CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS

QUARTERLY PROGRESS REPORT
OCTOBER-DECEMBER 1981

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ABSTRACT

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

An extensive series of measurements has been initiated to investigate the effect of irradiation dose rate on radiation damage formation in IRN-77 resin. Samples are being irradiated at dose rates between approximately 1.7×10^6 and approximately 4×10^4 rad/h. Thus far, there is no evidence for a pronounced radiation-dose effect in the radiation-induced decomposition of (fully-swollen) IRN-77 resin. There is a substantial interaction between mild steel coupons and acidic species produced in the irradiation induced decomposition of IRN-77 resin. For a given radiation dose, experiments at accelerated dose rates may tend to underestimate the net corrosion at low dose rates under field conditions. The corrosion behavior depends sensitively on resin loading - in some cases, long-term (or "asymptotic") corrosion rates may be much lower than initial rates. The mechanistic and regulatory implications of this behavior are discussed. Substantial amounts of hydrogen gas can be generated in the corrosion of mild steel in IRN-77 resin at the same time oxygen is unquestionably removed from the environment of irradiated resins. The scavenging does not rely on corrosion, and is quite effective at low dose rates and total doses. The O_2 scavenging may in part involve radiolytic conversion of O_2 to CO_2. Preliminary experiments indicate that the relatively low yield (or protective effect) in irradiated Na^+ form resin is at least qualitatively constant with an uptake of radiolytic H^+ ion by the resin itself.

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CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS
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1. INTRODUCTION

Brookhaven National Laboratory (BNL), under contract to the United States
Nuclear Regulatory Commission (NRC), is presently carrying out a research pro-
gram entitled, "Characterization of TMI-Type Wastes and Solid Products." The
present document is the second progress report issued under this contract.
Subsequent reports will be issued on a quarterly schedule. In this section,
background information is provided which is intended to define the scope and
objectives of the program. The various tasks within the program are described
to provide an initial context for evaluating the progress that is reported in
subsequent sections.

1.1 Background and Program Objectives

The objective of this program is to develop a data base applicable to NRC
licensing considerations for the storage and disposal of unique radioactive
wastes. As unique wastes, the program specifically considers organic and in-
organic ion exchange media subjected to high internal irradiation doses as a
result of heavy radionuclide loadings. Typical of such wastes are the resins
and zeolites either employed or contemplated for use in water decontamination
procedures at TMI-II as mentioned above. Previous experience has indicated
that in such materials, internal irradiation can produce degradation effects
of potential consequence in regard to licensing considerations. Briefly, the
properties of the wastes may undergo a more or less continuous evolution as
the irradiation dose builds up, both during storage and following incorpora-
tion of the wastes in an ultimate disposal form. This program is aimed at
generating information and developing test procedures which will permit char-
acterization of the anticipated properties of unique waste products under
field conditions. This involves four separate phases. First, a scoping study
to determine the manner in which material properties of engineering interest
might be altered by irradiation effects; second, an examination and delinea-
tion of those factors which govern the relationship between laboratory evalua-
tions and field performance; third, a phenomenological/mechanistic description
of the important radiation effects that may be anticipated for several generic
materials under field conditions; and fourth, a specification of the type of
tests which would adequately assess the radiation durability of a particular
ion exchange waste product in a given licensing application.

The project is organized as five separate tasks. Task 1 involves a char-
acterization of field experience with heavily loaded ion exchange media. This
is intended to provide a basis for comparison of laboratory and field results.
Task 2 is a parametric study of the radiation induced degradation of organic
ion exchange media. In Tasks 3 and 4, irradiation effects on inorganic ex-
change media and on solidified forms containing ion exchange media are to be
characterized. Task 5 will assess mechanistic issues specifically dealing

with qualifying test procedures for assessing the significance of radiation effects on the use, storage and disposal of ion exchange media under field conditions.*

1.2 Scope of the Present Report

Previous work (Swyler and Weiss, 1981) has largely involved the first two phases of this program - a scoping study to identify effects of practical significance, and preliminary experiments to identify the key external variables on parameters which govern these phenomena. Effects of practical significance include radiation induced (sulfuric) acid formation, radiation induced hydrogen generation, and radiation-induced oxygen scavenging in IRN-77 resin; radiation-induced corrosion of mild steel coupons contacted with this resin; physical changes and agglomeration of irradiated resin. Key factors influencing the extent of these effects were found to be resin loading, moisture content, and radiation dose. The type of resin or ion exchangers (i.e., backbone, exchange group, etc.) is, of course, a key factor also. The present effort concentrates on a few types which are representative of those widely used in the nuclear industry - styrene-divinylbenzene/sulfonic acid cation resin and styrene-DVB/quartenary ammonium anion resin (MacKenzie, Lin, and Barletta, 1981).

