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

**TOPICAL REPORT**

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

**October 1983**

**NUCLEAR WASTE MANAGEMENT DIVISION  
DEPARTMENT OF NUCLEAR ENERGY, BROOKHAVEN NATIONAL LABORATORY  
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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 resin loading. The acidity will be reduced first by a protective ion exchange effect in which  $H^+$  ion is exchanged for cation at undamaged resin sites. Second, some of the sulfate may be produced by a mechanism in which  $H^+$  ion is not generated in the oxidation of  $SO_3^-$  to  $SO_4^{2-}$ . In any event, the acidity is substantially reduced for loadings other than  $H^+$ . 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 capacity 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 high-integrity containers at burial.

For the cation resin, 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.

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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 ion-exchange 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.

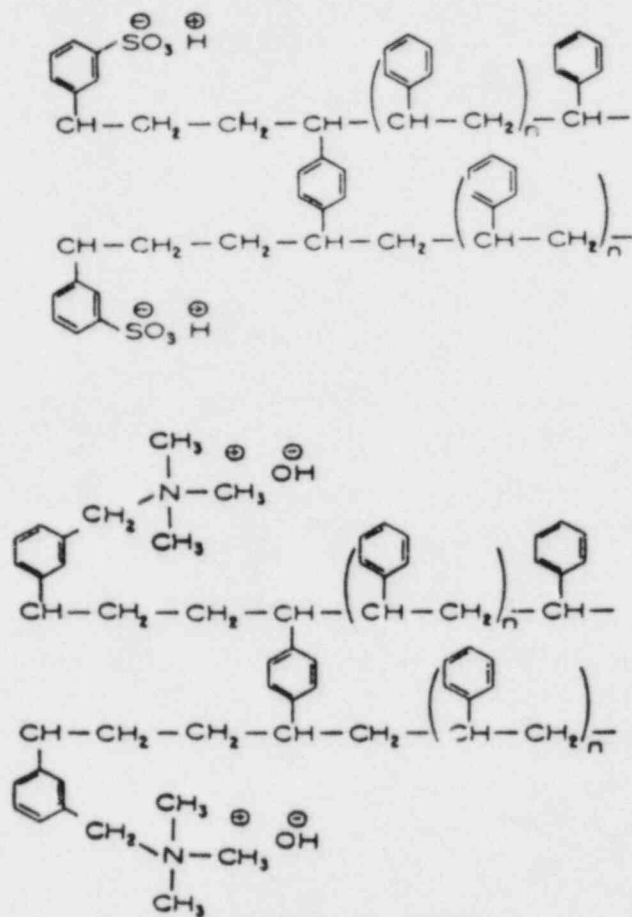


Figure 1.1 Structures of polystyrene/DVB sulfonic acid cation resin (IRN-77, upper) and polystyrene/DVB quaternary ammonium anion resin (IRN-78, lower).

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, quaternary 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 mixed 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, radiolytic 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 the irradiated 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 from containers or waste forms. Initial 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).

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. This was done both to make certain radiation damage effects (such as loss of exchange 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.

## 2. 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 ( $-\text{SO}_3^-$ ) on a polystyrene/divinylbenzene polymer backbone. IRN-78 contains quaternary ammonium ( $-\text{CH}_2\text{N}(\text{CH}_3)_3^+$ ) 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  $\text{H}^+$  form, and IRN-78 is provided with an  $\text{OH}^-$  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 Media<sup>a</sup>

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

<sup>a</sup>Nominal 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 resins were further oven dried in air at  $70^\circ\text{C}$ . Residual moisture content of the various samples was determined by measuring percentage weight loss following prolonged drying at  $100^\circ\text{C}$  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  $\text{Na}^+$  form,  $\text{Fe}^{++}$  form,  $\text{Fe}^{+++}$  form and  $\text{NH}_4^+$  form, from the as-delivered  $\text{H}^+$  form. The  $\text{Na}^+$  conversions were carried out according to standard batch procedures developed in our laboratory and described elsewhere (Weiss and Morcos, 1980). Conversion to  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$  and  $\text{NH}_4^+$  loadings was carried out with solutions of  $\text{FeSO}_4$ ,  $\text{FeCl}_3$  and  $\text{NH}_4\text{OH}$  respectively, using column techniques recommended by the manufacturer. Sulfuric acid was added to the  $\text{FeSO}_4$  solution to adjust the pH to 2.3, so as to maintain the iron in  $\text{Fe}^{++}$  form. IRN-78 samples were converted to  $\text{Cl}^-$  form and IRN-150 samples were converted to  $\text{NaCl}$  form by batch contact with excess  $\text{NaCl}$  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  $\text{Na}^+$  and  $\text{NH}_4^+$  form, the conversion was between 98 and 100% complete, as indicated by the residual  $\text{H}^+$  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 previously (Barletta et al., 1981).

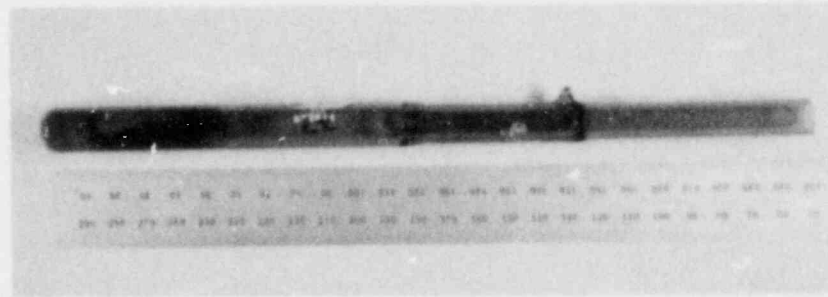


Figure 2.1 Break-seal vessel for resin irradiation.

The loaded 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

$$P_s = P_f + (P_f - P_i) \frac{V_c}{V_s} \quad (2.1)$$

$P_s$  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  $196 \text{ cm}^3$  and  $14 \text{ cm}^3$ , respectively. The large cell volume was chosen to handle the substantial gas pressure anticipated in  $\text{H}^+$  form resin containing corrosion coupons. In later experiments, the cell volume was reduced to  $100 \text{ cm}^3$ . Following the determination of  $P_i$  and  $P_f$ , 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  $\pm 1\%$  for components with concentration down to 1%. For lower concentration, the accuracy is  $\pm 5\%$  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 been 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.\*

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\*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 break-seal 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 properly. 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 irradiation 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.,  $\text{SO}_4^{2-}$ ) and counterions (e.g.,  $\text{Na}^+$ ) in solution. Sulfate ion concentrations were determined using a Dionex Model 10 ion chromatograph. Na and Fe concentrations were measured by atomic absorption spectroscopy.  $\text{Cl}^-$  concentrations were determined by colorometric techniques. In those cases where  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  were simultaneously present in solution,  $\text{Cl}^-$  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  $\text{Na}^+$  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 material 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  $\text{HNO}_3$ . 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  $\text{H}^+$  released by the resin. The resin moisture content is determined separately. Exchange capacity is given by meq  $\text{H}^+$  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

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 self-irradiation 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 ion-exchange 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 ( $\text{Na}^+$ ) and hydrogen ( $\text{H}^+$ ) 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  $\text{H}^+$  form resin is substantially more acidic than the  $\text{Na}^+$  form. The dependence of pH on radiation dose is also different for the two forms. For the hydrogen form resin, the hydrogen ion concentration  $[\text{H}^+]$ , as determined from pH, increases roughly as  $D^{2/3}$  over the range from  $\sim 10^7$  to  $10^9$  rad, where D is the dose in rad. In this relation, there is no evidence for any dependence of radiation damage yield upon radiation dose rate. For the  $\text{Na}^+$  form resin, the behavior is more complex.  $[\text{H}^+]$  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.

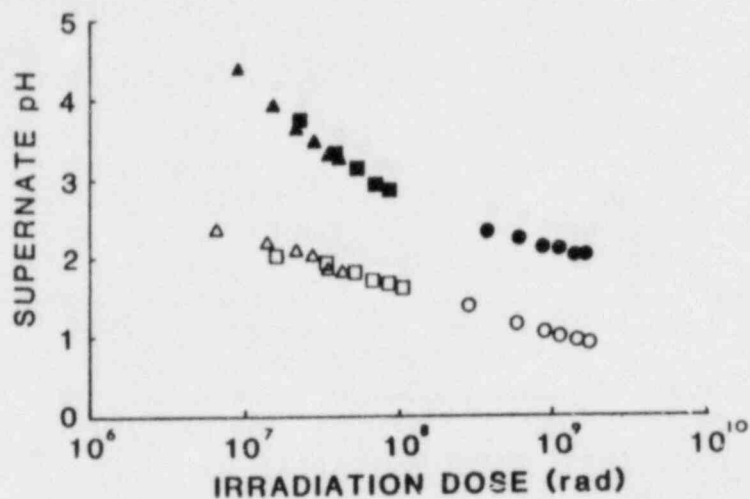


Figure 3.1 Supernate pH vs irradiation dose for irradiated  $H^+$  (open points) and  $Na^+$  form (solid points) resin. Dose rates (rad/h):  $\circ$   $-1.6 \times 10^6$ ;  $\square$   $-1 \times 10^5$ ;  $\Delta$   $-4 \times 10^4$ .

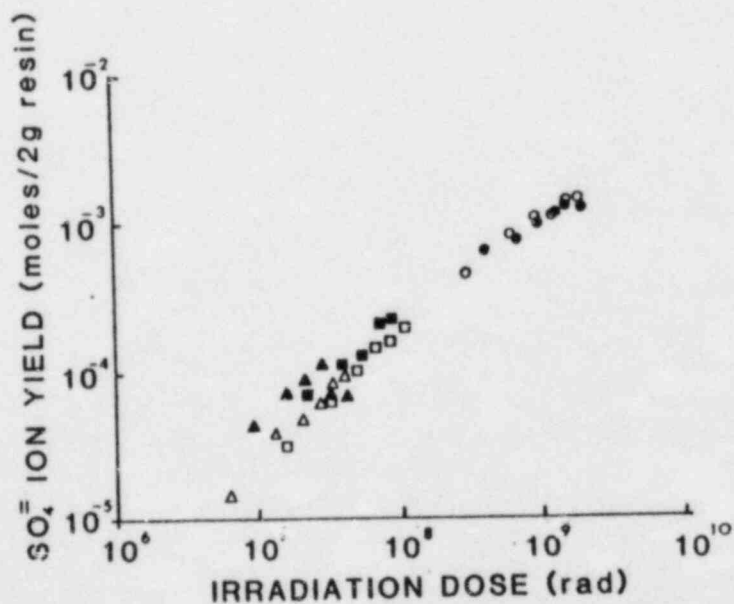


Figure 3.2 Soluble sulfate generation vs irradiation dose for fully swollen IRN-77  $H^+$  form resin (open points) and  $Na^+$  form resin (solid points). Dose rates (rad/h):  $\circ$   $-1.6 \times 10^6$ ;  $\square$   $-1 \times 10^5$ ;  $\Delta$   $-4 \times 10^4$ .

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  $-SO_3^-$  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  $SO_4^{2-}$ . Mechanisms are considered further in Section 4. For the present, solution analysis indicates that  $SO_4^{2-}$  is, indeed, the dominant species found in the supernate liquids. In selected samples, no significant concentration of  $SO_3^{2-}$  was detected by ion chromatography. Certain samples were oxidized with hydrogen peroxide and their  $SO_4^{2-}$  content redetermined. In no case did oxidation increase the  $SO_4^{2-}$  concentration by more than 15%. Gas analysis (Section 3.1.2) indicates that little, if any,  $SO_2$  escaped from the samples during irradiation. We cannot entirely rule out the possibility that species such as  $SO_3^{2-}$  present in the sealed irradiated tube are oxidized to  $SO_4^{2-}$  in the sampling process. Instability of  $SO_3^{2-}$  in soils, for example, is well known (Lindsay, 1979) and for irradiation in a sealed vessel, the atmosphere over resins quickly becomes anoxic (Section 3.1.2), which might favor  $SO_3^{2-}$ . 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  $SO_4^{2-}$  most probably results from the rapid hydrolysis of radiolytic  $SO_3$  during irradiation. Consequently, we interpret the  $SO_4^{2-}$  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  $H^+$  and  $Na^+$  forms, irradiated under the present conditions. Since the supernate pH of the  $Na^+$  and  $H^+$  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 (Kazanjan 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.

It is noteworthy that G values for  $SO_4^{2-}$  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

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

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

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<sub>4</sub><sup>=</sup> 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<sub>4</sub><sup>=</sup>. The fraction of the acidity attributable to H<sub>2</sub>SO<sub>4</sub> was then determined. This ranged from 60% at a dose of 2x10<sup>7</sup> rad to 100% at 10<sup>9</sup> 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 (NaHSO<sub>4</sub>) 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 (NaHSO<sub>4</sub>) 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).

\*This assumes a homogeneous distribution of SO<sub>4</sub><sup>=</sup> in 10 mL of liquid phase, both within and outside the resin. In the supernate, a certain fraction of the SO<sub>4</sub><sup>=</sup> will be incorporated in bisulfate, HSO<sub>4</sub><sup>-</sup>. In the measurement technique HSO<sub>4</sub><sup>-</sup> is determined as SO<sub>4</sub><sup>=</sup>.

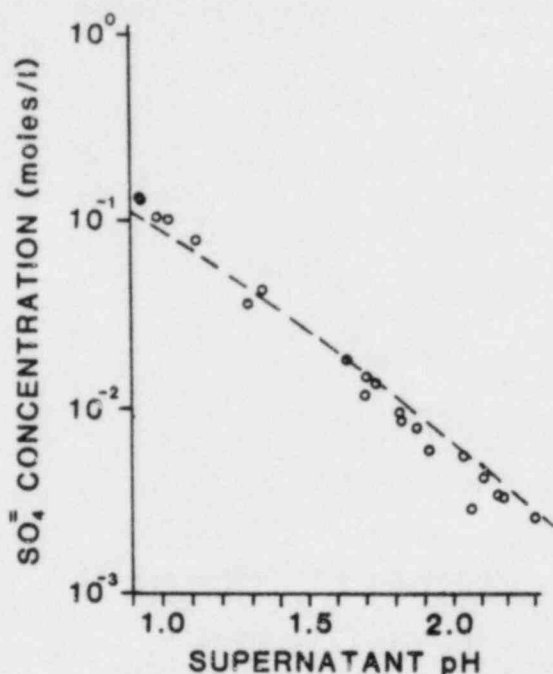


Figure 3.3  $\text{SO}_4^{=}$  yields vs pH in the supernate of IRN-77  $\text{H}^+$  form resin, subjected to various irradiation doses. The dashed line indicates the behavior expected for the dissociation of  $\text{H}_2\text{SO}_4$ . The  $\text{SO}_4^{=}$  yields include  $\text{SO}_4^{=}$  incorporated in  $\text{HSO}_4^-$  at the indicated pH.

