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CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS*

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ABSTRACT

Self-irradiation from sorbed radionuclides may affect properties of radwaste containing organic ion-exchange resins. Effects of gamma irradiation on cation (Amberlite IRN-77**), anion (Amberlite IRN-78**) and mixed bed (Amberlite IRN-150**) resins have been studied under conditions relevant to radwaste management. Sulfate ion is produced by the radiolytic scission of the cation resin functional group. Sulfate yields are not strongly dependent on pH conditions, resin chemical loading, or radiation dose rate, although radiation damage is reduced in dried resins. Acidity resulting from a given sulfate yield does depend on resin counter-ion loading; mechanisms are considered. In particular for heavy irradiation doses, use of cation and anion resin in a mixed bed does not prevent radiolytic acid formation. Irradiated anion resin may also release free liquid. The significance of these and other radiolysis effects in radwaste generated under off-normal conditions is discussed.

INTRODUCTION

In off normal reactor operations, ion exchange media may become heavily loaded with long-lived radionuclides. Consequently, the media may receive substantial doses of self-irradiation. Several 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.(1-4) However, little information is available to assess the practical consequences of radiation effects under actual storage and disposal conditions, including the presence of high-integrity container components and solidification agents. The present program is investigating how the properties of wastes containing organic ion-exchange media may be modified by heavy doses of internal radiation from sorbed nuclides. The object is

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to establish both guidelines and test procedures for assessing behavior under field conditions. The program involves four distinct areas of investigation:

- A parametric laboratory study of radiolysis effects (formation of acidic species, gas generation, agglomeration, counter-ion release, etc.) in organic ion-exchange media.
- A laboratory study of radiation effects on resin/container systems (e.g. irradiation enhanced corrosion) and resin solidification properties.
- An assessment of available field experience with heavily loaded ion exchange media (such as the Epicor-II liner studies carried out by Battelle Columbus Laboratory^(5,6) and our own investigations of this material).
- Mechanistic studies to support the development of test procedures for evaluating radiation effects in regulatory applications. Here, experimental information on radiation damage mechanisms (such as the role of peroxides in radiolytic resin degradation or the connection between functional group scission and loss of exchange capacity) will be generated. This will then be combined with results obtained in the areas mentioned above to consider what test procedures will provide the most useful assessment of radiation effects for regulatory applications.

Work in the first two areas is largely completed. Data analysis is continuing in the later two activities. Illustrative results are presented below.

Soluble Radiolysis Products and Acid Formation

Initial experiments were carried out with sulfonic acid cation resins (Amberlite IRN-77), quarternary ammonium anion resin (Amberlite IRN-78) and a mixed bed combination of the two (Amberlite IRN-150). These resins were chosen as typical of those used in the nuclear industry. IRN-77 contains sulfonic acid functional groups ($-SO_3^-$) and a polystyrene-divinyl benzene polymer backbone. IRN-78 contains quaternary ammonium ($-CH_2-N(CH_3)_3^+$) functional groups and the same backbone.

Strongly acidic conditions result from the irradiation of sulfonic acid resins. Acid formation is shown in Figure 1 for resins with both H^+ and Na^+ counter-ion loadings. pH values were measured in the supernate of 10 mL of deionized water contacted with 2 g of fully swollen (~50% moisture content) resins after the resin had been irradiated in a closed system.

Acidity is due to radiolytic scission of the $-SO_3^-$ functional group. In fully swollen IRN-77 resin, the scission products are largely oxidized to SO_4^{2-} . Attack on the functional group, as determined by sulfate yield, is largely insensitive to factors such as pH, sodium vs hydrogen loading and radiation dose rate (Figure 2).

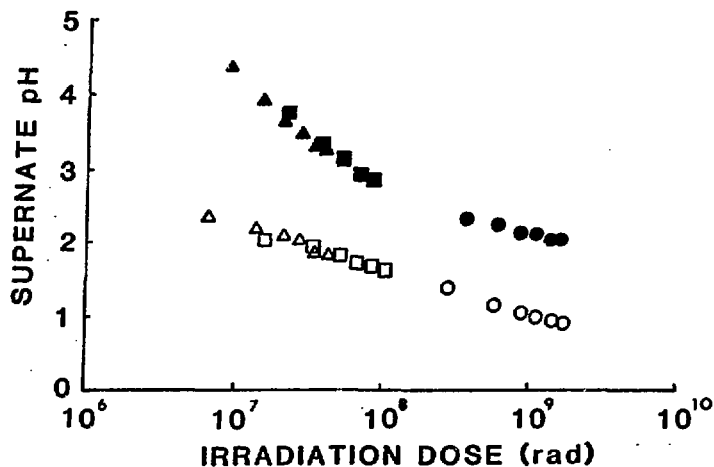


Figure 1. Supernate pH vs irradiation dose rate for irradiated H^+ (open points) and Na^+ form (solid points) resin. Dose rates (rad/h): o - 1.7×10^6 ; ■ - 1×10^5 ; ▲ - 4×10^4 .