Work carried out during this report period was primarily concerned with characterizing these various effects in terms of rates and yields, and with specifying the effect of external variables on these yields. Most of this work falls under Task 2. Major variables presently under investigation are resin loading (H^+ form vs Na^+ form) and radiation dose; synergistic interaction between corrosion and resin degradation are also being examined. Samples are being prepared for moisture content and mixed-bed studies. Experiments under Task 5 aimed at clarifying the role of irradiation-induced peroxides on resin degradation are continuing. A new experiment was initiated in this task to determine if the relatively low acid product yield (or protective effect) seen with Na^+ form resins might reflect a self-buffering mechanism. Progress in the various tasks is described below.

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*Note added in proof: Early in the second quarter of FY 1982, it was decided that Task 3, a specific study of inorganic ion exchange media, would no longer be included in this project.

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

During this report period, BNL personnel visited Battelle Columbus
Laboratories (BCL) to observe first-hand the characterization of an Epicor-II
liner used in the cleanup at TMI-II. Two recent BNL reports prepared under
separate contract to NRC were reviewed to identify field experience and po-
tential field sources of heavily loaded ion-exchange resins. Locally, steps
were initiated to obtain and characterize samples of resins used in BNL's High
Flux Beam Reactor. These activities are described in more detail below.

2.1 Monitoring Efforts on Epicor-II Liner Characterization

An Epicor-II liner used in decontamination of water in the TMI-II
auxiliary building is presently being characterized at Battelle Columbus
Laboratories. On November 14, 1981, K. J. Swyler visited this facility for a
briefing on techniques employed and results obtained in this characterization.

Much of the early work discussed is summarized in detail in a draft re-
port entitled "Preliminary Characterization of Epicor-II Prefilter 16 Liner,"
authored by Battelle Columbus Laboratories and published by EG&G under the
number, GEND-INF-015 (August 1981). While this document has not yet been re-
viewed in detail, it does not appear to contain extensive information of which
we were not previously aware, at least in a general sense.

Activities subsequent to those discussed in the draft report were ver-
bally described. These include additional visual examinations and a liner
pressurization measurement. The latter involves resealing the liner and
periodically sampling the atmosphere within the liner by a remote sampling
line feeding through the hot cell.

A number of effects seen in laboratory evaluations are observed under
field conditions. These include gas generation, oxygen gas uptake, and occur-
rence of liquid and solid phases with low pH. However, the present data do
not permit a detailed comparison of BNL's laboratory tests with field results.
For example, it will be difficult to obtain a comparison G-value for gas gen-
eration from the whole liner measurements. Similarly, the liner's (epoxy)
inner coating showed a number of small penetrations and rust spots in the
freeboard area above the resin bed. However, without baseline data, it is not
certain as to what extent, if any, this represents (radiation induced) corro-
sion during storage.* In having discussions, the importance of correlating
laboratory and field data was emphasized. It was pointed out that some of the
information generated in BCL's present characterization may be extremely use-
ful in this program. Future interaction between BCL and BNL along these lines
will be explored, including the possibility of obtaining loaded resin samples
from liner PF-16.

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*However, the existence of these penetrations argues against assigning any
 credit to the epoxy coating as a corrosion inhibitor.

In practical terms, the effects which most appear to warrant further characterization include:

- gas generation (and, in particular, oxygen uptake)

- pH changes and buffering effects in mixed-bed (or organic/inorganic) mixtures

- corrosion (including coating durability)

- radiation effects in the vapor phase above the resin.