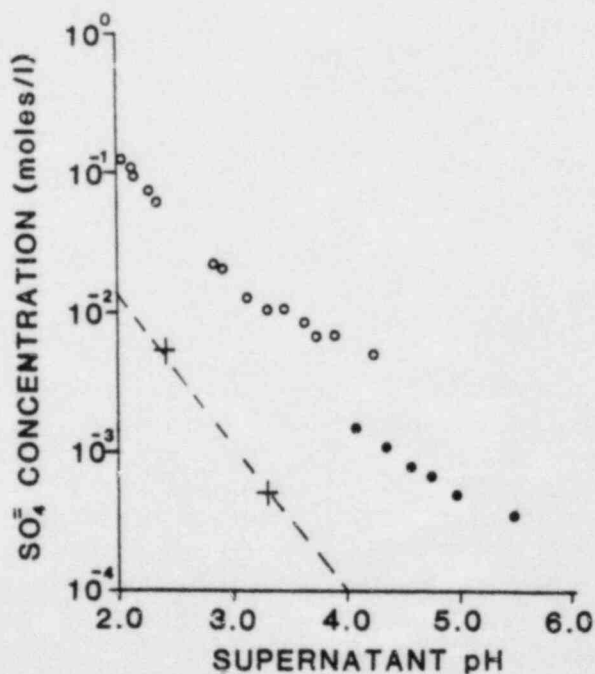


Figure 3.4  $\text{SO}_4^{=}$  yields vs pH in the supernate of IRN-77  $\text{Na}^+$  form resin, subjected to various irradiation doses. The dashed line indicates the behavior anticipated for the dissociation of  $\text{NaHSO}_4$ . The crosses indicate measured values for  $\text{NaHSO}_4$  solutions. The  $\text{SO}_4^{=}$  yields include  $\text{SO}_4^{=}$  incorporated in  $\text{HSO}_4^-$  at the indicated pH. Solid points = unirradiated control samples.

Table 3.2

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

Irradiation Dose (Rad)	Sulfuric Acid (Percent)	pH	Percent Dissociation
2.0 x 10 <sup>7</sup>	66	2.10	100
3.9 x 10 <sup>7</sup>	85	1.90	63
8.0 x 10 <sup>8</sup>	104	1.05	40
1.6 x 10 <sup>9</sup>	100	0.95	42

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>	[SO <sub>4</sub> <sup>=</sup> ] <sup>a</sup>	pH	Percent Dissociation
5.5 x 10 <sup>7</sup>	.005	N.M. <sup>b</sup>	0.03	3.0	20
3.0 x 10 <sup>8</sup> <sup>c</sup>	N.M.	0.11+.02	0.07+.01	2.1+.1	N.M.
9.1 x 10 <sup>8</sup>	.041	N.M.	0.18 <sup>-</sup>	2.1 <sup>-</sup>	20

<sup>a</sup>All values in meq per mL. Supernate formed from 10-mL deionized water and 2-g irradiated resin.

<sup>b</sup>N.M. = not measured.

<sup>c</sup>Data from Swyler and Weiss (1981).

The data in Table 3.3 confirm that the acidic species in the supernate of the Na<sup>+</sup> resin is not pure NaHSO<sub>4</sub>. The ratio of H<sup>+</sup> equivalents to SO<sub>4</sub><sup>=</sup> equivalents is only about 1:5 rather than 1:2, and the ratio of Na<sup>+</sup> equivalents to SO<sub>4</sub><sup>=</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 H<sup>+</sup> and Na<sup>+</sup> resin functional groups proceeds in a similar manner, the secondary processes which result in free acid formation are quite different. For H<sup>+</sup> resin, sensibly all the SO<sub>4</sub><sup>=</sup> production generates the acidic species H<sub>2</sub>SO<sub>4</sub>. In Na<sup>+</sup> form resin, less than 2/5 of the SO<sub>4</sub><sup>=</sup> production ultimately results in the analogous acidic

species  $\text{NaHSO}_4$ . 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 ( $1.6 \times 10^6$  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  $\text{Fe}^{++}$  form,  $\text{Fe}^{+++}$  form and  $\text{NH}_4^+$  form were carried out in sealed glass tubes, according to the procedures described earlier. Supernatant solutions were analyzed for radiolytic decomposition products, including sulfate ion and counterions released. pH data and  $\text{Fe}^{+++}$  form solution analysis results are shown in Figures 3.5 and 3.6, respectively.

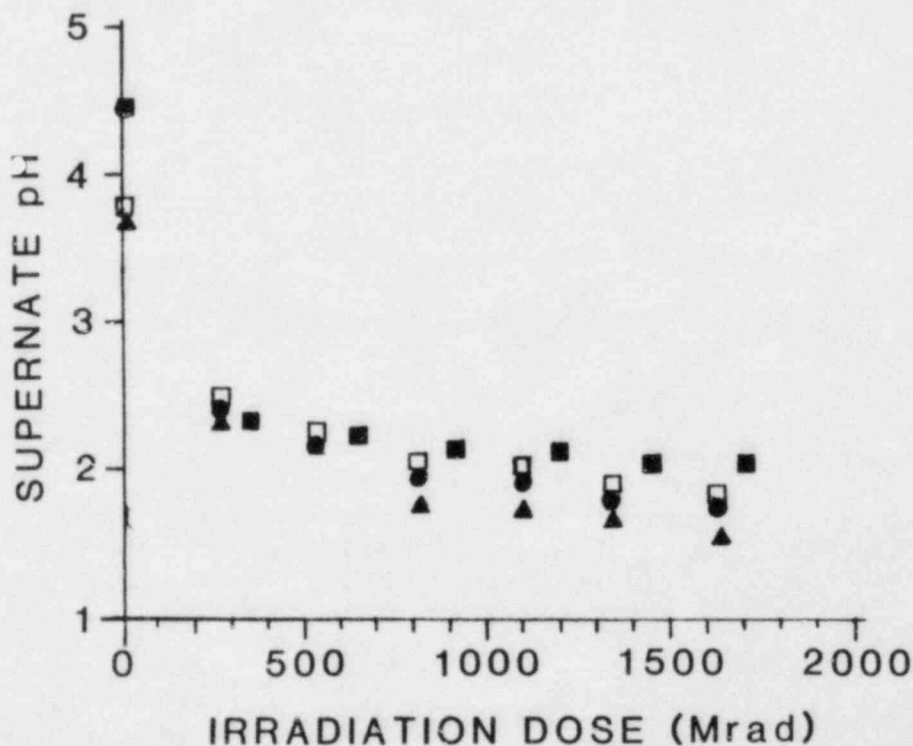


Figure 3.5 Supernatant pH vs irradiation dose for various forms of fully swollen IRN-77 resin. Dose rate =  $1.6 \times 10^6$  rad/h. Samples irradiated in sealed environment. ■ -  $\text{Na}^+$  form resin; ● -  $\text{NH}_4^+$  form; □ -  $\text{Fe}^{++}$  form; ▲ -  $\text{Fe}^{+++}$  form. Supernatant formed from 2-g irradiated resin and 10-mL de-ionized water.

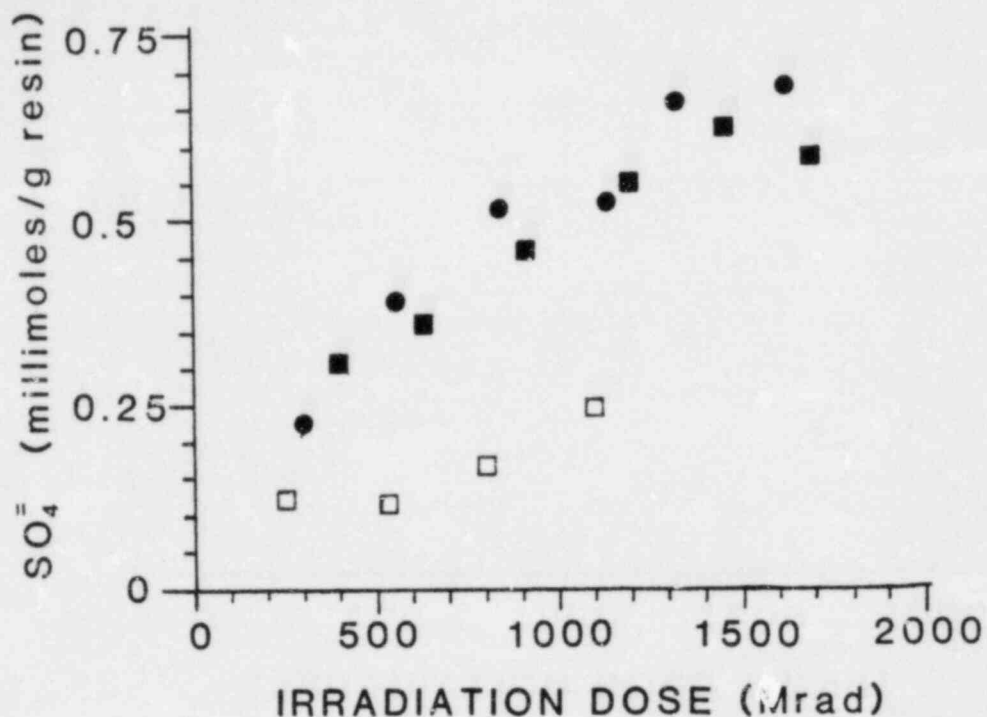


Figure 3.6 Sulfate ion supernate yields (moles per g of fully swollen resin) vs irradiation dose in different forms of fully swollen IRN-77 resin. ■ -Na<sup>+</sup> form; ● -H<sup>+</sup> form; □ -Fe<sup>+++</sup> form.

The data in Figure 3.5 indicate the same general trends observed in H<sup>+</sup> 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 NH<sub>4</sub><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<sup>9</sup> 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 functional group. A similar effect has been noted by others (Gangwer et al., 1978).

Table 3.4

Equivalents of  $\text{Fe}^{+++}$ ,  $\text{H}^+$  and  $\text{SO}_4^-$  in the Supernate of Irradiated  $\text{Fe}^{+++}$  Form IRN-77 Resin

Irradiation Dose (Rad)	Milliequivalents per mL of Supernate <sup>a</sup>		
	$\text{H}^+$	$\text{Fe}^{+++}$	$\text{SO}_4^-$
0			
$2.7 \times 10^8$	$1.3 \times 10^{-2}$	$4.2 \times 10^{-3}$	$4.8 \times 10^{-2}$
$5.4 \times 10^8$	$2.3 \times 10^{-2}$	$2.0 \times 10^{-2}$	$4.8 \times 10^{-2}$
$8.2 \times 10^8$	$3.3 \times 10^{-2}$	$3.3 \times 10^{-2}$	$6.8 \times 10^{-2}$
$1.1 \times 10^9$	$4.8 \times 10^{-2}$	$4.6 \times 10^{-2}$	$1.0 \times 10^{-1}$

<sup>a</sup>The equivalents for  $\text{H}^+$  are determined from pH data and include a calculated contribution from undissociated  $\text{HSO}_4^-$  at the indicated pH; supernate formed from 10-mL deionized water and 2 g irradiated resin.

<sup>b</sup> $\text{Fe}^{+++}$  equivalents are determined assuming that the measured iron in the supernate is entirely in the +3 state.

In  $\text{Na}^+$  form resin,  $5 \times 10^8$  rad results in supernatant sulfate levels corresponding to attack on 15% of the functional groups. In  $\text{Fe}^{+++}$  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  $\text{Fe}^{+++}$  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  $-\text{SO}_3^-$  groups for every  $\text{Fe}^{+++}$  ion in the resin. The average ratio of moles of  $\text{H}^+$  to moles of  $\text{SO}_4^-$  is 0.96. This means that  $\text{H}^+$  is produced on a very nearly 1:1 basis with the scission of the functional group.

This  $\text{H}^+$  is required to maintain the charge balance in the conversion of  $-\text{SO}_3^-$  to  $\text{SO}_4^-$ . There is no evidence that it is subsequently taken up by ion-exchange processes in the undamaged resin. The difference in selectivities between  $\text{H}^+$  and  $\text{Fe}^{+++}$  would probably prevent this effect. On the other hand, for  $\text{Na}^+$  form resin, more moles of sodium are released to the supernate than moles of sulfate. This "extra" sodium (which could be produced in the fundamental damage process or released in subsequent ion-exchange

processes on the undamaged resin) removes the 1:1  $\text{H}^+\text{SO}_4^-$  charge balance requirement observed in the  $\text{Fe}^{+++}$  resin. Consequently, although the  $\text{SO}_4^-$  yield is greater for  $\text{Na}^+$  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  $\text{H}^+$  and  $\text{Na}^+$  form were irradiated under wet and dry conditions to determine the effect of moisture on radiolytic attack. Irradiations were carried out on dry (7% moisture content) samples in sealed glass vessels, and on 2-g resin samples immersed in 10 mL of deionized water. For the samples irradiated under deionized water, the pH was determined periodically by removing the samples from the irradiation facility. Sulfate and pH analysis was performed on the supernatant liquids contacted with 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  $\text{Na}^+$  and  $\text{H}^+$  resins irradiated in the fully swollen form. It is interesting that the oxidized species,  $\text{SO}_4^-$ , is observed when water is contacted with resins which have been irradiated in the dry state. For the  $\text{Na}^+$  form resin, the soluble species is largely  $\text{Na}_2\text{SO}_4$ . For the hydrogen form resin the relationship between pH and  $\text{SO}_4^-$  agrees fairly well with the expected behavior for sulfuric acid.

Generally, the pH values of the  $\text{H}^+$  and  $\text{Na}^+$  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  $\text{Na}^+$  form samples immersed in water, large gas pockets formed which pushed the resin upward in the irradiation tube. This effect was not observed in the  $\text{H}^+$  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  $\text{HNO}_3$  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

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

Resin Form	Na <sup>+</sup> Dry			H <sup>+</sup> Dry	
	pH <sup>a</sup>	SO <sub>4</sub> <sup>=</sup> b	Na <sup>+</sup> b	pH <sup>a</sup>	SO <sub>4</sub> <sup>=</sup> b
Radiation <sup>c</sup> Dose (Rad)					
0	5.8	(9.6±0.4)×10 <sup>-7</sup>	(2.5±0.8)×10 <sup>-7</sup>	3.0	<3.5×10 <sup>-6</sup>
2.7×10 <sup>8</sup>	3.7	N.M. <sup>d</sup>	(2.0±1.4)×10 <sup>-4</sup>	2.3	N.M.
5.4×10 <sup>8</sup>	3.3	N.M.	2.8×10 <sup>-4</sup>	2.0	N.M.
8.2×10 <sup>8</sup>	3.2	(1.9±0.2)×10 <sup>-4</sup>	(3.5±0.7)×10 <sup>-4</sup>	1.8	(2.1±0.2)×10 <sup>-4</sup>
1.1×10 <sup>9</sup>	3.0	(2.3±0.2)×10 <sup>-4</sup>	(6.5±0.3)×10 <sup>-4</sup>	1.8	2.8×10 <sup>-4</sup>

<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 × 10<sup>6</sup> rad/h.

<sup>d</sup>N.M. = not measured.