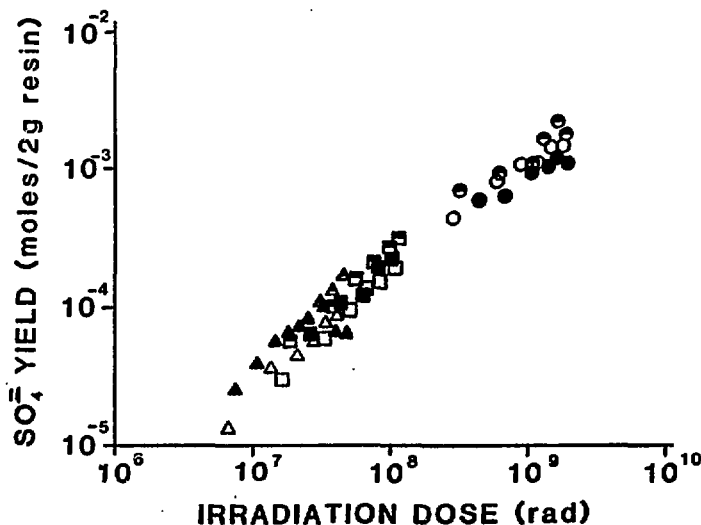


Figure 2. Soluble sulfate generation vs irradiation dose for fully-swollen IRN-77 H^+ form resin (open points) without corrosion coupons, and Na^+ form resin with (solid points) and without (half open points) corrosion coupons. Dose rates (rad/h): o - 1.7×10^6 ; ■ - 1×10^5 ; ▲ - 4×10^4 .

In fully-swollen resin, based on sulfate data, each 10 megarads of absorbed dose results in the scission of $\sim 0.3\%$ of the available exchange sites. The sulfate is most probably produced by direct radiolytic scission and subsequent hydrolysis of the radical products. Reducing the moisture

content from 50 to 5% protects the resin--radiolytic sulfate yields are reduced by 75%.

The amount of acidity resulting from a given sulfate yield depends on the resin loading. For H^+ resin, the sulfate ion forms almost pure sulfuric acid (Figure 3a). For resin in other forms the sulfate ion is present as a mixture of sulfuric acid and sulfate salts of the counter ion: although for Na^+ form resin, the resin is less acidic than would be expected on the basis of bisulfate salt formations such as $NaHSO_4$.⁽⁷⁾ See Figure 3b.