The mechanism of gas generation and uptake is of particular practical interest. According to personnel involved in the TMI cleanup, in Epicor-II liners, generation of explosive gas mixtures is not considered to be a problem due to the (irradiation-induced) oxygen uptake. The presently available oxygen uptake information is based almost entirely on characterization of one liner, where the activiity is contained almost entirely on (inorganic) zeolites, and on laboratory data whose correspondence to field conditions is not yet firmly established (Barletta, Swyler, Chan, and Davis, 1981). Since a number of the liners contain their activity entirely on organic media, and since it does not seem to have been demonstrated that the observed oxygen uptake results in a chemically stable species, it was suggested that some additional confirmatory characterization might be timely, particularly for the organic liners. In our program, we will attempt to establish, as well as possible, the general conditions under which irradiation-induced oxygen uptake can be relied on to prevent the formation of explosive mixtures.

2.2 Characterization of Spent Resins Generated in Commercial Reactor Operations

Recently, under a separate contract to the NRC (FIN A-3159), Piciulo (1981) and MacKenzie, Lin, and Barletta (1982) have completed review documents addressing the storage and disposal of spent ion-exchange media generated in normal reactor operations. As part of these efforts, a survey of field experiences with spent resins at various reactor sites was conducted. In this survey, the commercial reactor facilities have been identified which evidently generate resins with internal curie loadings large enough to be of potential interest in the present program. The Maine Yankee Atomic Power Company, has apparently loaded mixed bed (Rohm and Haas Amberlite IRN 150) resin to 125 Ci/ft^3. The E. I. Hatch Plant in Georgia has generated powdex resins (Epicor, H^+, OH^-) loaded to $\sim$60 Ci/ft^3.

As indicated by MacKenzie, Lin, and Barletta, the relationship between activity and radiation dose depends on the specific radionuclides involved and on geometry factors. It presently seems possible that these resins may least approximate the irradiation conditions anticipated in off-normal cleanup operations. Moreover, the mixed beds contain individual resin components which are already under study in our laboratory. Consequently, we have made initial inquiries to investigate the feasibility of obtaining field samples of these

resins for characterization. One important question is whether useful total internal doses can in fact be achieved with these resins in a convenient time frame.

2.3 Development of Standards for Activity Determination and Dosimetry of Ion Exchange Media

In characterizing actual field samples of radionuclide-loaded ion-exchange media, it will be necessary to determine specific activities and radiation dose rates. We intend to carry out such determinations by gamma counting samples on apparatus which presently exists in our laboratory. In order to determine specific activities, counting data from an unknown sample will have to be compared with data obtained on a standard activity sample of the same material. During this report period, work was initiated on developing standard activity samples. As a prototypical unknown, a sample of spent resin from BNL's high-flux beam reactor is being utilized. Development of counting standards and dosimetry techniques should be largely completed during the next quarter.

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

    Measurements examining the effect of radiation dose rates and chemical
loading on the radiation-induced degradation of IRN-77 resin continued during
this report period. These extend and refine the scoping measurements in the
earlier part of this program. As indicated earlier (Swyler and Weiss, 1981),
particular features of radiation-induced degradation which are being examined
include (1) formation of acidic species, (2) corrosion of mild steel contacted
with the resin, (3) physical changes in the resin (agglomeration and color),
and (4) nature of the soluble decomposition products.

    As an additional refinement, the previous measurements have been extended
to include an extensive series of irradiations in sealed Pyrex tubes. This
was motivated by two factors. First, data obtained in the previous scoping ex-
periments indicates that in those cases when large gas pressures are generated
by irradiation and/or corrosion, the atmosphere and moisture content of the
samples cannot be reliably maintained in simple stoppered tubes. Second, a
recent NRC technical assistance document (MacKenzie, Lin, and Barletta 1982)
has recommended irradiation in sealed tubes, followed by gas evolution mea-
surements as a standard test for resin licensing considerations. Sealed tube
irradiations thus provide improved control of experimental conditions, while
also affording a basis for evaluating test procedures proposed in the TA task.
This technique, of course, also permits study of an additional feature: gas
generation/uptake. It is recognized, however, that in actual field practices,
storage and disposal may incorporate vented or pseudo-vented conditions. Con-
sequently, experiments are also being carried out to establish the correspond-
ence between irradiation under sealed (isovolumetric) and vented (isobaric)
conditions. Results obtained during this report period are described below.

