MASTER

IRRADIATION EFFECTS IN THE STORAGE AND DISPOSAL OF
RADIOACTIVE ION-EXCHANGE RESINS[*]

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ABSTRACT

Research is under way to characterize the effects of self-
irradiation on radwastes which may be generated when organic
ion-exchange media are used in water demineralization or de-
contamination operations at nuclear facilities. External
factors affecting the relation between laboratory evalua-
tions and field performance are emphasized. Initial experi-
ments do not yet indicate substantial radiation dose-rate
effects on radiolytic gas yields or acid product formation,
when (fully swollen) sulfonic acid resins are irradiated in
a sealed air environment. At the same time, oxygen gas is
removed from the environment of irradiated resins. Inter-
action between mild steel coupons and acidic species pro-
duced in the irradiation induced decomposition of sulfonic
acid resin results in irradiation enhanced corrosion. Cor-
rosion rates depend on radiation dose rate, moisture content
and resin chemical loading. In some cases, corrosion rates
decrease with time, suggesting depletion of acidic species
within the resin bed, or a synergistic interaction between
resin and corrosion coupon. Implications of these and other
results on evaluating field behavior of radwaste containing
ion-exchange media are discussed.

INTRODUCTION

Under certain conditions, and particularly in cleanup procedures following
off-normal reactor operations, ion-exchange media used in demineralization may
incorporate a substantial loading of long lived radionuclides. This program is
investigating how the properties of wastes 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 opera-
tions at TMI-II.[1-4] However, little information is available to relate
existing laboratory results to the anticipated effects of irradiation on ion-
exchange resin wastes under actual storage and disposal conditions, including
the presence of solidification agents or high integrity container components.
The present paper describes measurements of three separate effects resulting
from the irradiation of organic ion-exchange media:
- Formation of chemically aggressive, soluble decomposition products.
- Radiolytic generation or uptake of combustible or corrosive gases.
- Enhanced corrosion of mild steel contacted with irradiated resins.
Special emphasis is placed on variables such as radiation dose, dose rate,

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chemical loading on the resins, moisture content, and composition of external media, which may affect the relation between laboratory test results and field behavior of resin wastes.

EXPERIMENTAL

Initial experiments have been carried out with sulfonic acid cation resins (Amberlite IRN-77), and quatenary ammonium anion resin (Amberlite IRN-78).[*] These resins were chosen as typical of those used in the nuclear industry. IRN-77 contains sufonic acid functional groups ($-SO_3^-$) on a polystyrene/ divinyl benzene polymer backbone. IRN-78 contains quatenary ammonium ($-N(CH_3)_3^+$) functional groups on the same backbone.

Resin samples were prepared with different counter-ion loadings using batch 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 dried by heating in air. Residual moisture content of the various samples was determined by measuring percentage weight loss following prolonged drying. The present results refer largely to irradiations in a sealed environment simulating waste storage. Two sample configurations were used. In one, 6 g resin-samples were weighed into Pyrex break-seal tubes, which were then flame-sealed in air. Where desired, mild steel corrosion coupons (ASTM 1018 steel, 33 x 6.4 x 0.53 mm^3) were embedded in the resin prior to flame sealing. 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 loaded sample tubes are either set aside as zero dose control samples or irradiated in Brookhaven National Laboratory'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 1.65×10^6 rad/h, 9.6×10^4 rad/h, and 3.7×10^4 rad/h. All these values should be considered accurate to $\pm 10\%$.

Following removal of the resins from the irradiation source, sample cell pressure was determined. For the Pyrex cells, this involved breaking the cell in an evacuated chamber equipped with a pressure transducer. Where desired, the gases were then sampled for compositional determination by mass spectroscopy. Corrosion coupons were next withdrawn from the resin. Corrosion weight loss was determined after removing the corrosion layer by vigorously stirring for 3-4 minutes in Clarks' solution. Generally the coupons were photographed before and after removal of the corrosion film.

For anion and mixed bed resins free liquids released from the resins during irradiation were removed by centrifuging. For all resins, a second liquid fraction was then formed by contacting 2 g of the individual 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 are to provide a basis for comparison with future results obtained on resins irradiated while immersed in water.