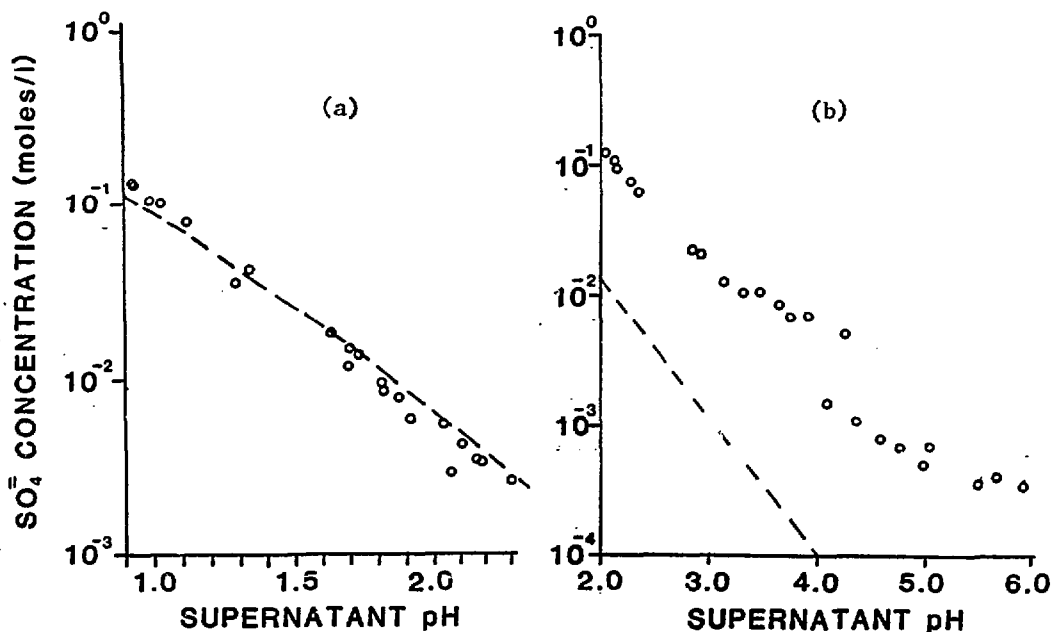


Figure 3. Correlation of supernatant pH with sulfate yield in the supernate of irradiated sulfonic acid resins. (a) H^+ form resin. The dashed line indicates the behavior expected for $SO_3^- H^+ \rightarrow H_2SO_4$. (b) Na^+ form resins. The dashed line indicates the behavior expected for $SO_3^- Na^+ \rightarrow NaHSO_4$.

The reduced acidity in Na^+ form resin (relative to bisulfate salt formation) may be attributed to a protective ion-exchange effect in which H^+ is exchanged for Na^+ at some undamaged ion-exchange sites. The mechanism apparently operates for other counter-ions as well. Also, 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, which may be favored in dry resins, the oxygen could 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 completely protect the resin against radiolytic sulfuric acid formation, unless 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.

IRN-78 anion resins in the OH^- form become increasingly basic upon irradiation. In the Cl^- form, the resins remain nearly neutral upon irradiation. In both cases, the fully swollen resins release free liquid upon irradiation to a dose of $\geq 3 \times 10^8$ rad. (Figure 4.)

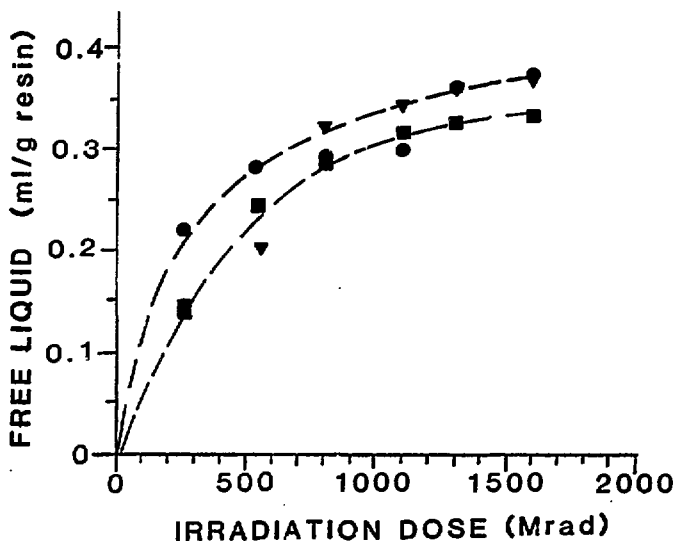


Figure 4. Free liquid release in irradiated IRN-78 and IRN-150 resin.

For Cl^- form resin, analysis of resin-water mixtures and free liquid for chloride release indicate that the resin has largely lost its functionality after a dose of $\sim 3 \times 10^8$ rad - the quarternary ammonium anion functional group is much more readily attacked than the sulfonic acid functional group.

Use of IRN-77 and IRN-78 resins in the mixed bed form did not prevent formation of acidic conditions radiation (Figure 5).

Partial neutralization has occurred in the IRN-150 HOH^- form resin. The acidity probably reflects the equilibrium between a strong acid (H_2SO_4) and a weak base such as trimethyl ammonium hydroxide. Since, at these doses, the anion resins has largely lost its functionality, acidity cannot be neutralized by the exchange of radiolytic SO_4^{2-} for OH^- on the anion component.⁽⁸⁾ The $NaCl$ form mixed bed, also became strongly acidic for heavy irradiation doses. Solution analysis suggests that positive ions (e.g., trimethyl ammonium) released in the decomposition of the anion resin functional group may promote the release of positive ions (including radionuclides) sorbed on the cation resins: in the mixed bed $NaCl$ form resin, nearly all the sodium ion was released to solution, although the cation component had not lost its functionality.