3.1 Sample Preparation and Irradiation Procedures

    Samples of IRN-77 in the hydrogen and sodium forms were prepared accord-
ing to standard procedures developed in other programs in our laboratory
(Weiss and Morcos, 1981). The IRN-77 resin is obtained in hydrogen form from
the manufacturer. Prior to use, this material was rinsed several times in de-
ionized water. Free water was then removed by suction. The residual moisture
content was determined by measuring percentage weight loss following air dry-
ing for 18 hours at $110°C$.

    A second portion of the as-received resin was converted to the sodium
form by procedures described earlier. In this procedure, the converted resin
is rinsed until the resin pH becomes neutral. Free water was then removed and
the moisture content determined as before. The moisture contents of the H^+
and Na^+ for resins were determined to be 50% and 52%, respectively.

    Samples in stoppered tubes are being irradiated in configurations de-
scribed earlier. For irradiation in a sealed environment, 6.0 g resin samples
are weighed into Pyrex tubes, which are then flame-sealed in air. Where

designed, mild steel corrosion coupons are embedded in the resin prior to
flame sealing. Coupon preparation has been described previously (Swyler and
Weiss, 1981). A typical break-seal is shown in Figure 3.1.
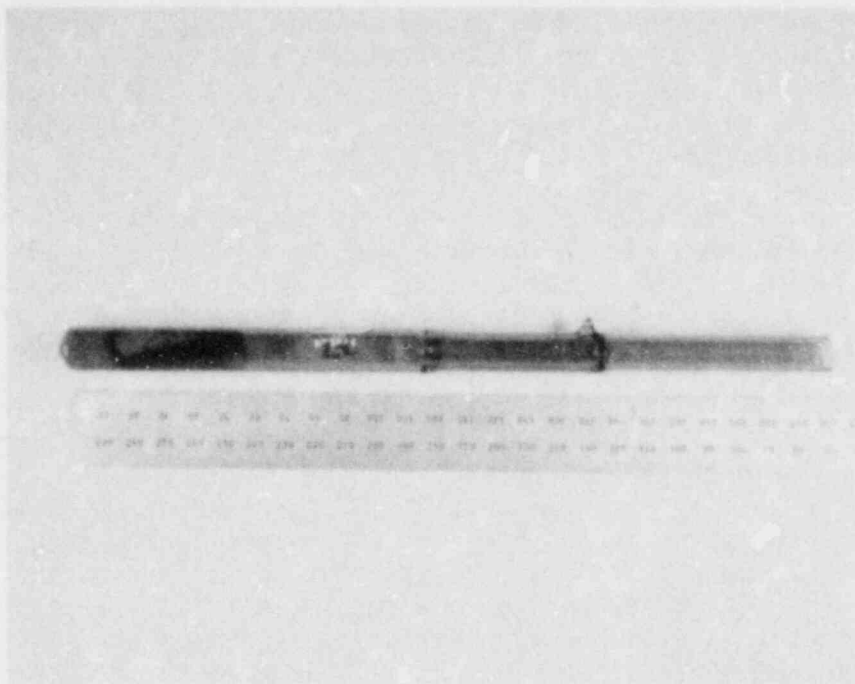
Figure 3.1 Break-seal vessel for resin irradiation.

The loaded sample tubes are either set aside as zero dose control sam-
ples or irradiated in BNL's Co-60 gamma pool. This facility incorporates a
number of air tubes, each of which provides a different radiation dose rate.
Sample vessels are irradiated six at a time in a given air tube. As the irra-
diation proceeds, samples are sequentially removed from the air tubes, provid-
ing an ensemble of six samples, irradiated to different total doses at a given
gamma dose rate. The gamma flux varies locally with position in each air
tube. The dose rate at the individual sample tube positions were determined
in situ with radiochromic foils taped to the sample tubes. The variation in
relative dose rate was less than 10%. The average dose rates employed 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 $\pm 10\%$. Results obtained to date are
observed below.

