulfate by hydrogen-sodium exchange at an undamaged functional site on the sodium form resin:

This mechanism will be considered in future studies. If it is effective, a buffering action should be evident when irradiated sodium form resin is contacted with a solution of sodium hydrogen sulfate.

Results thus far indicate that sulfuric acid (or its derivative) is the corrosive species formed by irradiating nuclear sulfonic resin. Other acids, such as sulfonic acids, could result from radiation induced attack on the resin backbone. The available evidence, however, suggests that in the present case, it is sulfuric acid that is produced by attack at the resin functional group. Consequently, it seems useful to consider the corrosion data from the viewpoint of sulfuric acid attack.

The available corrosion rate data are very preliminary; however, some interesting early trends are evident. For example, Figure 3.1 suggests an initially linear relationship between corrosion weight loss and contact time. If this relationship is confirmed by more extensive data, an initial corrosion rate may be uniquely defined by the slope of such a curve. Corrosion rates defined in this manner may then be compared for various conditions of radiation dose rate, resin chemical and radioactivity loading, etc. For longer contact times (>30 days), the weight loss appears to saturate at about 25%. At the same time, the initial pH decrease slows down and the pH tends toward a constant or slightly increasing value (Figure 3.2). For contact times up to about 15 days (approx. 3.6×10^8 rad), the pH data in the corrosion studies are in quantitative agreement with the data in Tables 3.1 and 3.3. For longer times the pH values are somewhat higher than those which would be expected in the absence of corrosion coupons (Table 3.1).

Presently, then, it appears that some mechanism exists whereby both corrosion and the formation of acidic species are inhibited as the irradiation dose increases. The practical consequences of such an effect are obvious: In the present case, assuming uniform corrosion, the initial weight loss rate corresponds to a penetration rate of approximately 1.6 mm per year. This rate approaches zero after a total penetration of only approximately 0.13 mm. At this point we will not speculate on the details of such a mechanism; a number of factors may be involved. For example, Figures 3.1 and 3.2 indicate two points (20 and 24 days) where anomalously high corrosion is coupled with the presence of anomalously high pH. This suggests a substantial uptake of acidic species in the corrosion process. We have earlier described the visual evidence (darkening of the resins near corrosion coupons) which indicates an interaction between the resins and species formed during corrosion. The fact that the entire resin volume is not affected suggests that transport limitations on corrosive species may be important. Such factors will be explicitly considered in future studies aimed at clarifying this effect. Recent experiments on thermally induced corrosive behavior in nuclear sulfonic resins⁽¹¹⁾ suggest that it will be useful to examine the corrosive behavior of resin-sulfuric acid solutions. Such examinations are planned for the near future.

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