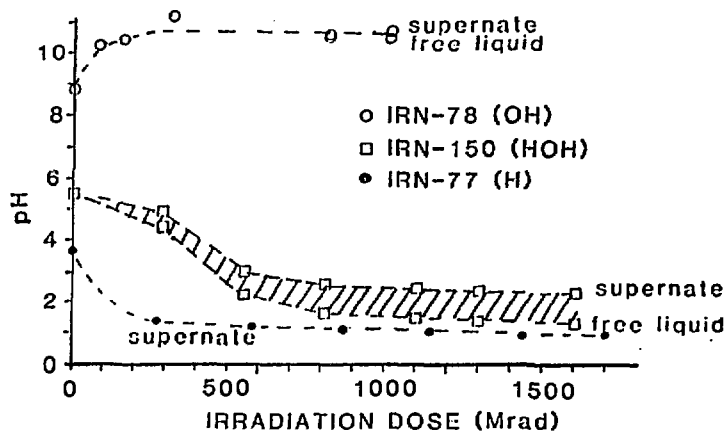


Figure 5. pH vs irradiation dose for irradiated IRN-77, IRN-78 and IRN-150 resins.

Radiolytic Gas Generation

Hydrogen is the principal gas generated on irradiation of cation, anion and mixed bed resins. Hydrogen generation proceeds linearly with irradiation dose and at least for the cation resin, the amount of hydrogen produced by a given radiation dose does not depend on the radiation dose rate (Figure 6).

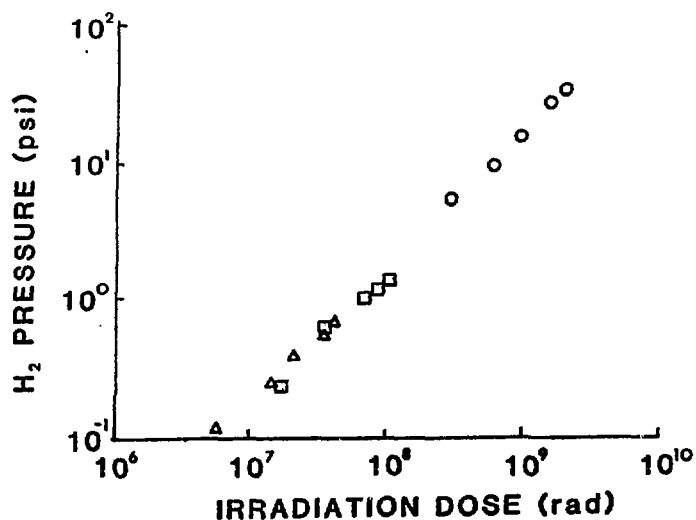


Figure 6. Hydrogen pressure over irradiated IRN-77 H⁺ form resin. Dose rates (rad/h); o - 1.7×10^6 ; \square - 1×10^5 ; Δ - 4×10^4 .

In cation resins, hydrogen generation probably results primarily from the radiolysis of incorporated water. In the anion resin hydrogen yields are several times greater and may reflect resin decomposition as well. In mixed bed resin, the net hydrogen generation can be well represented by the sum of the individual anion and cation component values.

Under sealed conditions, explosive conditions will probably not result from radiolytic hydrogen formation,^(4,10) since oxygen is rapidly scavenged from the atmosphere over irradiated resins (Figure 7).