The various liquid phases were analyzed for pH, decomposition products of functional groups (e.g., SO_4^-) and counter ions (e.g., Na^+) in solution. Several resin samples were also characterized for uptake of corrosion products (i.e. iron) and for changes in swelling behavior.

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[*]Amberlite is a trademark of the Rohm and Haas Company, Philadelphia, PA.

RESULTS

Formation of Soluble Decomposition Products

Formation of acidic species in irradiated IRN-77 resin is shown in Figure 1.
The pH values were measured in the supernate of 10 mL of deionized water con-
tacted with 2 g of fully swollen resin irradiated in a sealed environment.
Data are given for resins in both the hydrogen and sodium forms .

The hydrogen form resin is substantially more acidic than the sodium form.
However, radiolytic attack on the functional group, as measured by the release
of soluble sulfates, is sensibly the same for both forms (Figure 2).
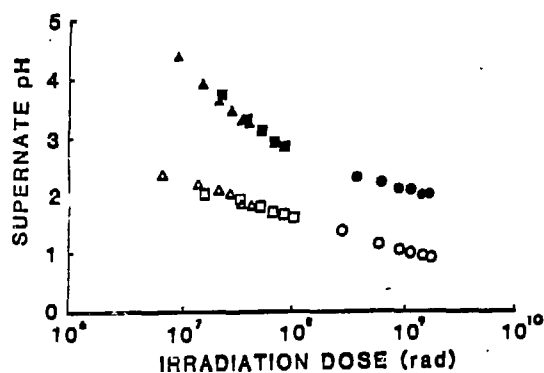
Fig. 1. Supernate pH vs irradiation dose rate for irradiated H^+ (open
points) and Na^+ form (solid points) resin. Dose rates (rad/h): o - 1.7 x
10^6; □ - 1 x 10^5; △ - 4 x 10^4.

Fig. 2. Soluble sulfate generation vs irradiation dose for fully swollen
IRN-77 H^+ form resin (open points) and Na^+ form resin (solid points) with-
out corrosion coupons; and Na^+ form resin with corrosion coupons (half open
points). Dose rates (rad/h): o -1.7 x 10^6; □ -1x10^5; △ - 4 x 10^4.

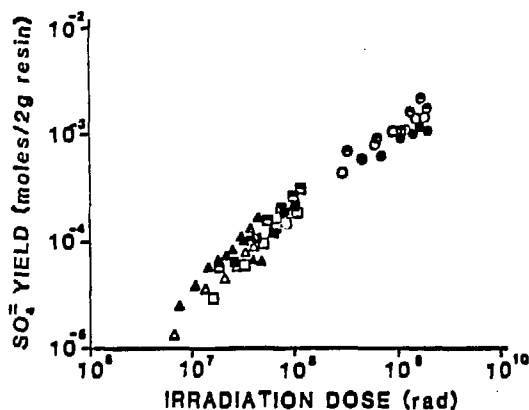Strongly acidic conditions in irradiated sulfonic acid resins may be attributed to radiolytic scission of the $-SO_3$ functional group.[1] In dewatered (fully swollen) IRN-77 resin, the scission products are largely oxidized to sulfates, presumably by radiochemical processes. Attack on the functional group, as measured by sulfate yield is largely insensitive to external factors, such as pH, sodium vs hydrogen loading, and (apparently) radiation dose rate (Figure 1). G values for sulfate formation from Figure 1 are ~0.7 near 10^8 rad and ~0.4 near 10^9 rad. The present data cannot entirely rule out the possibility that the apparent decrease of G-value actually represents a dose rate effect. Other studies, however,[5,6] reported decreased radiation sample yields in resins at high irradiation doses.

The acidity resulting from a given yield of sulfate depends on resin loading. In hydrogen form resin, the supernate acidity can be qualitatively accounted for as sulfuric acid. The sodium form resin is less acidic than would be expected on the basis of $NaHSO_4$ formation. The relatively low acidity and the sodium to sulfate ratios in the supernate suggests a "protective effect," in which acidity is reduced by exchange of hydrogen for sodium at undamaged exchange sites in the sodium form resin.