3.2 Gas Generation

In the sealed tube irradiations, both the pressure and composition of gases generated during irradiation are measured. Pressure is determined by breaking the sealed sample cell in an evacuated chamber equipped with a pressure transducer. The pressure is determined from the relation

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

where 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 cm^3 and 14 cm^3, respectively. The large cell volume was chosen to handle the substantial gas pressure anticipated in the H^+ forms resin containing corrosion coupons. In later experiments the cell volume was reduced to 100 cm^3. Following the determination of P_i and P_f, gas was transferred into an evacuated glass vessel for compositional analysis by mass spectroscopy. The accuracy of the compositional determination by this technique is +1% for components with concentration down to 1%. For lower concentration, the accuracy is +5% until 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.[*]

Figure 3.2 shows the buildup of cell pressure vs irradiation time for irradiation of Na^+ form IRN-77 near at three different radiation dose rates. Data for an irradiated control sample is also given. Similar data are shown in Figure 3.3 for Na^+ form resin containing an embedded cold steel corrosion coupon. Figure 3.4 gives data for H^+ from resin containing a corrosion coupon.

For the sodium form resin, pressure changes in controlled samples and in samples irradiated at low dose rates are marginally detectable. Indeed, the data suggest a slight pressure decrease. For irradiation at approximately 10^6 rad/h fairly unsubstantial pressures are achieved at approximately 10^9 rad, following what may be an initial induction dose the pressure shows a roughly linear increase with irradiation dose. The G-value for total gas

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[*]The amount of water present in the vapor phase should be less than approximately 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%.

generation determined from the curve slope is approximately 0.25. In the Na+
form resin, it does not appear that the gas generation is strongly influenced
by the presence of corrosion coupons.