Table 3.6

## Supernatant pH for IRN-77 Resin Irradiated Under Deionized Water

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

<sup>a</sup> -: not measured.



### 3.1.1.2 Quaternary Ammonium Anion Resin (IRN-78)

#### 3.1.1.2.1 Radiation and Resin Loading Effects 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  $\text{Cl}^-$  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
$\text{Cl}^-$	0	<0.2	N.M. <sup>b</sup>	6.1±0.7
	$2.7 \times 10^8$	0.84	5.7	7.1
	$5.4 \times 10^8$	1.20	6.4	6.8
	$8.1 \times 10^8$	1.93	7.4	5.8
	$1.1 \times 10^9$	2.06	7.3	5.6
	$1.3 \times 10^9$	2.13	7.0	5.3
$\text{OH}^-$	0	<0.1	N.M.	8.6±0.8
	$8.0 \times 10^7$	N.M.	N.M.	10.4*
	$1.6 \times 10^8$	N.M.	N.M.	10.6*
	$3.2 \times 10^8$	N.M.	N.M.	11.0*
	$8.0 \times 10^8$	2.38	10.5	10.6
	$1.1 \times 10^9$	2.49	10.4	10.7

<sup>a</sup>All irradiations carried out at  $1.6 \times 10^6$  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.

<sup>b</sup>N.M. = not measured

The centrifuged free liquid and supernate were measured for  $\text{Cl}^-$  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  $\sim 1.7$  meq/g; Table 3.8 indicates that, for doses  $> 8 \times 10^8$  rad, sensibly all the available  $\text{Cl}^-$  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  $8 \times 10^8$  rad.

Table 3.8

Physical Changes and  $\text{Cl}^-$  Ion Release in Irradiated IRN-78 Resin in the  $\text{Cl}^-$  Form<sup>a</sup>

Irradiation Dose (rad)	Free Liquid Release (mL/g)	Bulk Resin Density $\text{g/cm}^3$	Cl <sup>-</sup> Release (Moles/g)		
			Free Liquid	Supernate	Total
0	.027±.02	0.63±.01	N.M. <sup>b</sup>	$< 10^{-6}$	N.M.
$2.7 \times 10^8$	0.14	0.62	N.M.	$2.9 \times 10^{-4}$	N.M.
$5.4 \times 10^8$	0.20	0.63	N.M.	$3.7 \times 10^{-4}$	N.M.
$8.1 \times 10^8$	0.32	0.62	$8.5 \times 10^{-4}$	$4.1 \times 10^{-4}$	$1.3 \times 10^{-3}$
$1.1 \times 10^8$	0.34	0.69	$9.0 \times 10^{-4}$	$3.6 \times 10^{-4}$	$1.3 \times 10^{-3}$
$1.3 \times 10^9$	0.36	0.69	$9.0 \times 10^{-4}$	$3.2 \times 10^{-4}$	$1.2 \times 10^{-3}$
$1.6 \times 10^9$	0.35	0.78	$1.0 \times 10^{-3}$	$3.9 \times 10^{-4}$	$1.4 \times 10^{-3}$

<sup>a</sup>All per gram quantities refer to 1 g of fully swollen resin.

<sup>b</sup>N.M. = not measured.

For the irradiated  $\text{OH}^-$  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 following 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  $\text{OH}^-$  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  $\text{OH}^-$  concentration is maintained at about  $3 \times 10^{-4}$  moles/liter. This is

substantially lower than the concentration ( $3 \times 10^{-1}$  moles/liter) that would be expected on the basis of complete release and subsequent stabilization of  $\text{OH}^-$  ion. Either the released  $\text{OH}^-$  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  $\text{Cl}^-$  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  $1 \times 10^9$  rad is shown in Figure 3.7.

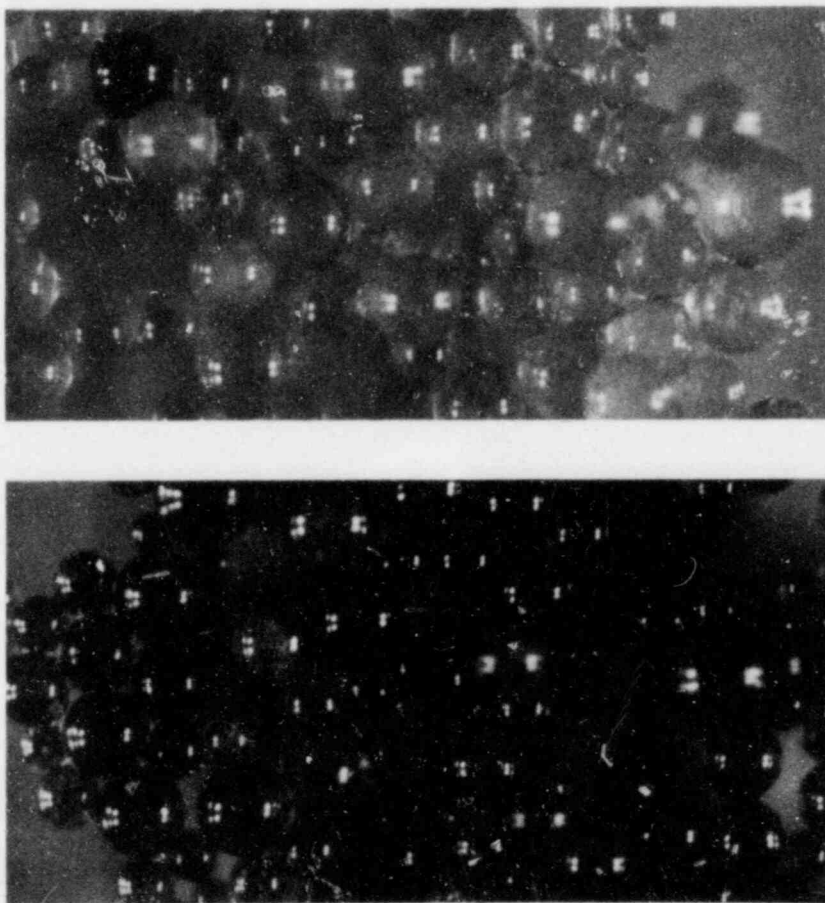


Figure 3.7 Photomicrograph of IRN-78 resin beads before (upper) and after (lower) irradiation to  $1 \times 10^9$  rad at  $1.6 \times 10^6$  rad/h. The beads were centrifuged prior to photographing to remove free liquid released during irradiation.

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% (0.35 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 moisture 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

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

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

<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.

Table 3.10

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

Irradiation Dose (rad) $\times 10^{-8}$	Free Liquid					Supernate Over Centrifuged Resin <sup>b</sup>					
	Amount Released (mL/g)	SO <sub>4</sub> <sup>=</sup> (mole/g)	Na <sup>+</sup> (mole/g)	Cl <sup>-</sup> (mole/g)	pH	SO <sub>4</sub> <sup>=</sup> (mole/g)	Na <sup>+</sup> (mole/g)	Cl <sup>-</sup> (mole/g)	pH	Total Dissolved Na <sup>+</sup> (mole/g)	Total Dissolved Cl <sup>-</sup> (mole/g)
0	<0.02	N.M. <sup>c</sup>	N.M.	N.M.	N.M.	<10 <sup>-6</sup>	<10 <sup>-5</sup>	<10 <sup>-6</sup>	5.8±0.9	N.M.	N.M.
2.7	.13	6.9×10 <sup>-5</sup>	N.M.	1.0×10 <sup>-4</sup>	2.0	9.8×10 <sup>-6</sup>	2.6×10 <sup>-4</sup>	2.2×10 <sup>-4</sup>	2.8	N.M.	3.2×10 <sup>-4</sup>
5.4	.24	1.8×10 <sup>-4</sup>	5.0×10 <sup>-4</sup>	3.7×10 <sup>-4</sup>	1.6	5.4×10 <sup>-5</sup>	3.2×10 <sup>-4</sup>	2.9×10 <sup>-4</sup>	2.3	8.2×10 <sup>-4</sup>	6.6×10 <sup>-4</sup>
8.1	.27	2.7×10 <sup>-4</sup>	5.2×10 <sup>-4</sup>	4.8×10 <sup>-4</sup>	1.5	7.5×10 <sup>-5</sup>	3.2×10 <sup>-4</sup>	1.5×10 <sup>-4</sup>	2.2	8.4×10 <sup>-4</sup>	6.3×10 <sup>-4</sup>
11	.31	1.7×10 <sup>-4</sup>	4.6×10 <sup>-4</sup>	2.5×10 <sup>-4</sup>	1.2	9.2×10 <sup>-5</sup>	2.5×10 <sup>-4</sup>	3.4×10 <sup>-4</sup>	2.1	7.1×10 <sup>-4</sup>	5.9×10 <sup>-4</sup>
13	.32	2.0×10 <sup>-4</sup>	5.5×10 <sup>-4</sup>	2.6×10 <sup>-4</sup>	1.1	N.M.	2.3×10 <sup>-4</sup>	3.3×10 <sup>-4</sup>	2.1	7.8×10 <sup>-4</sup>	5.6×10 <sup>-4</sup>
16	.33	1.9×10 <sup>-4</sup>	7.0×10 <sup>-4</sup>	2.6×10 <sup>-4</sup>	1.0	8.4×10 <sup>-5</sup>	2.8×10 <sup>-4</sup>	4.2×10 <sup>-4</sup>	2.0	9.3×10 <sup>-4</sup>	5.4×10 <sup>-4</sup>

<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.<sup>c</sup>N.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<sup>+</sup> and SO<sub>4</sub><sup>=</sup> concentrations in the supernate and free liquid of HOH form resin (Table 3.11) indicate that the liquids are less acidic than H<sub>2</sub>SO<sub>4</sub>. Since H<sub>2</sub>SO<sub>4</sub> is the acid produced in the irradiation of IRN-77 (H<sup>+</sup>) 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 [SO<sub>4</sub><sup>=</sup>]<sup>a</sup> and [H<sup>+</sup>]<sup>b</sup> in  
Liquids Contacting Irradiated IRN-150 HOH Form Resin

Resin Form	Irradiation Dose (rad)	Free Liquid (meq/mL)		Supernate (meq/mL)	
		[SO <sub>4</sub> <sup>=</sup> ]	[H <sup>+</sup> ]	[SO <sub>4</sub> <sup>=</sup> ]	[H <sup>+</sup> ]
HOH	<0.02	N.M. <sup>c</sup>	N.M.	<10 <sup>-6</sup>	2x10 <sup>-6</sup>
	2.7x10 <sup>8</sup>	6.8x10 <sup>-2</sup>	4.0x10 <sup>-5</sup>	N.M.	N.M.
	5.4x10 <sup>8</sup>	4.6x10 <sup>-1</sup>	9.6x10 <sup>-2</sup>	1.3x10 <sup>-3</sup>	1.5x10 <sup>-3</sup>
	8.1x10 <sup>8</sup>	1.1	4.0x10 <sup>-1</sup>	2.6x10 <sup>-2</sup>	5.1x10 <sup>-3</sup>
	1.1x10 <sup>9</sup>	4.0x10 <sup>-1</sup>	1.8x10 <sup>-1</sup>	3.4x10 <sup>-2</sup>	6.5x10 <sup>-3</sup>
	1.3x10 <sup>9</sup>	N.M.	N.M.	3.8x10 <sup>-2</sup>	9.3x10 <sup>-3</sup>
	1.6x10 <sup>9</sup>	7.2x10 <sup>-1</sup>	3.5x10 <sup>-1</sup>	4.4x10 <sup>-2</sup>	1.4x10 <sup>-2</sup>

<sup>a</sup>The value for [SO<sub>4</sub><sup>=</sup>] is total sulfate concentration and may include species such as NaHSO<sub>4</sub>, HSO<sub>4</sub><sup>-</sup> 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

Ion Balance in Liquids Contacting Irradiated IRN-150 ( $\text{Na}^+\text{Cl}^-$ ) Resin<sup>a</sup>

Irradiation Dose (rad)	Free Liquid		Supernate	
	$\text{SO}_4^{=}$ + $\text{Cl}^-$	$\text{Na}^+$ + $\text{H}^+$	$\text{SO}_4^{=}$ + $\text{Cl}^-$	$\text{Na}^+$ + $\text{H}^+$
$2.7 \times 10^8$	---	---	0.56	0.060
$5.4 \times 10^8$	3.0	2.5	0.099	0.092
$8.1 \times 10^8$	3.7	2.8	0.082	0.10
$1.1 \times 10^8$	1.9	2.1	0.15	0.08
$1.3 \times 10^8$	2.0	2.4	---	---
$1.6 \times 10^8$	1.9	2.7	0.14	0.10

<sup>a</sup>All values given in meq/mL resin;  $\text{H}^+$  values from pH, including the computed amount of  $\text{H}^+$  incorporated in bisulfate 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  $\text{SO}_4^{=}$  yields in the mixed bed system are comparable with those measured in the pure cation resin.  $\text{SO}_4^{=}$  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 cation-exchange 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.

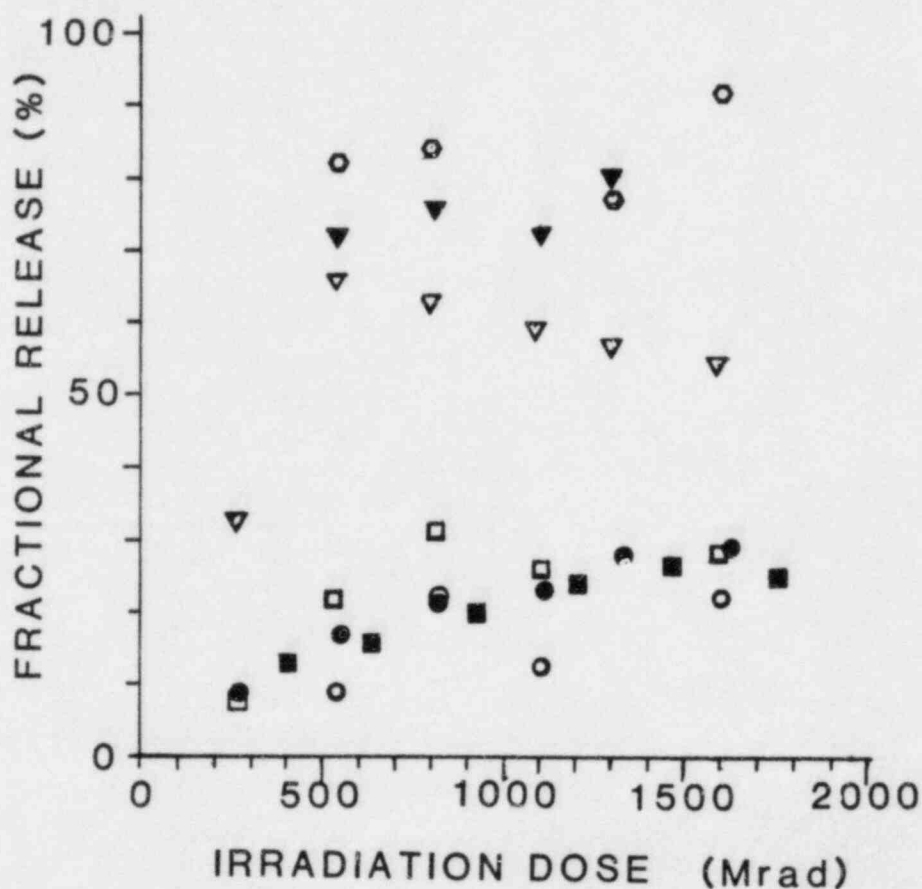


Figure 3.8 Fractional release of functional group decomposition products and exchangeable ions. ○ - Na<sup>+</sup>, IRN-150, NaCl form; ▼ - Cl<sup>-</sup>, IRN-78 Cl<sup>-</sup> form; ▽ - Cl<sup>-</sup>, IRN-150, NaCl form; □ - SO<sub>4</sub><sup>=</sup>, IRN-150, NaCl form; o - SO<sub>4</sub><sup>=</sup>, IRN-150, HOH form; ■ - SO<sub>4</sub><sup>=</sup>, IRN-77, Na<sup>+</sup> form; ● - SO<sub>4</sub><sup>=</sup>, IRN-77, H<sup>+</sup> form.