Measurements were also carried out on liquids contacting the various forms of IRN-78 resin. Results are shown in Table I.

TABLE I
Properties of liquids contacting irradiated[a] IRN-78 resin

Sample Type	Irradiation or Holding Time (h)	Free Liquid Yield (mL)	Free Liquid pH	Supernatant pH Fresh	Aged 9-12 Weeks
Cl⁻	168	0.84	5.71	7.08	
	336	1.20	6.42	6.75	
	504	1.93	7.37	5.91	
	672	2.06	7.28	5.64	
	840	2.13	7.03	5.31	
Cl⁻ Control	168	<0.1	—	6.89	
	336	<0.1	—	6.17	
	504	<0.1	—	5.13	
	672	<0.1	—	—	
	840	<0.1	—	6.24	
OH⁻	50	NM	NM	10.35*	10.00
	100	NM	NM	10.57*	9.40
	200	NM	NM	11.01*	9.53
	504	2.38	10.52	10.57	
	672	2.49	10.35	10.69	
OH⁻ Control	50	<0.1	—	9.79	9.83
	100	<0.1	—	8.59	9.85
	200	<0.1	—	9.41	9.96
	504	<0.1	—	7.38	
	672	<0.1	—		

[a]All irradiations carried out at 1.6×10^6 rad/h. NM = not measured.
Control - Unirradiated samples, stored for times indicated.
Liquid yield - Amount of liquid removed by centrifuging 6 g of resin.
Liquid pH - pH of liquid removed by centrifuging.
Supernatant pH - pH of supernatant formed from 2 g centrifuged resins plus 10 mL deionized water. For samples indicated by an asterisk (*) the free liquid was decanted from the resins, rather than centrifuged.

For irradiation doses approaching 3×10^8 rad the fully swollen resins lose their ability to retain water, and a free liquid phase becomes evident.

For OH^- form resin, a relatively low ($\sim 8 \times 10^7$ rad) dose increases the pH by about 1.5 to 2 units. Subsequently, and unlike the case for cation resin, the freshly measured pH remains relatively stable at about 10.5 as the irradiation proceeds. For resin in the Cl^- form, the pH remains nearly neutral, while the concentration of chloride in solution increases with irradiation dose. For several of the OH^- form samples, the supernatant pH was remeasured after aging for 9-12 weeks in polyethylene vials. In general, this aging produced a pH decrease in the supernate of irradiated resins, and a pH increase for unirradiated control samples.

Substantial amounts of free liquid are released by both Cl^- and OH^- form resins as the irradiation dose increases. As the free liquid is released, the resin undergoes a considerable shrinkage. For OH^- form resins, the maximum yield of 2.5 mL per 6 g of swollen resin corresponds to a release of about 60% of the water originally present.

Radiolytic Gas Generation

Hydrogen is the principal radiolytic gas produced when fully swollen IRN-77 and IRN-78 resins are irradiated in a sealed environment.

The hydrogen pressure increases in a closely linear manner with irradiation dose. A plot of the hydrogen pressure vs irradiation dose at different dose rates is given in Figure 3. The departure from linearity lies within present experimental uncertainty. Between 10^6 and 10^9 rad, the G value derived from the fit is $0.12 \pm .01$. Both the G-value and total pressure correspond reasonably well to those found for Na^+ form resin.

CO_2 is also produced by radiolysis of IRN-77 resin. Under the present conditions, the ratio of H_2 to CO_2 is roughly 4:1 at high total doses. Gases such as SO_2, which would result directly from attack on the functional group, were not observed.