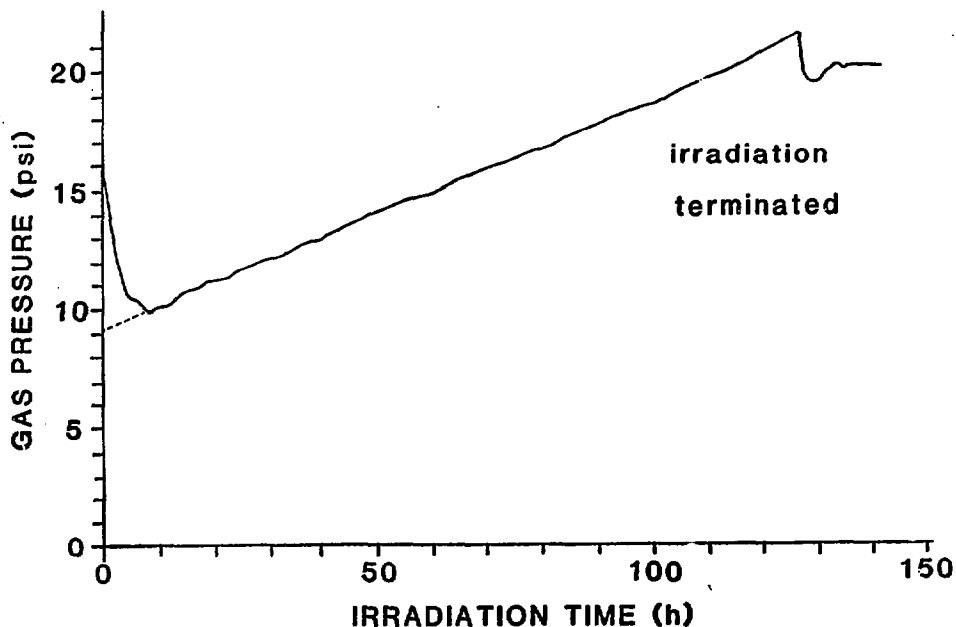


Figure 7. Gas pressure over H^+ IRN-77 resin during irradiation at 8×10^6 rad/h. The sample originally contained 6.4 psi of O_2 .

The pressure decrease during the first 10 h of irradiation is due to oxygen uptake and can be represented by a first-order kinetic process (Figure 8).

The rate constant derived from the data corresponds to an uptake of 90% of the available oxygen ($\sim 10^{-3}$ moles) by 12 g of resin after a dose of $\sim 4 \times 10^7$ rad. If the oxygen scavenging involves only attack at carbon atoms, a maximum of $\sim 0.3\%$ of the carbon atoms were oxidized in this measurement. Radiolytic oxidation above this level (as in samples irradiated in open atmospheres) evidently contributes to the agglomeration of resins reported in earlier scoping studies.⁽³⁾ See Figure 9.

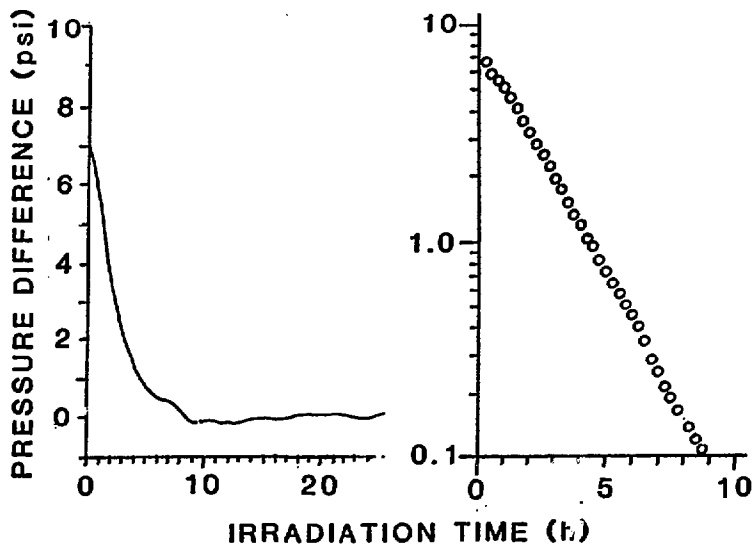


Figure 8. Linear (a) and semilogarithmic (b) plots of the difference between the data and the fitted straight line in Figure 7.




Figure 9. IRN-77 Na⁺ form irradiated to 1x10⁹ rad in open (left) and closed (right) systems.

Corrosion of Resin Corrosion Materials

Mild steel corrosion in fully swollen resins is promoted by the acidic species produced in the irradiation of cation or mixed bed resins (Figure 10). For the anion resin alone, corrosion was not observed.



H resin



Na resin



HOH resin



NaCl resin



HOH unirradiated Na

Figure 10. Mild steel (1018) coupons contacted with IRN-77 and IRN-150 resins during irradiation in sealed environments. Irradiation dose, 1.3×10^9 rad. Contact time 5 weeks.

Hydrogen form cation resin is the most corrosive. Corrosion rates are reduced when this resin is used in a mixed bed with anion resin in the OH^- form. Interestingly, during irradiation corrosion is somewhat greater in Na^+ form resin than in NaCl form mixed bed although the mixed bed releases strongly acidic free liquid. This is probably because the free liquid actually dilutes the acidity within the individual resin beads and produces a more uniform and less extensive corrosion. On the other hand, for the Na^+ form cation resin, corrosion occurs primarily by pitting at the resin coupon contact.