#### 3.1.1.3.4 Relative Free Liquid Release 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 Baumann (1966). The shrinkage (and subsequent liquid release) is confined largely to the anion component, as shown in Figure 3.10.



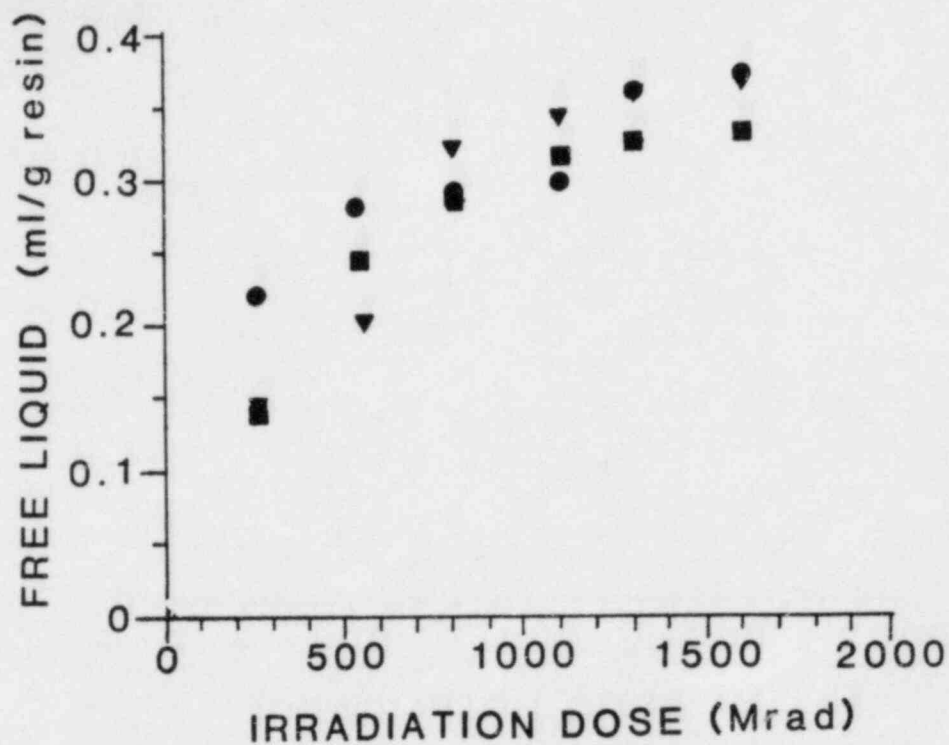


Figure 3.9 Free liquid release vs irradiation dose in IRN-78,  $\blacktriangledown$  - (Cl<sup>-</sup>); IRN-150,  $\bullet$  - (HOH); and IRN-150,  $\blacksquare$  - (NaCl) resins.

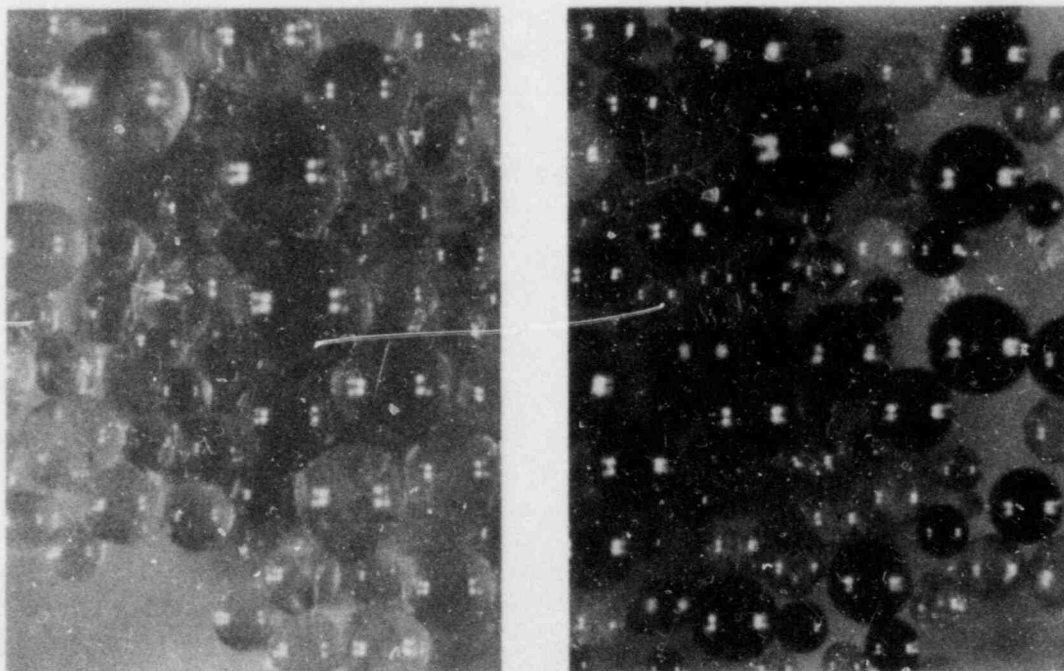


Figure 3.10 IRN-150 (HOH) form resin before (left) and after (right) irradiation to  $1 \times 10^9$  rad. The cation component darkens under irradiation but does not undergo extensive shrinkage.

### 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<sup>+</sup> 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.

Table 3.13  
Gas Pressures in the Atmosphere Over Irradiated H<sup>+</sup> Form IRN-77 Resin

Dose Rate (rad/h)	Time (h)	Pressure (psi)						Total
		H <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	Ar	
0	0	0	0	0	11.5	3.08	0.14	14.7 <sup>a</sup>
"	165	N.D. <sup>b</sup>	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	---	---	---	---	---	---	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	14.7 <sup>a</sup>
"	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
"	675 <sup>d</sup>	0.02	0.35	1.98	9.8	1.89	0.12	14.2
"	845 <sup>d</sup>	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
1x10 <sup>5</sup>	0	0	0	0	11.5	3.08	0.14	14.7 <sup>a</sup>
"	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
"	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
1.6x10 <sup>6</sup>	0	0	0	0	11.5	3.08	0.14	14.7 <sup>a</sup>
"	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

<sup>a</sup>Assumes initial composition of standard air at 1 atmosphere.

<sup>b</sup>N.D. = not detected; pressure <0.01 psi.

<sup>c</sup>Gas composition not analyzed.

<sup>d</sup>Compositional 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  $\pm 0.41$  psi. These values should be taken to reflect, respectively, the average initial pressure for these experiments, and the experimental uncertainty ( $\pm 3\%$ ) 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 power-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  $0.13 \pm .02$ .

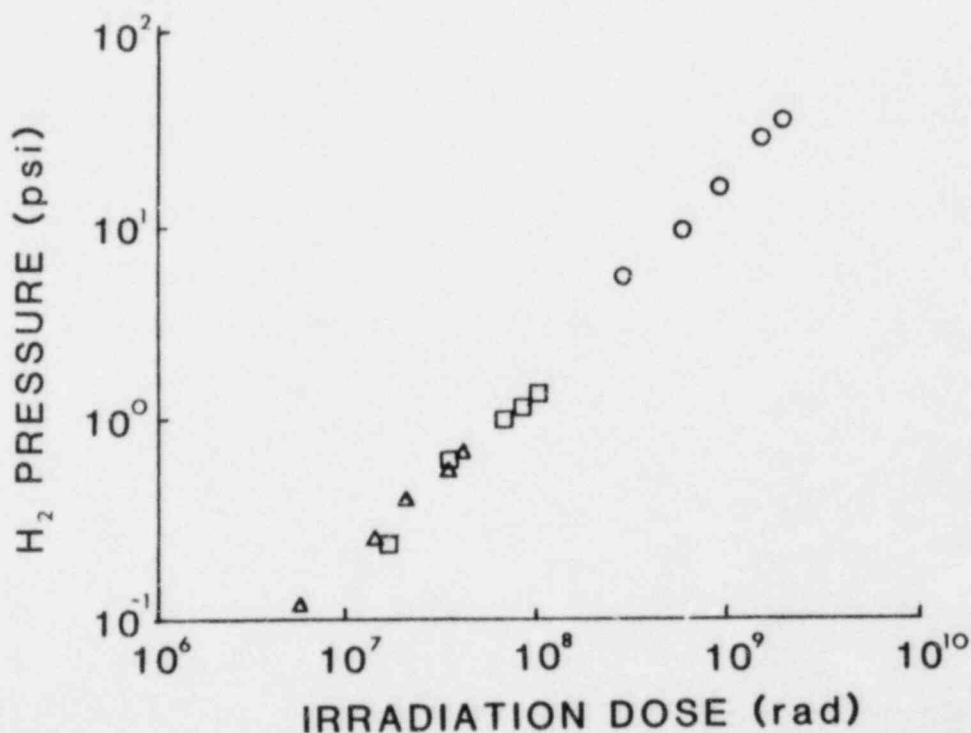


Figure 3.11 Hydrogen pressure over irradiated IRN-77  $H^+$  form resin.  
 Dose rates (rad/h): 0 -  $1.6 \times 10^6$ ;  $\square$  -  $1 \times 10^5$ ;  
 $\triangle$  =  $4 \times 10^4$ .

A second major radiolytic gaseous component is carbon dioxide. This appears in two stages. In unirradiated control samples and in samples irradiated at  $4 \times 10^4$  and  $10^5$  rad/h,  $\text{CO}_2$  levels, remains fairly stable with time at roughly 2 psi. For irradiation at  $1.6 \times 10^6$  rad/h, a second stage of  $\text{CO}_2$  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,  $\text{CO}_2$  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.

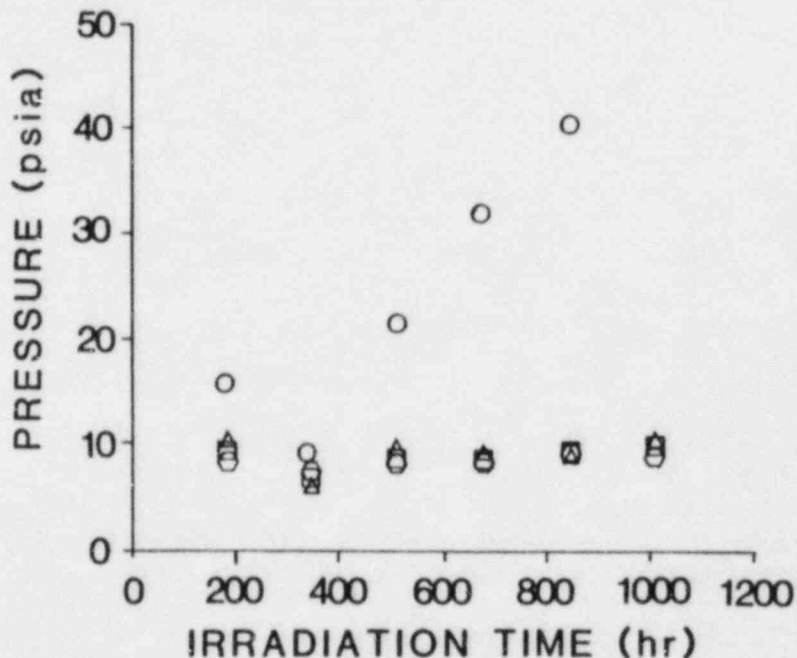


Figure 3.12 Sample cell pressure vs irradiation time at different dose rates for Na<sup>+</sup> form IRN-77 resin. Irradiation dose rates (rad/h): o -  $1.6 \times 10^6$ ; □ -  $1 \times 10^5$ ; △ -  $4 \times 10^4$ ; ◇ - unirradiated.

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

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

Dose Rate (rad/h)	Time (h)	Percent Composition								
		H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	CO	CO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>	H <sub>2</sub> O
0	1030	N.D. <sup>a</sup>	20.1	76.6	0.91	0.6	1.68	N.D.	N.D.	.06
4 x 10 <sup>4</sup>	1030	0.56	19.8	76.1	0.91	0.7	1.79	N.D.	N.D.	.09
1 x 10 <sup>5</sup>	1030	--	--	--	--	--	--	--	--	--
1.6 x 10 <sup>6</sup>	1030	65.8	0.42	19.9	0.26	N.D.	13.4	N.D.	N.D.	0.17

<sup>a</sup>N.D. = not detected; pressure <0.01 psi; --- = not determined.

Samples irradiated at low dose rates show an uptake of atmospheric oxygen which is approximately balanced by the formation of CO<sub>2</sub>. In samples irradiated at high dose rates, which show substantial hydrogen generation, the amount of CO<sub>2</sub> present is greater than that anticipated on the basis of conversion of O<sub>2</sub> to CO<sub>2</sub>.

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<sub>2</sub>. At greater doses (or higher dose rates), additional CO<sub>2</sub> 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  $NH_4^+$  Form Resins - Fully Swollen

Gas generation measurements were also made on IRN-77 resin in  $Fe^{++}$ ,  $Fe^{+++}$ , and  $NH_4^+$  forms (Table 3.15). Gas compositional data for these experiments are less extensive than for  $H^+$  and  $Na^+$  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.