Thus far, there is no evidence for a radiation dose rate or resin loading (hydrogen vs sodium) effect on gas generation in fully swollen IRN-77 resin (Figure 3). Hydrogen G-values for IRN-78 resin ($\sim 60\%$ moisture content) are about three times greater than those in IRN-77 resin ($\sim 50\%$ moisture content). Sulfate G-values in IRN-77 resin are also several times those for hydrogen generation. Taken together with the evidence for a characteristic ratio of H_2 to CO_2, these results suggest that in IRN-77 resin, radiolytic attack on the resin backbone, rather than direct water radiolysis or attack on the functional group, may be a rate determining step in hydrogen gas generation. In all cases, oxygen is quickly removed from the atmosphere over irradiated resins. A radiation dose of $\sim 10^7$ rad is sufficient to promote consumption of at least 1×10^{-3} moles of O_2 per gram of resin. Initial data on samples irradiated in an oxygen atmosphere indicate that this oxygen scavenging follows first order kinetics, with a rate constant of $1.9 \ h^{-1}$ at a dose rate of 7×10^6 rad/h and a resin mass of 12 g.
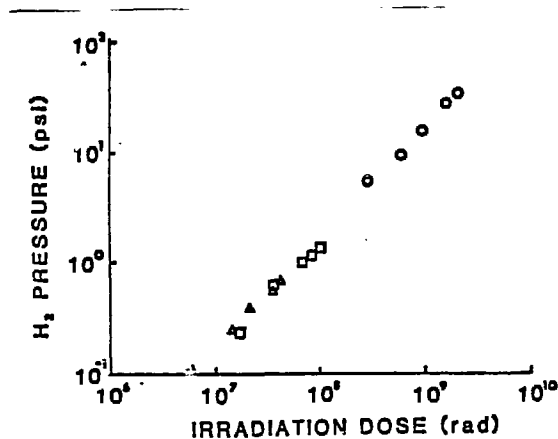
Fig. 3. Hydrogen pressure over irradiated IRN-77 H$^+$ form resin. Dose rates (rad/h): o - 1.7 x 10^6; □ - 1 x 10^5; Δ - 4 x 10^4.

Corrosion of Mild Steel Coupons Contacted with Irradiated Resins

Weight loss determinations have been carried out on mild steel coupons contacted with IRN-77 resin during irradiation at different dose rates. Figure 4a shows weight loss for coupons contacted with fully swollen sodium form resin and irradiated at various dose rates. Similar data for hydrogen form resin are shown in Figure 4b.
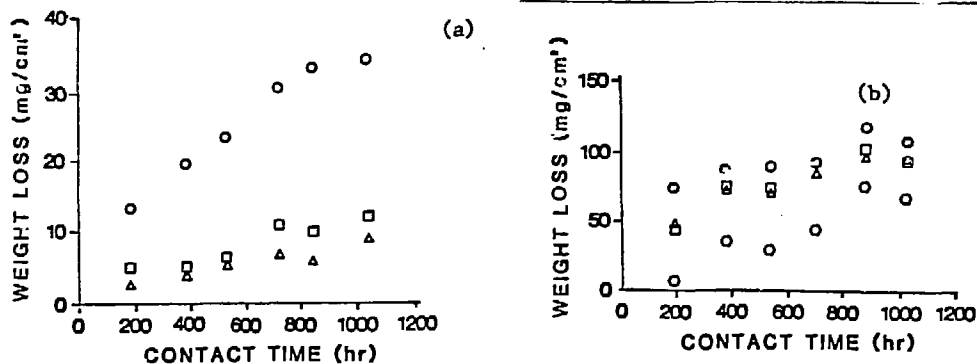

Fig. 4. Corrosion weight loss for mild steel coupons contacted with Na$^+$ form IRN-77 resin and irradiated at different dose rates. Dose rates (rad/h): o - 1.7 x 10^6; □ - 1 x 10^5; Δ - 4 x 10^4; ◯ - unirradiated. a - sodium form resin; b - hydrogen form resin.

Corrosion weight loss is barely detectable in unirradiated sodium form resin. In irradiated samples, corrosion weight loss shows a roughly linear increase with irradiation time. The corrosion rate, as measured by the values of

linear fits to the weight loss curves, increases with increasing dose rate; 0.05, 0.009 and 0.03 mg/cm^2-h are obtained for dose rates of 4 x 10^4, 1 x 10^5 and 1.7 10^6 rad/h, respectively. Since there is some evidence for leveling off at 1.7 x 10^6 rad/h, the last point was not included in the fit.

Significant corrosion occurrs in coupons contacted with unirradiated samples of IRN-77 resin in the hydrogen form. Figure 4 indicates a weight loss of 60 mg/cm^2 after approximately 1000 h contact time. In irradiated samples, initial corrosion is even more rapid. As contact time increases, weight loss rates decrease in the irradiated samples. The curves evidently start to level off for a weight loss of approximately 80 mg/cm^3.