In this case, corrosion may actually be retarded by excess water, which reduces pitting behavior. Some moisture, however, is necessary if corrosive species are to be transported to the resin-container interface. Irradiation corrosion is not observed in dry H^+ form resin. In samples with corrosion coupons, pH tends to steady values which are substantially higher than those measured in the absences of corrosion, indicating a significant consumption of acidic species. Transport measurements show that acidic species and corrosion products can be transported (by diffusional processes) over a distance of several centimeters in a bed of fully swollen resin. The corrosion rate thus reflects the balances between the generation/transport and the consumption of corrosion species. This produces effects which depend on irradiation dose rate. For example, for a dose of 10^9 rad at a dose rate of 4×10^4 rad, the extrapolated weight loss of mild steel in Na^+ form resin was 125 mg/cm^2 . For the same dose at 1.7×10^6 rad, the extrapolated weight loss is 18 mg/cm^2 . Consequently testing for radiation corrosion effects at accelerated dose rates may significantly underestimate total corrosion under field conditions. Finally, it is worth noting that the radiolysis of cation resin is not significantly influenced by the uptake of corrosion products.

DISCUSSION AND SUMMARY

Practical implications results obtained in this study 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 resulting in:
 - (1) Generation of strongly acidic conditions ($\text{pH} < 2$) in aqueous solutions of irradiated resins, leading to a potentially corrosive environment.
 - (2) Release of sulfate ion and/or SO_2 gas. Sulfate ion may interact with solidification agents while SO_2 is a corrosive gas in moist environment.
 - (3) Loss of ion-exchange capacity, with the accompanying release of exchangeable counterions including radionuclides.
- Relative insensitivity to parameters such as radiation dose rate, pH and resin loading makes the radiolytic sulfate yield a convenient measure of radiation durability for regulatory considerations. 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. For 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. In this case the acidity will be reduced first by a protective ion-exchange effect in which H^+ ion is exchanged for cation at undamaged resin sites. Some of the sulfate may also be produced by a mechanism in which H^+ ion is not generated in the oxidation of SO_3^- to SO_4^- . In any event, the acidity is substantially reduced for loadings other than H^+ . Acidity and radiolytic attack can be further reduced (but not eliminated) by drying the sulfonic acid resin.
- 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 heavy doses, the anion resin evidently loses its capacity to exchange OH^- for anions (sulfate) released in the degradation of the cation resin. The basic species produced in the radiolytic degradation of the anion functional group did not completely 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 radiolytic hydrogen yield from the anion component is several times greater than for the cation component.

- (b) Decomposition products from the anion resin will tend to convert the undamaged cation resin into an ammonium form by ion-exchange processes, promoting the release of radioactive cations.
- (c) The irradiated anion resin component releases substantial amounts of free liquid. This liquid can serve as a transport medium for radionuclides or corrosive species released from the cation resin. On the other hand, it may also dilute local acidity.
- For the fully swollen cation resin, hydrogen gas generation most probably involves the radiolysis of incorporated water. Hydrogen yields can be substantially reduced by drying the resin. However, unlike the case for pure water, considerable hydrogen pressures can be achieved without saturation. At 10^8 rad, an unvented cation resin container with a void volume of 33% would experience a hydrogen overpressure of ~ 0.5 atmospheres. For anion resin, the H_2 over-pressure would be of the order 1.5 to 2.5 atmospheres. Radiolytic hydrogen yields are not dependent on radiation dose rate; this supports the validity of accelerated testing.
 - 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 radiolytic hydrogen and oxygen. Observations on samples irradiated in open systems indicate that radiolytic resin agglomeration is probably associated with extensive radiolytic oxidation. This will not occur in a sealed environment.
 - There is a substantial interaction between mild steel and the acidic species produced in the irradiation-induced decomposition of dewatered IRN-77 sulfonic acid resins. Initial corrosion rates are increased by irradiation in a closed system and depend strongly on radiation dose rates. Subsequent behavior may vary with resin loading. In some cases (H^+ form resin), corrosion rates tend toward asymptotic values, which are lower than those observed initially. Decreasing corrosion rates may indicate a depletion of acidic species in the resin sample. For others (Na^+ form resin) although corrosion rates are lower, this asymptotic behavior has not yet been observed.
 - A linear extrapolation of the corrosion rate data for sodium form resins to a total dose of 10^9 rad indicates a greater net corrosion at lower dose rates. Assuming uniform corrosion, the extrapolated weight loss corresponds to a thickness decrease of less than 1 mm. The dominant form of corrosive attack, however, is by pitting. (10)

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