Table 3.15

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

Resin Loading	Irradiation Dose Rad	Total Pressure (psi)	Partial Pressure of Component Gases (psi)									
			H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	CO	CO <sub>2</sub>	CH <sub>4</sub>	SO <sub>2</sub>	H <sub>2</sub> O	
$Fe^{++}$	0	13.1±.07										
	2.7x10 <sup>8</sup>	16	3.2	.02	9.3	.11	.2	2.5	---	---	---	
	5.4x10 <sup>8</sup>	18										
	8.2x10 <sup>8</sup>	22	9.9	.01	9.5	.13	.18	2.2	---	---	---	
	1.1x10 <sup>9</sup>	28										
	1.3x10 <sup>9</sup>	31	19	---	9.6	.12	---	2.0	---	---	.04	
1.6x10 <sup>9</sup>	37	25.	25.	.01	9.0	.12	.2	2.0	---	---	---	
$Fe^{+++}$	0	16.6±1.8	.04	2.2	11.0	.16	1.0	2.0	---	---	---	
	2.7x10 <sup>8</sup>	17	2.2	1.6	11.2	.14	.21	2.1	---	---	---	
	5.4x10 <sup>8</sup>	22										
	8.2x10 <sup>8</sup>	23	8.2	---	10.5	.15	1.2	3.4	---	---	---	
	1.1x10 <sup>9</sup>	33										
	1.3x10 <sup>9</sup>	37	24	---	7.1	.10	---	5.6	---	---	---	
1.6x10 <sup>9</sup>	47	31	---	9.1	.13	.40	5.8	---	---	---		
$NH_4^+$	0	15.2±0.6	---	1.7	11.3	.13	.23	2.1	---	---	---	
	1.7x10 <sup>8</sup>	24.5										
	2.9x10 <sup>8</sup>	24.5±.3	7.6	---	13.5	.17	0	3.3	.02	---	.03	
	5.7x10 <sup>8</sup>	29										
	1.0x10 <sup>9</sup>	45										
	1.3x10 <sup>9</sup>	51										
1.6x10 <sup>9</sup>	65	46	---	10.7	.14	.23	8.5	.12	---	.04		

Blank entry - not measured; --- not detected; pressure <0.01 psi.  
 Irradiation dose rate:  $Fe^{++}$ ,  $Fe^{+++}$  -  $1.6 \times 10^5$  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 indicative of a decomposition mechanism such as biodegradation.

### 3.1.2.1.4 Na<sup>+</sup> and H<sup>+</sup> 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 3.16  
Radiolytic Gas Generation in Dried IRN-77 Resin<sup>a</sup>

Resin <sup>b</sup> Loading	Irradiation Dose Rad	Total Pressure (psi)	Partial Pressure of Component Gases (psi)									
			H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	CO	CO <sub>2</sub>	CH <sub>4</sub>	SO <sub>2</sub>	H <sub>2</sub> O	
H <sup>+</sup>	0	13.8±.07										
	2.7x10 <sup>8</sup>	13.3±.07	0.5±.1	0.8±.6	10.3±.01	1.22	---	1.3±.5	--- <sup>c</sup>	0.09	---	
	5.4x10 <sup>8</sup>	14.7										
	8.2x10 <sup>8</sup>	16.5	1.7	0.1	10.1	0.13	---	3.2	---	0.6	---	
	1.1x10 <sup>9</sup>	17.7										
Na <sup>+</sup>	0	14.2±1.6										
	2.7x10 <sup>8</sup>	11.5±.6	0.6	0.8	9.5	0.11	---	0.8	---	---	---	
	5.4x10 <sup>8</sup>	11.7±.6										
	8.2x10 <sup>8</sup>	12.0±.6	1.6	.01	9.2	0.12	---	0.6	---	---	---	
	1.1x10 <sup>9</sup>	13.4±.4	2.3	---	9.4	0.10	0.3	0.6	---	---	---	

<sup>a</sup>Pressure 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<sub>2</sub> and possibly CO<sub>2</sub> 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 at a dose rate of  $1.6 \times 10^6$  rad/h. Gas generation rates do not depend sensitively on the resin form ( $\text{OH}^-$  vs  $\text{Cl}^-$ ) or the presence of corrosion coupons. The total gas generation rate is about five times that observed with IRN-77 cation resin.

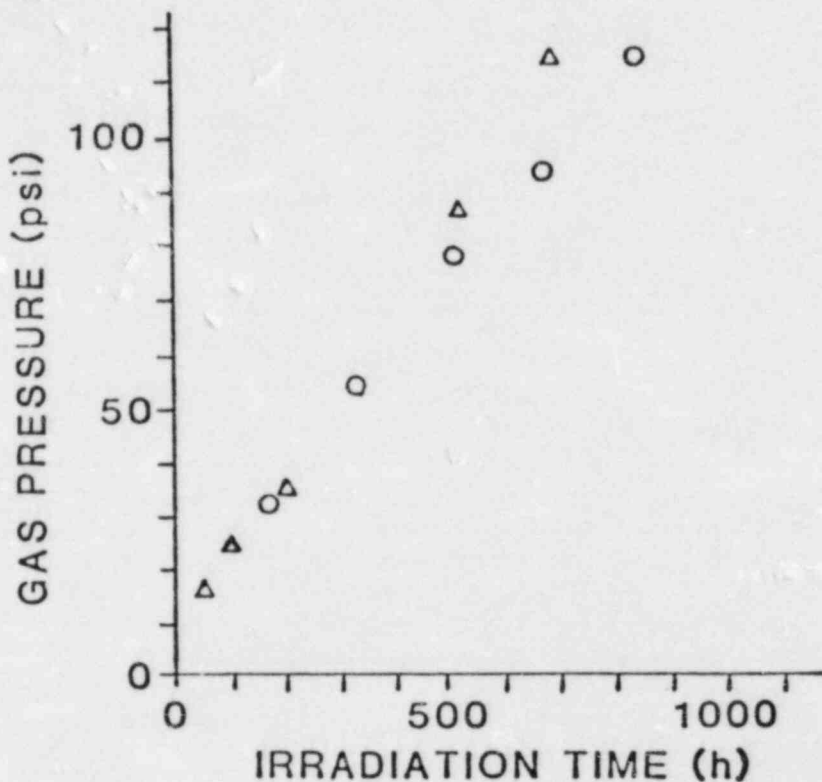


Figure 3.13 Gas pressure over IRN-78 resin vs irradiation time at  $1.6 \times 10^6$  rad/h. O =  $\text{Cl}^-$  form, Δ =  $\text{OH}^-$  form.

The partial pressures of the various gases found in the atmosphere over irradiated IRN-78  $\text{OH}^-$  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  $\text{OH}^-$  form resin. Hydrogen G values are 0.62 and 0.34 for  $\text{OH}^-$  and  $\text{Cl}^-$  forms, respectively. In all cases, atmospheric oxygen is scavenged.



Table 3.17

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

Sample Form	Irradiation Time (h)	Pressure (psi)							
		H <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	Ar	CH <sub>4</sub>	N(CH <sub>3</sub> ) <sub>3</sub>
Cl <sup>-</sup>	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.
OH <sup>-</sup>	50	4	0.20	N.D.	11	N.D.	0.15	0.11	1.18
	100 <sup>b</sup>	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

<sup>a</sup>N.D. = None detected; pressure <0.01 psi.

<sup>b</sup>Correction made for air introduced in sampling.

For Cl<sup>-</sup> form resin, CO<sub>2</sub> is produced with an apparent H<sub>2</sub>:CO<sub>2</sub> ratio of about 5.5:1. Methane formation is also observed. CO<sub>2</sub> 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 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 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<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Ar and CH<sub>4</sub> 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.

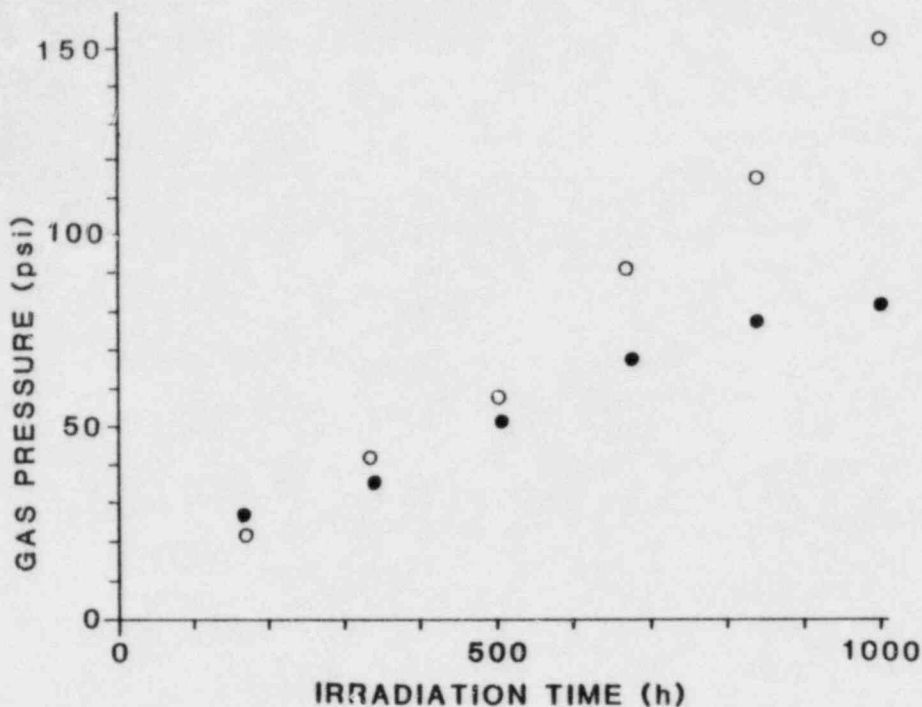


Figure 3.14 Gas generation in IRN-150 resin irradiated at  $1.6 \times 10^6$  rad/h.  
 o = HOH form resin; ● = NaCl form resin.

Table 3.18

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

Sample Form	Irradiation Time (h)	Pressure (psi)						
		H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	CO <sub>2</sub>	CO	CH <sub>4</sub>
NaCl	0 <sup>a</sup>	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
	840 <sup>c</sup>	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
HOH	0 <sup>a</sup>	0.02	2.0	12.6	0.15	N.D.	0.01	N.D.
	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

<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.

<sup>c</sup>Correction made for air introduced in sampling.

As in all previous experiments, hydrogen is the major radiolytic gas generated and oxygen is rapidly scavenged 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:

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

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-Values for Radiolytic Hydrogen Generation

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

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 irradiated 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<sub>2</sub>. In the OH<sup>-</sup> form resin, free CO<sub>2</sub> generation was barely detectable. In the mixed bed system, however, more CO<sub>2</sub> is produced in the HOH form than in the NaCl form. Again, one may speculate that CO<sub>2</sub> 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

Radiolytic Gas Generation for Resins Irradiated in Various Atmospheres

Sample <sup>a</sup> Form	Radiation Dose (Rad)	Gas Composition									
		Before Irradiation <sup>b</sup> (psi)			After Irradiation (psi)						
		Air	He	O <sub>2</sub>	He	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	Ar	CO	CO <sub>2</sub>
(1) IRN-77 (H <sup>+</sup> )	1.3x10 <sup>9</sup>	5.3	9.4		9.4	7.7	0.01	4.2	0.08	0.35	2.2
(3) IRN-77 (H <sup>+</sup> )	8.0x10 <sup>8</sup>	15.0			---b	5.9	0.06	11.6	0.15	.58	1.9
(4) IRN-77 (H <sup>+</sup> )	7.2x10 <sup>8</sup>		15.2		14.9	4.6	0.06	0.47	0.14	0.58	1.1
(5) IRN-77 (H <sup>+</sup> )	8.0x10 <sup>8</sup>	14.7			---	7.1	0.04	11.1	0.13	0.05	2.4
(6) IRN-77 (H <sup>+</sup> )	9.8x10 <sup>8</sup>	14.7			---	4.5	0.02	11.1	0.13	0.17	2.0
(7) IRN-77 (H <sup>+</sup> )	9.6x10 <sup>8</sup>		15.7		15.2	7.9	---	---	---	0.50	1.9
(8) IRN-77 (H <sup>+</sup> )	9.9x10 <sup>8</sup>	6.2	2.4	5.1 <sup>d</sup>	2.4	8.5	---	4.9	0.05	0.67	3.9
(9) IRN-78 (OH <sup>-</sup> )	4.2x10 <sup>8</sup>		4.0	13.5	3.9	13.5	---	---	---	0.23	---
(10) IRN-77 (H <sup>+</sup> )	5.5x10 <sup>8</sup>		1.2	17	1.3	6.7	0.01	0.01	---	0.31	1.3

<sup>a</sup>All samples contained 12 g of fully swollen resin except (6), which contained 6 g.

<sup>b</sup>The gas was not sampled prior to irradiation. Post-irradiation nitrogen analysis indicates air was accidentally introduced in measurements 1 and 8.

<sup>c</sup>--- not detected; pressure <0.01 psi.

<sup>d</sup>The oxygen added to this sample was <sup>18</sup>O<sub>2</sub>. <sup>13</sup>C<sup>18</sup>O<sub>2</sub> was not detected. <sup>12</sup>C<sup>16</sup>O<sup>18</sup>O was present at a partial pressure of 0.3 psi; <sup>12</sup>C<sup>18</sup>O was present at a partial pressure of 0.07 psi.

The data do not indicate any pronounced variation in hydrogen generation in H<sup>+</sup> form resin with atmospheric composition. G-values for H<sub>2</sub> generation in an inert He environment are 0.10±.02; for irradiation in an atmosphere originally containing air, G(H<sub>2</sub>) = 0.12±.02. For samples irradiated in excess oxygen, G(H<sub>2</sub>) = 0.12 for an initial oxygen pressure (air plus added oxygen) of 6 psi and G(H<sub>2</sub>) = 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<sup>+</sup> form resin irradiated in an inert atmosphere showed a release of free liquid, which was not observed for irradiation under oxygen. The maximum free liquid loss was ~.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 oxic conditions. CO<sub>2</sub> formation was studied by isotope doping techniques. In this measurement the initial ratio of <sup>18</sup>O<sub>2</sub> to <sup>16</sup>O<sub>2</sub> in the atmosphere was about 4:1. Following irradiation, the ratio of C<sup>18</sup>O<sub>2</sub> to C<sup>16</sup>O<sub>2</sub> was ~1:10; C<sup>18</sup>O<sub>2</sub> was not detected, and the ratio of C<sup>16,18</sup>O to C<sup>16</sup>O<sub>2</sub> was 1:10. 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).

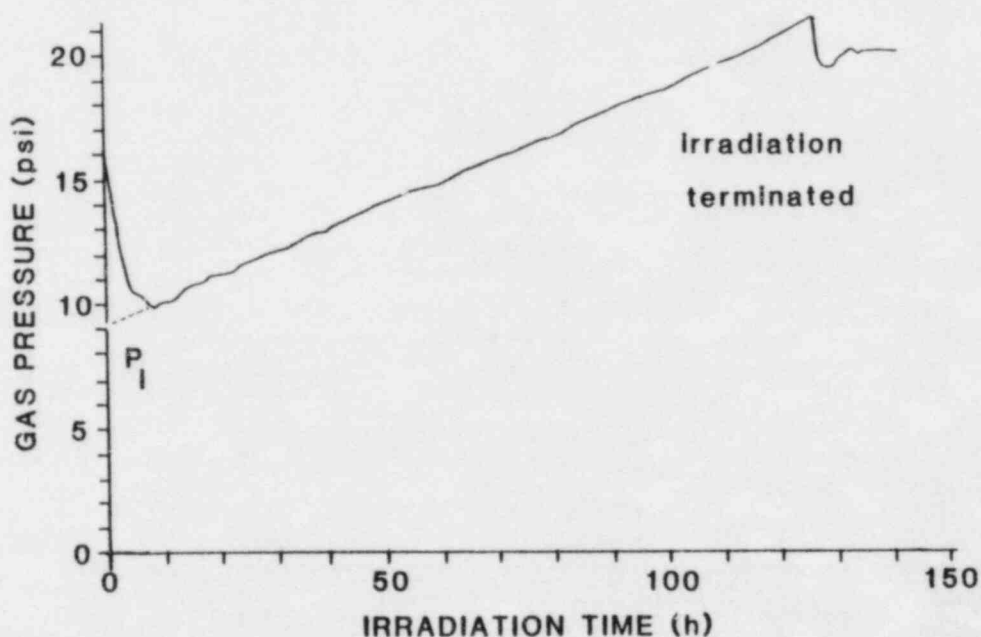


Figure 3.15 Gas pressure over H<sup>+</sup> IRN-77 resin during irradiation at  $8 \times 10^6$  rad/h. The sample originally contained 6.4 psi of O<sub>2</sub>.