In both resin forms, pH is strongly influenced by the corrosion process. In samples with corrosion coupons, the supernate pH tends to steady values, which are substantially higher than those measured in the absence of corrosion. Comparative values are shown in Table II. Soluble sulfate formation, however, is not significantly affected by interaction with mild steel corrosion coupons (Figure 1).

TABLE II
Supernatant pH values for IRN-77 resins irradiated with and without corrosion coupons[a]

Sample Form	Dose Rate (rad/h)	Supernatant pH	
		No coupon	Coupon
Na$^+$	0	4.7	5.9
Na$^+$	4 x 10^4	3.3	4.0
Na$^+$	1 x 10^5	2.9	3.8
Na$^+$	1.7 x 10^6	2.1	2.8
H$^+$	0	3.8	2.6
H$^+$	4 x 10^4	1.8	2.7
H$^+$	1 x 10^5	1.6	2.6
H$^+$	1.7 x 10^6	0.9	2.4

[a]Irradiation/contact times = 1000 h.

In sodium form resin, corrosion does not dramatically affect gas generation. In the hydrogen form resin, containing corrosion coupons, there is a remarkable similarity between the gas generattion curves and the corrosion weight loss curves. If the data are combined in a plot of weight loss vs gas pressure, the resulting curve indicates that approximately one mole of H$_2$ is produced for every mole of Fe lost in corrosion, independent of dose rate. This results in hydrogen pressures in excess of 100 psi for the endpoints of the curves in Figure 4b. (Compare Figure 3.)

To the extent that supernate pH values reflect actual conditions in the resin, corrosion evidently tends to stabilize or reduce the radiolytic H$^+$ ion concentration. This may happen in several ways. First, corrosion reactions may effectively convert H$^+$ ion to H$_2$ gas, which is subsequently released. Second, corrosion products may provide a sink for H$^+$ ion. Last, the resin itself may be protected against further degradation by uptake of corrosion products.[7]   It appears that the first of these mechanisms may be operating for the H$^+$ form resin. For the Na$^+$ form resin, it is less clear which mechanism predominates, although the formation of soluble sulfate, which reflects radiation damage at the exchange sites, is evidently not retarded by corrosion. In any event, the corrosion rate will reflect the balance between the generation/transport and uptake of corrosive species. Finally, corrosion depends sensitively on resin moisture content. In short-term tests on samples

irradiated to 3×10^8 rad, corrosion was not observed in samples of H^+ form resin that had been dried to $\leq 14\%$ moisture. Supernate pH data, however, indicate that drying the resin does not greatly reduce the yield of acidic species produced by radiolysis.

SUMMARY AND CONCLUSIONS

Thus far, there is no clear evidence for a substantial radiation dose rate effect in the irradiation-induced decomposition of dewatered (fully swollen) IRN-77 resin irradiated in closed systems. Additional data are required to confirm this early trend. Dose rate effects, presumably associated with oxidation effects, have been observed when certain polymers are irradiated under oxic conditions.[8] The results, however presently support the validity of accelerated resin testing at high radiation dose rates.[9] Further, gas generation data indicate that, in sealed storage or disposal, the atmosphere over irradiated (dewatered) resins will rapidly be depleted in oxygen, reducing explosion hazard.

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 substantially 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. For others (Na^+ form resin) although corrosion rates are lower, this asymptotic behavior has not yet been observed.

Decreasing corrosion rates may indicate a depletion of acidic species in the resin sample. A linear extrapolation of the corrosion rate date 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 coresponds to a thickness decrease of less than 1 mm. The dominant form of corrosive attack, however, is by pitting, as indicated by Gangwer and Pillay.[10]

In contrast to the results of Gangwer and Pillay, obtained under somewhat different conditions, significant mild steel corrosion in irradiated anion (IRN-78) resin was not observed in the present experiments. The release of free liquid by this resin, however, provides a possible mode of transport for corrosive species generated in the cation component of a mixed or layered bed. The interaction between anion and cation resins under irradiation is presently being investigated.

ACKNOWLEDGMENTS

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