For H+ form resins containing corrosion coupons, there is substantial
gas generation in unirradiated control samples. Irradiation evidently in-
creases the initial gas generation rate but the gas generation slows down as
the irradiation time increases. Interestingly, the limiting gas generation
rate in irradiated samples does not appear to depend on radiation dose rate.
Data are not yet available for gas generation in H+ form resin without cor-
rosion coupons. Almost certainly, however, a large fraction of the gas gener-
ation indicated in Figure 3.4 is due to corrosion of the mild steel coupons in
H+ form resins.
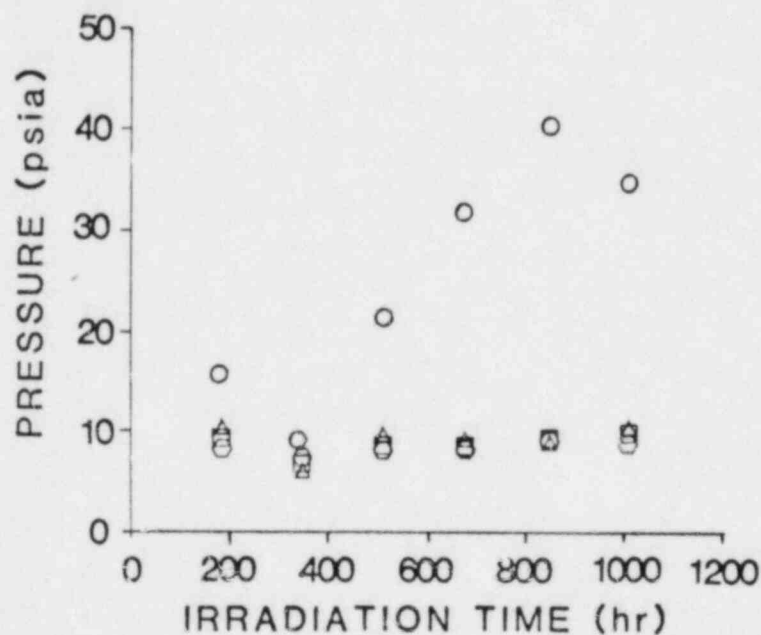
Figure 3.2   Sample cell pressure vs irradiation time at different dose
rates for Na+ form IRN-77 resin. Irradiation dose rates
(rad/h): o - 1.7×10^6; □ - 1×10^5; △ - 4×10^4;
⬡ - unirradiated.
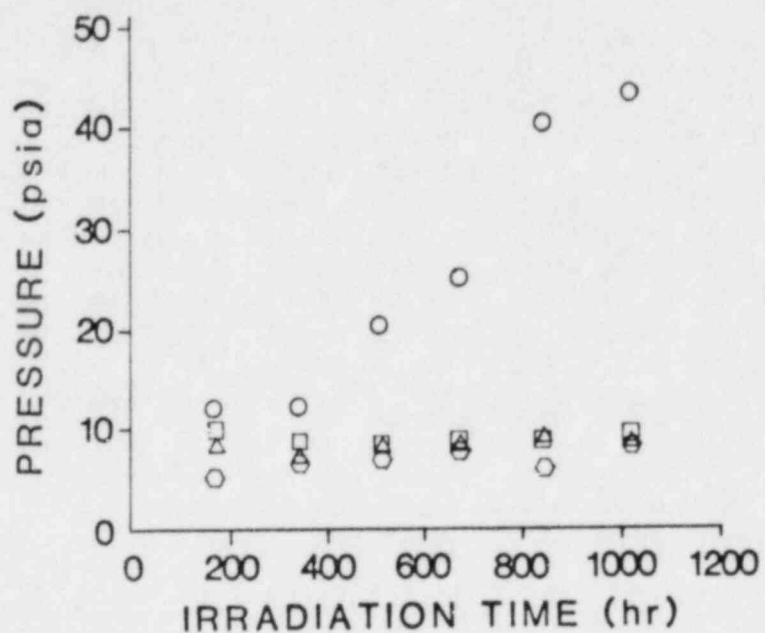
Figure 3.3   Sample cell pressure vs iradiation time at different dose rates for Na$^+$ form IRN-77 resin, contacted with mild steel coupons. Irradiation dose rates (rad/h):   o - 1.7 x 10^6; □ - 1 x 10^5; △- 4 x 10^4; ◯ - unirradiated.
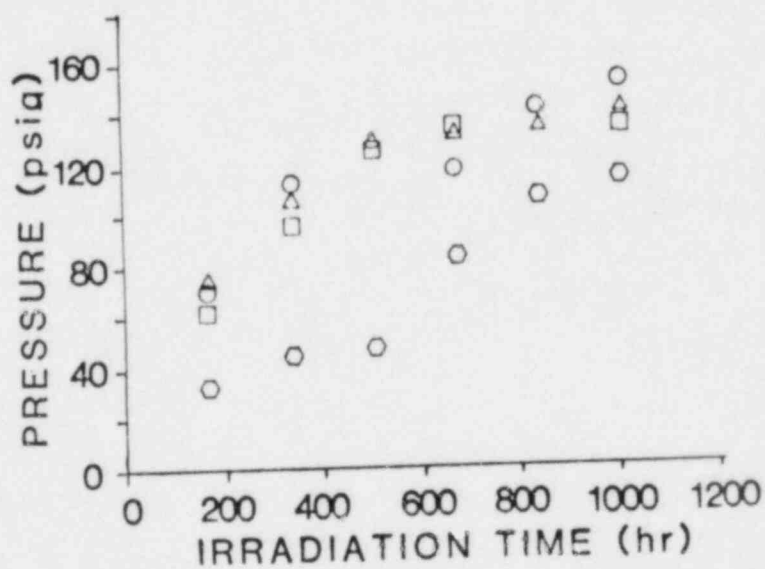
Figure 3.4   Sample cell pressure vs irradiation time at different dose rates for H$^+$ form IRN-77 resin, contacted with mild steel coupons. Irradiation dose rates (rad/h):   o - 1.7 x 10^6; □ - 1 x 10^5; △ - 4 x 10^4; ◯ - unirradiated.

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Table 3.1 gives the percent composition of the gas phase over the resins in the various experiments. Without exception, the nitrogen/argon ratios agree closely with the expected value for air; there is no evidence for nitrogen uptake. The gases which are generated are hydrogen and carbon dioxide. These two gases do not occur in a fixed ratio for all conditions. In the sodium form resin containing corrosion coupons, samples irradiated at low dose rates show an uptake of atmospheric oxygen which is approximately balanced by the formation of CO_2. In samples irradiated at high dose rates which show substantial hydrogen generation, the amount of CO_2 present is greater than that anticipated on the basis of conversion of O_2 to CO_2. This is demonstrated in Table 3.2 giving the ratios O_2/Ar and CO_2/Ar and their sum, which should remain at approximately 22.4 if the only mechanism involved is the conversion of O_2 to CO_2.