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 supported 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. Semilogarithmic 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:

$$\frac{d[O_2]}{dD} = K[O_2] \quad (3.2)$$

Where  $[O_2]$  = amount of oxygen in the gas phase over the irradiated resin sample,  
 $D$  = radiation dose, in rad.

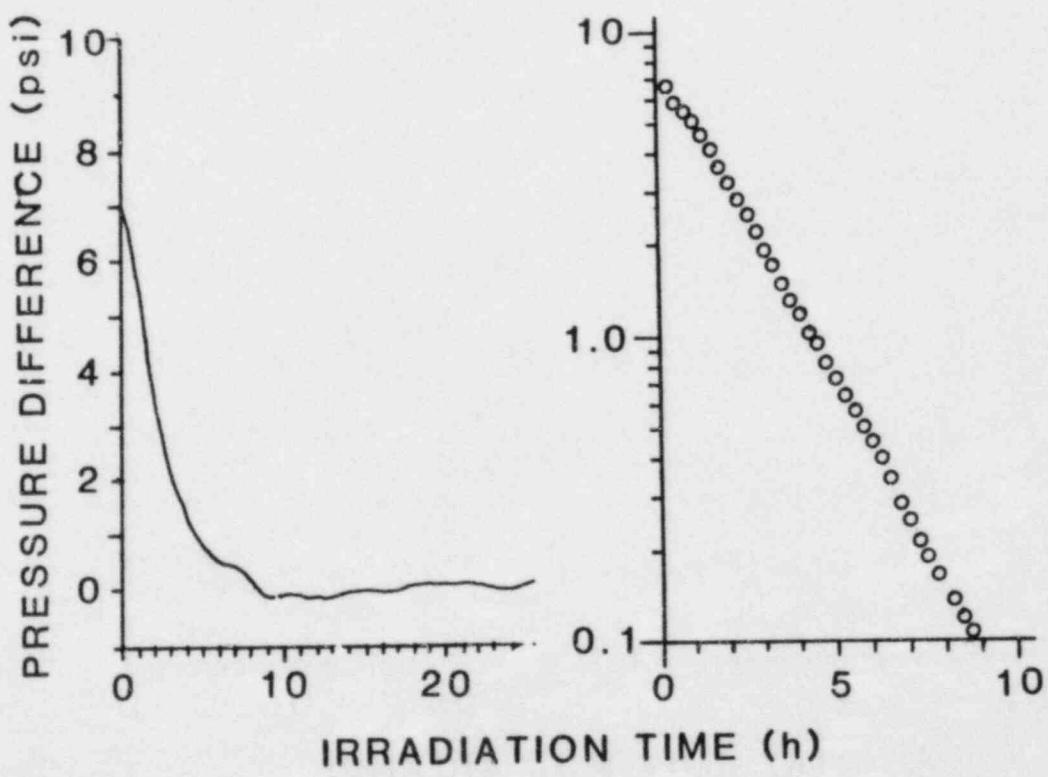


Figure 3.16 Linear (a) and semilogarithmic (b) plots of the difference between the data and the fitted straight line in Figure 3.14.

For the experimental conditions of measurement 8,  $K = 6.4 \times 10^{-8}$   $\text{rad}^{-1}$ , corresponding to an uptake of 90% of the available oxygen by 12 g of resin after a dose of  $\sim 3.0 \times 10^7$  rad. The maximum oxygen uptake observed in these experiments was  $\sim 3.01 \times 10^{-3}$  moles, (measurement No. 10) at a dose of  $3 \times 10^7$  rad in 12 g of resin. There are approximately  $3 \times 10^{-1}$  moles of carbon (and  $3 \times 10^{-2}$  moles of  $-\text{SO}_3\text{H}$ ) in 12 g of fully swollen resin. If the oxygen scavenging involves only attack at the carbon atoms, a maximum  $\sim 1\%$  of the available carbon atoms are oxidized 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  $\text{CO}_2$  data. Mohoric and Kramer (1968) have also observed  $\text{CO}_2$  evolution for resin samples irradiated in evacuated vessels. The ratio of  $\text{H}_2$  to  $\text{CO}_2$  in their experiments ( $\sim 4:1$ ) is roughly similar to that in the present experiments. Extensive oxidation might contribute to agglomeration of resins irradiated in open systems.\* 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  $4 \times 10^4$  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 unirradiated resin did not consistently produce a freestanding product (Manaktala and Weiss, 1980).

A number of small cylindrical (2-in. diameter x 4-in. long) resin-cement forms were cast from irradiated ( $9 \times 10^8$  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 soaked for 28 days in deionized water at

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\*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 ~53% before mixing. Test conditions and results to date are shown in Table 3.21.

Table 3.21  
Compression Test Data on Resin-Cement Waste Forms

Formulation	Waste/ Cement +Water	Swollen Resin (g)	Water (g)	Portland Cement (g)	Resin Condition	Compressive Strength (psi)
1	0.07	13.8	55.0	137.5	R <sup>a</sup>	} 2.7 x 10 <sup>3</sup>
		-	-	-	R	
		-	-	-	R	
2	0.14	27.5	55.0	137.5	NR <sup>b</sup>	} (2.1 ± 0.4) x 10 <sup>3</sup>
		-	-	-	NR	
		-	-	-	NR	
		-	-	-	R	} (2.2 ± 0.1) x 10 <sup>3</sup>
		-	-	-	R	
		-	-	-	R	
3	0.29	48.9	48.9	122.5	NR	} F <sup>c</sup>
		-	-	-	NR	
		-	-	-	NR	
		-	-	-	R	} 1.5 x 10 <sup>3</sup>
		-	-	-	R	
		-	-	-	R	
4	0.39	66.0	48.9	122.5	R	} 1.1 x 10 <sup>3</sup>
		-	-	-	R	
		-	-	-	R	

<sup>a</sup>R = Resin irradiated prior to solidification.

<sup>b</sup>NR = Unirradiated resin.

<sup>c</sup>F = 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.

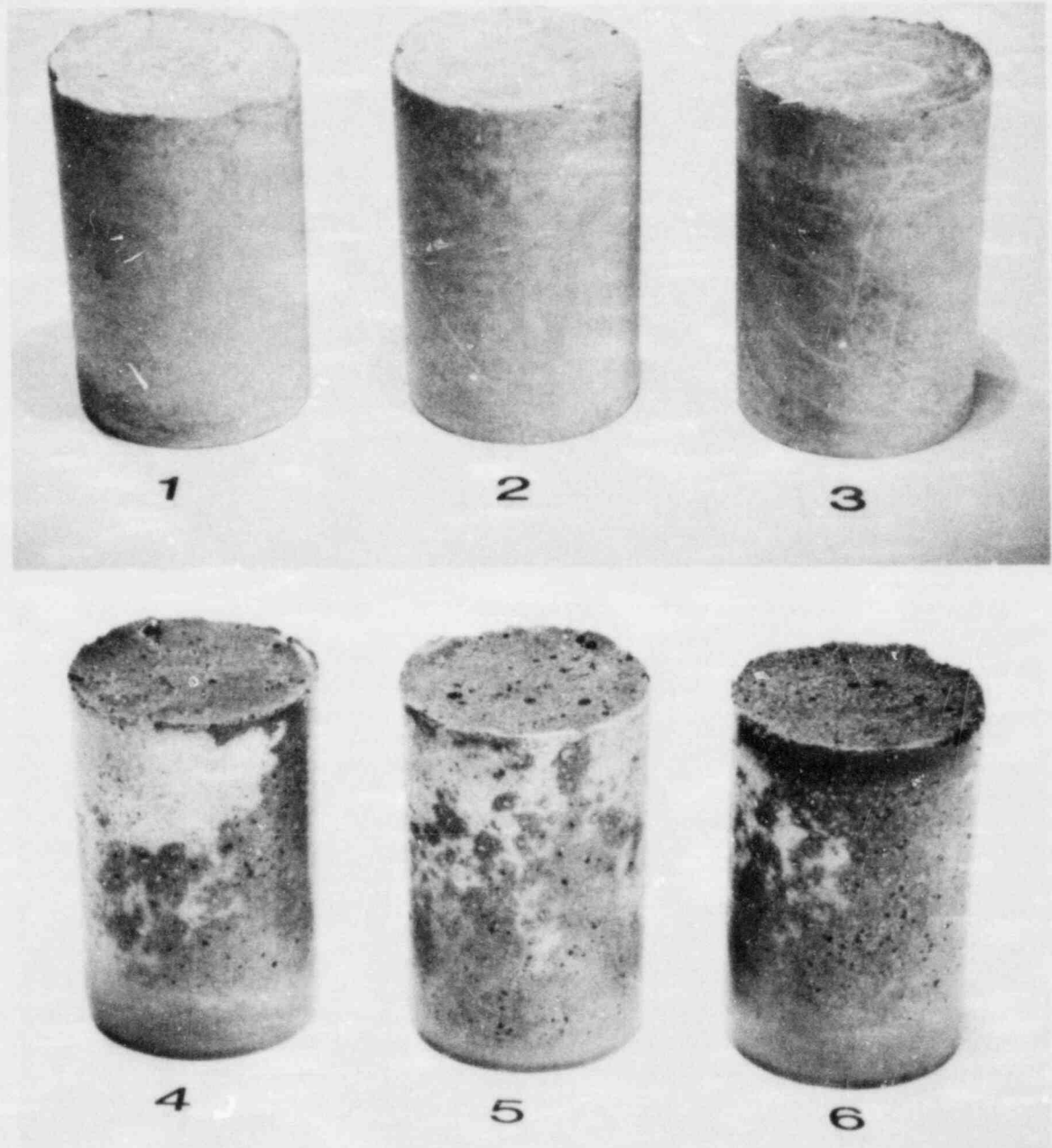


Figure 3.17 Resin-cement forms made with irradiated (upper) and unirradiated (lower) resin after soaking for 28 days in deionized water.

### 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 ( $\text{Na}^+$  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  $^{137}\text{Cs}$  and  $^{85}\text{Sr}$  as radiotracers. For forms incorporating irradiated resin, the spiked resin was irradiated to  $9 \times 10^8$  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.

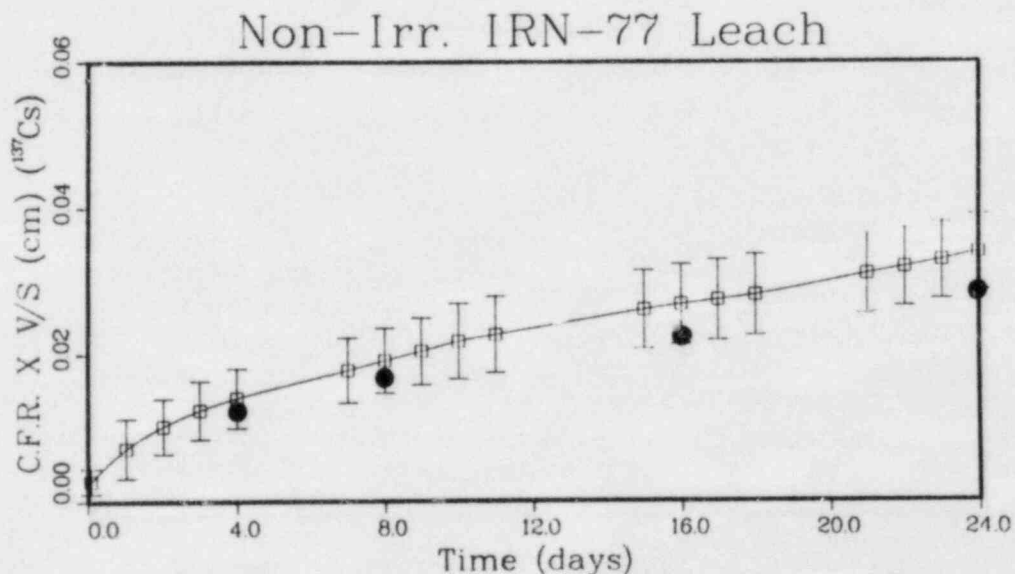


Figure 3.18 Cumulative fractional cesium release from 2 in. x 2 in. resin-cement composite made with unirradiated resin. V/S = volume-to-surface ratio = 0.85 cm. ● = data for similar forms from "scale-up" study of Dayal et al. (1983).

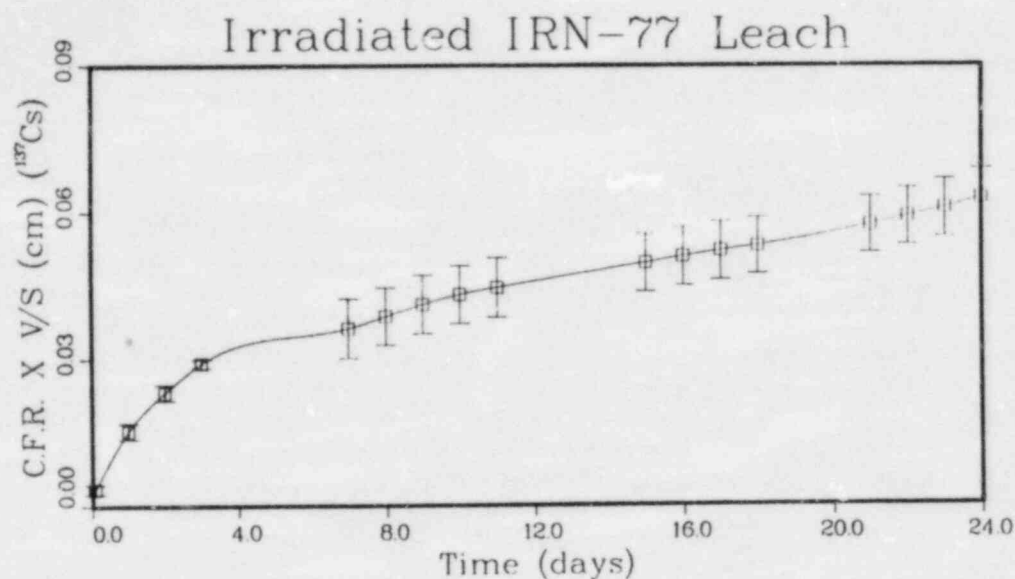


Figure 3.19 Cumulative fractional cesium release from 2 in. x 2 in. resin-cement composite made with resin exposed to  $9 \times 10^8$  rad.  $V/S = 0.85$  cm.

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 ( $10^9$  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

Swelling Force Exerted by Irradiated IRN-77 Resin

Resin Form	Irradiation Dose (rad)	Irradiation Environment	Swelling Pressure <sup>a</sup> (psi)
H+	0	----	335 + 43
H+	$2.4 \times 10^5$	sealed	208
H+	$4.5 \times 10^8$	sealed	278 + 60
H+	$1 \times 10^9$	sealed	21 + 4
H+	$1 \times 10^9$	vented	8 + 3
Na+	0	----	257 + 4
Na+	$1 \times 10^5$	sealed	218 + 1
Na+	$7.5 \times 10^8$	sealed	143 + 41
Na+	$1 \times 10^9$	sealed	33 + 1
Na+	$1 \times 10^9$	vented	14 + 6

<sup>a</sup>Pressure exerted against a 0.5 in.-diam piston upon rewetting the dried resin in a fixed volume.

The somewhat precipitous decrease in swelling force between  $\sim 7 \times 10^8$  and  $1 \times 10^9$  rad may be due to somewhat different experimental conditions - samples irradiated to  $10^9$  rad were exposed to different radiation dose rates and resin-oxygen ratios than those at lower doses. Samples irradiated under vented conditions (i.e., exposed to atmospheric  $O_2$ ) 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.

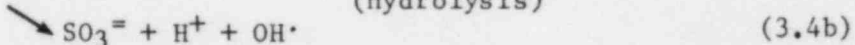
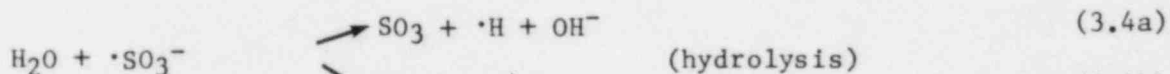
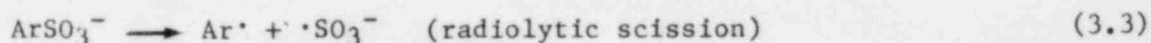
### 3.3 Mechanistic Studies

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.

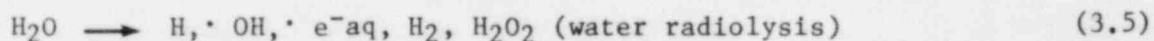
#### 3.3.1 Radiolytic Degradation Mechanisms

Several physically distinct processes may act to produce overall radiolytic scission of the functional group. Proposed mechanisms fall into three classes, as described in the literature (Karpukhina et al., 1976; Hall and Streat, 1963; Tulupov et al., 1973; Ichikawa and Hagiwara, 1973). These are illustrated below for sulfonic acid cation resin.

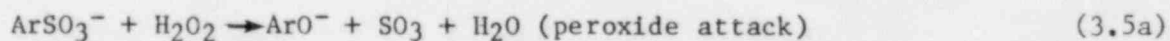
- I. Direct radiolytic scission of the functional group, possibly followed by free radical hydrolysis:



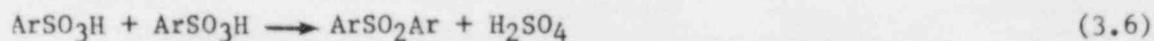
- II. Attack on the functional group by aqueous radiolysis products:



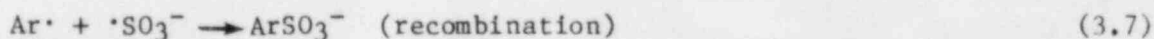
possible subsequent processes: e.g.,



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



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



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  $\text{SO}_3^-$  group to  $\text{SO}_4^-$ , which is observed in solution. For Class (I) reactions, the oxidation could occur, for example, via



A number of agents might oxidize the sulfite ion in solution. In any event, for loadings other than  $\text{H}^+$ , the bisulfate salt (e.g.,  $\text{NaHSO}_4$ ) would then result. The bisulfate salt solution can of course be considered an acidic mixture of  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ . On the other hand, in a Class III process, redox considerations do not require that  $\text{H}^+$  is produced in the oxidation of  $\text{SO}_3^-$  to  $\text{SO}_4^-$ . One functional group is oxidized and another simultaneously reduced. In this case, no acidity accompanies functional group scission for loadings other than  $\text{H}^+$ . Only pure salts are produced and conversion from the  $\text{H}^+$  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  $\text{H}^+$  form resin were contacted with 50-mL solutions of 10, 1,  $10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ , and  $10^{-5}$  M  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  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.

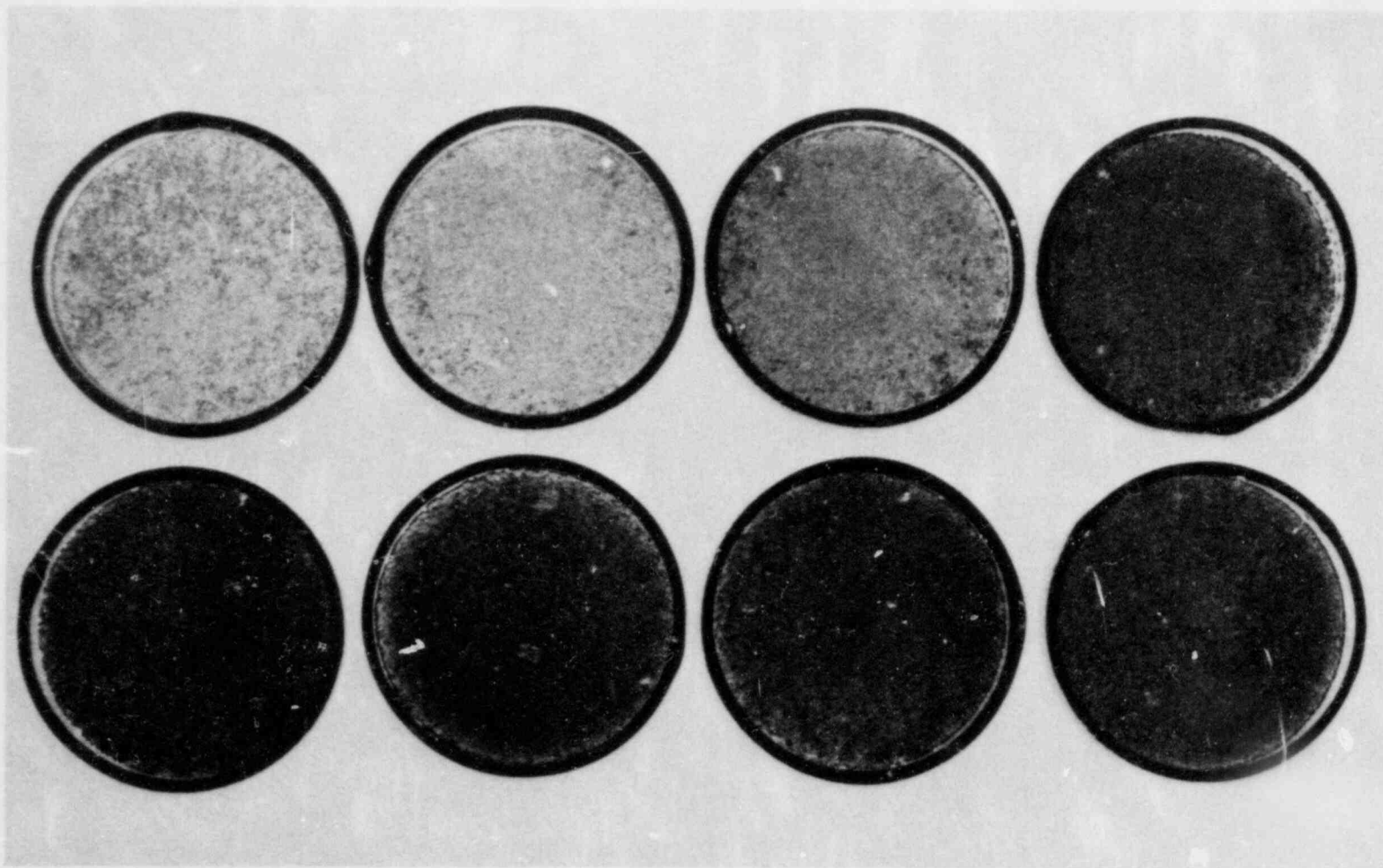


Figure 3.20 IRN-77 resin in various  $H_2O_2$  solutions (5.0 g resin/50.0-mL  $H_2O_2$  solution).  
Top (left to right): 10 M, 1 M,  $1 \times 10^{-1}$  M,  $1 \times 10^{-2}$  M  $H_2O_2$ . Bottom (left to right):  $1 \times 10^{-3}$  M,  $1 \times 10^{-4}$  M,  $1 \times 10^{-5}$  M  $H_2O_2$ , and deionized water only.

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

pH and Sulfate Content of Peroxide-Resin Solutions

(H <sub>2</sub> O <sub>2</sub> ) <sup>a</sup> Moles/L	pH			(SO <sub>4</sub> <sup>2-</sup> ) Moles/L			SO <sub>4</sub> <sup>2-</sup> Yield Moles/g Resin		
	Day 1	Day 22	Day 45	Day 1	Day 22	Day 45	Day 1	Day 22	Day 45
0	3.4	3.4	3.1	3.8x10 <sup>-5</sup>	5.7x10 <sup>-5</sup>	8.0x 10 <sup>-7</sup>	1.5x10 <sup>-7</sup>	2.3x10 <sup>-7</sup>	3.2x10 <sup>-7</sup>
8.8x10 <sup>-6</sup>	3.4	3.3	3.2	4.1x10 <sup>-5</sup>	5.0x10 <sup>-5</sup>	5.4x10 <sup>-5</sup>	1.6x10 <sup>-7</sup>	2.0x10 <sup>-7</sup>	2.2x10 <sup>-7</sup>
8.8x10 <sup>-5</sup>	3.6	3.1	3.0	4.0x10 <sup>-5</sup>	6.3x10 <sup>-5</sup>	1.1x10 <sup>-4</sup>	1.6x10 <sup>-7</sup>	2.5x10 <sup>-7</sup>	4.4x10 <sup>-7</sup>
8.8x10 <sup>-4</sup>	3.4	2.9	2.7	3.7x10 <sup>-5</sup>	1.2x10 <sup>-4</sup>	1.5x10 <sup>-4</sup>	1.5x10 <sup>-7</sup>	4.8x10 <sup>-7</sup>	6.0x10 <sup>-7</sup>
8.8x10 <sup>-3</sup>	3.4	2.7	2.5	5.4x10 <sup>-5</sup>	3.3x10 <sup>-4</sup>	5.1x10 <sup>-4</sup>	2.2x10 <sup>-7</sup>	1.3x10 <sup>-6</sup>	2.0x10 <sup>-6</sup>
8.8x10 <sup>-2</sup>	3.6	2.7	2.4	6.1x10 <sup>-5</sup>	4.8x10 <sup>-4</sup>	7.5x10 <sup>-4</sup>	2.4x10 <sup>-7</sup>	1.9x10 <sup>-6</sup>	3.0x10 <sup>-6</sup>
8.8x10 <sup>-1</sup>	3.3	2.7	2.6	7.4x10 <sup>-5</sup>	3.9x10 <sup>-4</sup>	7.8x10 <sup>-4</sup>	3.0x10 <sup>-7</sup>	1.6x10 <sup>-6</sup>	3.1x10 <sup>-6</sup>
8.8	2.5	1.7	1.5	2.5x10 <sup>-4</sup>	1.5x10 <sup>-3</sup>	7.9x10 <sup>-3</sup>	1.0x10 <sup>-6</sup>	6.0x10 <sup>-6</sup>	1.2x10 <sup>-5</sup>

<sup>a</sup>Samples made from 5 g of IRN-77 fully-swollen resin plus 20 mL of peroxide solution.

Peroxide reacts with the resin to form acidic species and free sulfate. The pH values for the greatest H<sub>2</sub>O<sub>2</sub> concentrations (~10 molar) approach those found in heavily irradiated samples. The correlation between SO<sub>4</sub><sup>2-</sup> ion concentration and pH, however, is quite different from that found in the supernate irradiated samples. Free SO<sub>4</sub><sup>2-</sup> 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 SO<sub>4</sub><sup>2-</sup> increases with increasing irradiation time; the pH and SO<sub>4</sub><sup>2-</sup> yields are sensibly independent of H<sub>2</sub>O<sub>2</sub> concentration. The SO<sub>4</sub><sup>2-</sup> yields per gram of swollen resin irradiated in the peroxide solutions are comparable to those found for resins irradiated in the swollen form at corresponding doses. The



pH values are comparable to those found earlier for resins irradiated in de-ionized water (allowing for the difference in resin-water ratios). Accordingly, in the present experiments, any effect of added  $H_2O_2$  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

pH and Sulfate Content of Irradiated and Unirradiated Resin-Peroxide Solutions<sup>a</sup>

Irradiation Dose Rate (rad/h)	Supernatant Initial ( $H_2O_2$ ) (moles/L)	pH		( $SO_4^{2-}$ ) (moles/L)		$SO_4^{2-}$ Yield (moles/g resin)	
		day 10	day 20	day 10	day 20	day 10	day 20
		0	0	3.8	3.2	$2.4 \times 10^{-5}$	$5.3 \times 10^{-4}$
0	$8 \times 10^{-3}$	3.0	N.M.	$2.3 \times 10^{-4}$	$3.7 \times 10^{-4}$	$4.0 \times 10^{-7}$	$6.1 \times 10^{-7}$
0	8.8	2.8	2.5	$5.1 \times 10^{-4}$	$1.1 \times 10^{-3}$	$8.7 \times 10^{-7}$	$1.9 \times 10^{-6}$
$1.5 \times 10^6$	0	0.83	0.66	0.18	0.32	$3.0 \times 10^{-4}$	$5.5 \times 10^{-3}$
$1.5 \times 10^6$	$8 \times 10^{-3}$	0.92	0.64	0.15	0.31	$2.5 \times 10^{-4}$	$5.0 \times 10^{-3}$
$1.5 \times 10^6$	8.8	0.85	<0.6	0.18	0.31	$3.0 \times 10^{-4}$	$5.0 \times 10^{-3}$

Solution = 5 mL of  $H_2O_2$  solution contacted with 3-g fully-swollen IRN-77 resin and then held as control samples or irradiated for the times indicated.

<sup>a</sup>N.M. = not measured.