Table 3.1

Atmospheric Compositions Over
Irradiated Resins (Contact Time 1030 h)

Sample	Percent Composition								
Form	H_2	O_2	N_2	Ar	CO	CO_2	NO_x	SO_2	H_2O
Na^+/Coupon:									
0 rad/h	0	20.5	77.4	0.93	0.6	0.41	0	0	0.14
4×10^4 rad/h	2.31	1.70	75.1	0.89	0	19.2	0	0	0.60
1×10^5 rad/h	7.31	0.92	70.4	0.95	0	19.6	0	0	0.40
1.7×10^6 rad/h	82.3	0.13	11.4	0.16	0	5.90	0	0	0.12
Na^+:									
0 rad/h	0	20.1	76.6	0.91	0.6	1.68	0	0	.06
4×10^4 rad/h	0.56	19.8	76.1	0.91	0.7	1.79	0	0	.09
1×10^5 rad/h	--	--	--	--	--	--	--	--	--
1.7×10^6 rad/h	65.8	0.42	19.9	0.26	0	13.4	0	0	0.17
H^+/Coupon:									
0 rad/h	73.2	4.1	21.0	0.26	0	1.00	0	0	0.21
4×10^4 rad/h	80.3	2.7	15.7	0.20	0	0.68	0	0	0.20
1×10^5 rad/h	76.3	4.8	18.9	0.23	0	0.48	0	0	0.20
1.7×10^6 rad/h	90.3	2.9	15.4	0.20	0	0.82	0	0	0.20

Table 3.2

Relative Concentrations of O_2 and CO_2 in the Atmosphere of Irradiated Resin Samples

Sample Form	O_2/Ar	CO_2/Ar	$CO_2 + O_2$/Ar
Na^+/Coupon:			
0 rad/h	22	0.44	23
4×10^4 rad/h	1.9	23	23
1×10^5 rad/h	0.92	21	22
1×10^6 rad/h	0.81	37	38
Na^+:			
0 rad/h	22	1.9	24
4×10^4 rad/h	21	2.0	24
1×10^5 rad/h	--	--	--
1×10^6 rad/h	1.8	52	54
H^+Coupon:			
0 rad/h	16	3.9	20
4×10^4 rad/h	14	3.4	17
1×10^5 rad/h	17	2.1	19
1×10^6 rad/h	15	4.1	19

Evidently, for the Na^+ form samples, oxygen may initially be taken up by a mechanism which can be described as the conversion of atmospheric oxygen to CO_2. At greater doses (or higher dose rates), CO_2 is generated by another mechanism, presumably involving oxygen initially present in the resin or incorporated water. For the H^+ resin with corrosion coupons, the net concentration of O_2 and CO_2 is lower than anticipated on the basis of a constant inventory of oxygen in the gas phase. In this case, it is likely that oxygen is consumed in some additional process - possibly corrosion.

3.3 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. Coupon preparation and weight loss determination methods have been described previously (Swyler and Weiss, 1981). As indicated earlier, the present results refer to irradiations carried out in sealed glass vessels. Figure 3.5 shows weight loss for coupons contacted with sodium form resin and irradiated at various dose rates. Similar data for H^+ form resin are shown in Figure 3.6.

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 slope of the curve in Figure 3.5, increases with increasing dose rate.