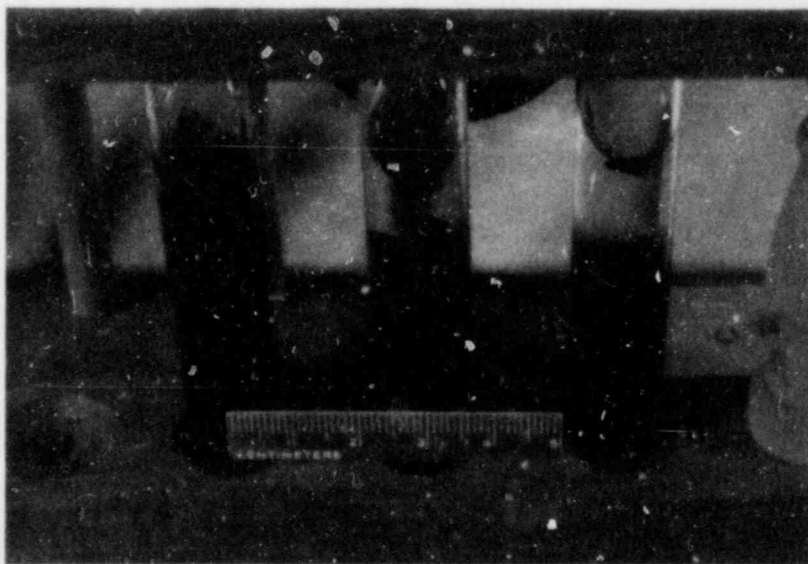
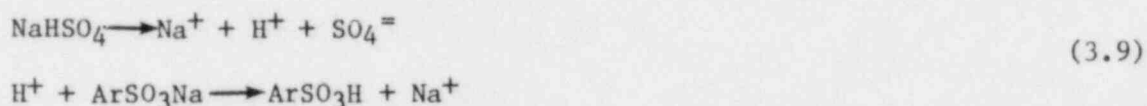


Figure 3.21 IRN-77 resin irradiated in  $H_2O_2$  solutions.  
 Left: resin + 8 M  $H_2O_2$ ; center - resin + 0.008 M  $H_2O_2$ ; right - resin + deionized water.

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  $\text{NaHSO}_4$ , 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:



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

To determine if this mechanism is plausible, measurements first were carried out to investigate the ability of  $\text{Na}^+$  form resin to take up  $\text{H}^+$  from  $\text{NaHSO}_4$  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  $\text{H}^+$  is contained in the resin. A weaker acid is also present in solution and ~2% of the sites in unirradiated resin were in  $\text{H}^+$  form. The residual  $\text{H}^+$  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  $\text{NaHSO}_4$  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  $\text{NaHSO}_4$  formation.

Table 3.25

pH Elevation of NaHSO<sub>4</sub> Solutions (10 mL) by  
Sodium Form IRN-77 Resin (2 g)

NaHSO <sub>4</sub> 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	3.7	3.4	2.3	2.0	1.6

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

Table 3.26

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

Radiation Dose (rad)	Supernate <sup>a</sup> pH		meq H <sup>+</sup> /g Resin		
			Supernate		Resin
	Fresh	Aged <sup>b</sup>	Calculated <sup>c</sup>	Titrated	Titrated
0	5.00	4.00	.005	0.037	0.05
4.7 x 10 <sup>7</sup>	4.10	4.18	.003	0.009	0.06
1.0 x 10 <sup>8</sup>	3.65	3.83	.007	0.020	0.10
1.7 x 10 <sup>9</sup>	2.75	2.82	.083	0.160	0.19

<sup>a</sup>2-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 SO<sub>4</sub><sup>=</sup> produced. For Class III processes, exchange capacity decreases by two equivalents per mole of SO<sub>4</sub><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.

Table 3.27

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

Resin Type	Irradiation Dose Rate rad/h	Irradiation Dose (rad)	% Moisture	Total Exchange Capacity (meq/g dry resin)
H <sup>+</sup> with coupon	0	0	54.6	5.83
	0	0	56.7	5.94
	4 x10 <sup>4</sup>	2.0x10 <sup>7</sup>	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 coupon	0	0	55.2	5.53
	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>	4.8x10 <sup>7</sup>	55.0	5.46
	1 x10 <sup>5</sup>	9.9x10 <sup>7</sup>	55.2	5.42
	1.6x10 <sup>6</sup>	8.0x10 <sup>8</sup>	55.4	4.93
	1.6x10 <sup>6</sup>	1.6x10 <sup>9</sup>	51.8	4.45
Na <sup>+</sup>	0	0	55.4	5.49
	0	0	55.0	5.50
	4 x10 <sup>4</sup>	2.2x10 <sup>7</sup>	55.5	5.67
	4 x10 <sup>4</sup>	4.2x10 <sup>7</sup>	55.6	5.42
	1 x10 <sup>5</sup>	5.5x10 <sup>7</sup>	57.8	5.66
	1 x10 <sup>5</sup>	8.8x10 <sup>7</sup>	56.5	5.56
	1.6x10 <sup>6</sup>	9.1x10 <sup>8</sup>	56.0	5.47
	1.6x10 <sup>6</sup>	1.7x10 <sup>9</sup>	52.2	4.90

<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 SO<sub>4</sub><sup>=</sup> 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  $H^+$ .

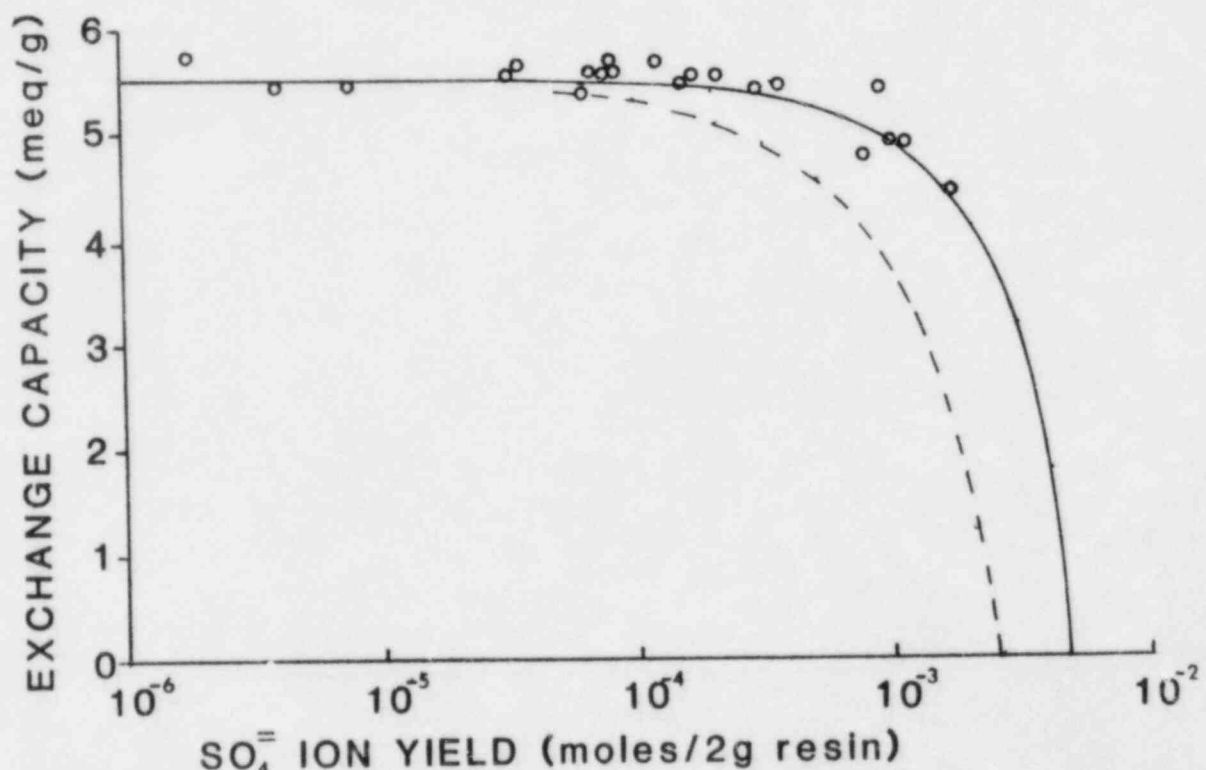


Figure 3.22 Cation exchange capacity vs soluble sulfate supernate yields for irradiated IRN-77 resin. Solid line: Hypothetical curve assuming 1 mmol of  $SO_4^{=}$  represents a decrease in total exchange capacity of 1 meq. (class I or II process), dashed line: hypothetical curve assuming 1 mmol of  $SO_4^{=}$  represents a decrease in total exchange capacity of 2 meq (class III process).

#### 4. CONCLUSIONS AND SUMMARY

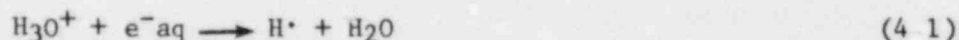
At this point, it is possible to qualitatively interpret certain features of the experimental results. Conclusions are discussed in Sections 4.1 and 4.2. The practical consequences of this work are summarized in Section 4.3.

##### 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,

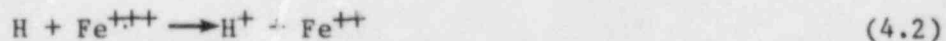
(1) The lack of pH dependence (Section 3) argues against a significant role for e<sup>-</sup><sub>aq</sub>, since the hydrated electron would be scavenged by the reaction



(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<sup>•</sup> and OH<sup>•</sup> 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 scavenger for OH<sup>•</sup>; this suggests that OH<sup>•</sup> 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



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 <sup>•</sup>SO<sub>3</sub><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  $H_2SO_4$  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  $H^+$  and  $Na^+$  form sulfonic acid resin, sulfate yields in the supernate at first increase in a roughly linear manner with increasing irradiation dose. For higher doses ( $>5 \times 10^8$  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 correspondence 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):

$$\frac{dE}{dD} = -k_1 E \quad (4.3)$$

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):

$$\frac{dE}{dD} = -k_2 E^2 \quad (4.4)$$

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

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

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

$$S = S_{\infty} \left( \frac{k_2 D E_0}{k_2 D E_0 + 1} \right) \quad (4.6)$$

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  $\sim 10^9$  rad, this distinction is not pronounced. The sulfate release is practically linear with doses up to  $\sim 5 \times 10^8$  rad.

• For dry sulfonic acid resins, the principal mechanism for radiolytic scission 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  $\cdot SO_3^-$ . However, for resin loadings other than  $H^+$ , Class (III) reactions, if they occur, would be expected to produce only pure salts (e.g.,  $Na_2SO_4$ ). A definite pH decrease was in fact observed



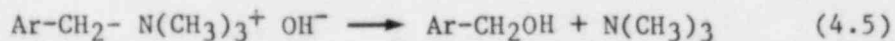
for irradiated oven-dry resins in the Na<sup>+</sup> form. Still, we believe with the Russian workers (Tupulov and Butaev, 1980) that Class (III) reactions become more favored at low moisture content.

- 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 radiolytic 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.\*

- 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:



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

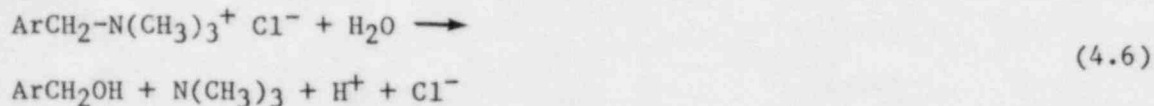
In our experiments, trimethylamine is observed in the gas phase for irradiated OH<sup>-</sup> form anion resins. For resins in the Cl<sup>-</sup> form, and for HOH and NaCl form mixed bed resin, trimethylamine was not observed as a gas. This may reflect either a change in decomposition mechanism or,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

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

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\*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  $\text{OH}^-$  form resin. The irradiated  $\text{Cl}^-$  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:

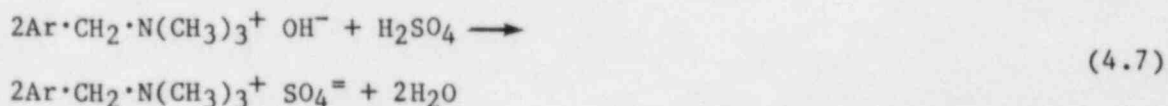


The result of Eq. 4.6 would be a solution of trimethylammonium chloride.

- 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  $\text{Na}^+$  form yields acidic species, while the  $\text{Cl}^-$  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  $\text{H}^+$  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  $e^-_{\text{aq}}$  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  $\text{OH}^-$  form anion resin, e.g.,



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.,  $\text{HN(CH}_3)_3^+ + \text{OH}^-$ ) and a strong acid ( $\text{H}_2\text{SO}_4$ ). 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.

- 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 probably analogous to the liquid release observed in our experiments. Several possible mechanisms could account for this effect.

#### 4.2 Radiolytic Gas Generation

- In sulfonic acid resin  $G(H_2)$  values for hydrogen generation in fully-swollen resins are somewhat lower than expected on the basis of pore water radiolysis:

$G(H_2)$  for pure water is  $\sim 0.45$  (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  $H^+$  form resin,  $G(H_2)$  is  $\sim 0.13$  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 scavenge species (e.g., OH) which back-react with  $H_2$  to limit saturation pressures in pure water radiolysis. At the same time, if most of the hydrogen is due to water radiolysis, some mechanisms must act to reduce the G-value. In tritiated water experiments, Mohorcic et al. (1974) have found that H atom is taken up by fully swollen Dowex resin with a G-value of 0.52. 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,  $G(H_2)$  is substantially greater than in cation resins:

The G-value for  $OH^-$  resin is significantly larger than for  $Cl^-$  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  $H_2$  yield in  $Cl^-$  and  $OH^-$  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  $CO_2$  generation, may also occur in closed systems involving oxygen present in the

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\*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  $\text{SO}_3^-$  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  $\sim 10^8$  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 ( $\text{pH} < 2$ ) in aqueous solutions of irradiated resins, leading to a potentially corrosive environment.
  - (b) Release of sulfate ion and/or  $\text{SO}_2$  gas. Sulfate ion may interact with solidification agents while  $\text{SO}_2$  is a corrosive gas in moist environment.
  - (c) Loss of ion-exchange capacity, with the accompanying release of exchangeable 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  $\text{H}^+$  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 sulfonic 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  $H^+$  ion is exchanged for cation at undamaged resin sites. Second, some of the sulfate may be produced by a mechanism in which  $H^+$  ion is not generated in the oxidation of  $-SO_3^-$  to  $SO_4^{=}$ . 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  $H^+$  form would protect the resin against radiolytic sulfuric acid formation, unless substantial residual  $H^+$  remains in the resin after conversion. In any event, the acidity is substantially reduced for loadings other than  $H^+$ . 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  $2ArSO_3^- \rightarrow Ar-SO_2-Ar + SO_4^{=}$  with the formation of a sulfone cross-link -- one functional group is oxidized and the other reduced.
- For doses in excess of  $\sim 3 \times 10^8$  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  $OH^-$  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 radio-nuclides 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 ( $\sim 1.2 \times 10^{-6}$  moles  $H_2$  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  $\sim 0.5$  atmospheres. For anion resin, the  $H_2$  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 scavenging 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 resin will take up  $\sim 20\%$  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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