Figure 3.5   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;
             △ - 4 x 10^4
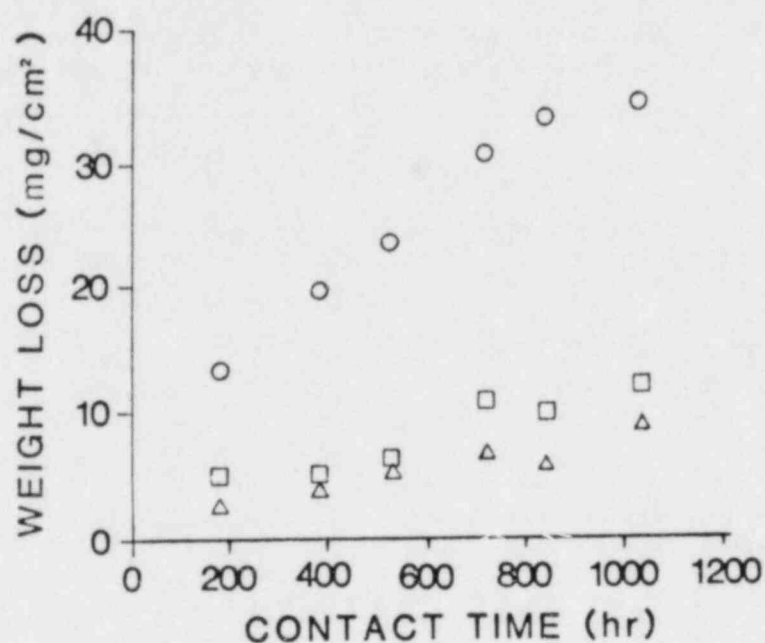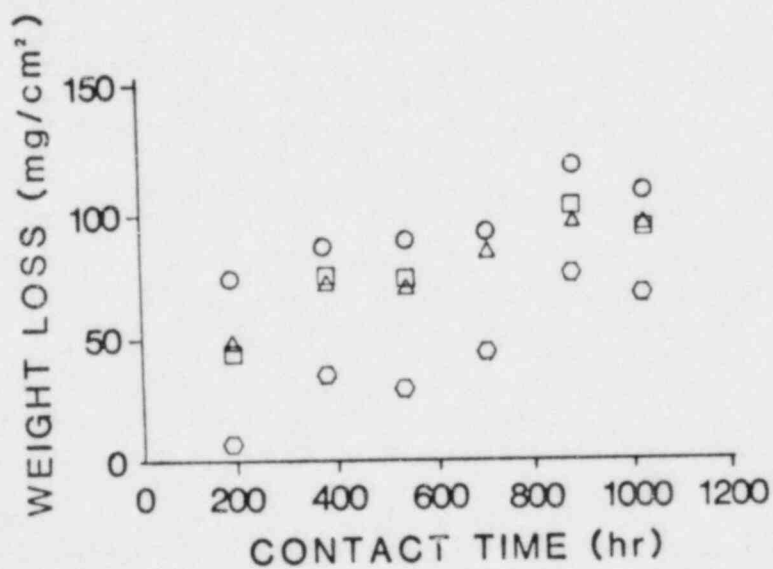

Figure 3.6   Corrosion weight loss for mild steel coupons contacted with
             H$^+$ form IRN-77 resin and irradiated at different dose rates.
             Dose rates (rad/h):   o - 1.7 x 10^6; □ - 1 x 10^5;
             △ - 4 x 10^4; ⊘ - unirradiated.

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In contrast, there is significant corrosion occurring in coupons contacted with unirradiated samples of IRN-77 resin in the H^+ form. Figure 3.6 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. There is some evidence that the curves start to level off for a weight loss of approximately 120 mg/cm^3. Figure 3.6 suggests that the rate at which this "asymptotic" region is approached may depend on radiation dose rate, but the asymptotic corrosion behavior is not strongly influenced by dose rate.

There is a remarkable similarity between the gas generation curves for the H^+ form resin in Figure 3.4 and the corrosion weight loss curves in Figure 3.6. If the data from Figure 3.4 and 3.6 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.

In Table 3.3, we have listed corrosion rates estimated from the slopes of the curves shown in Figure 3.5 and 3.6. At this point, the values are subject to considerable uncertainty. They demonstrate however, that in hydrogen form resin, the major radiation dose rate effects on corrosion rate occur during the early stages of corrosion. The corrosion rate values do not seem to depend strongly on dose rate. For the sodium form, corrosion rates are at least an order of magnitude lower than the initial corrosion rates in the corresponding samples of H^+ form resin. Also, saturation conditions have not been clearly reached in the Na^+ form resin. Corrosion rates still appear to depend on dose rate after 1000 hours contact time. Finally, the corrosion rate in the sodium form resin apparently does not scale linearly with radiation dose. The present data for sodium form resin suggest that, at a given total dose, corrosion will be greater at lower dose rates. In Figure 3.7, weight loss is plotted vs total dose for Na^+ form resin. Extrapolation of the low dose rate data indicates that under conditions of constant radiation dose, corrosion at 4×10^4 rad/h may be about 4 times greater than that at 1.7×10^6 rad/h. Long-term irradiations (up to 10^9 rad) at 10^5 and 4×10^4 rad/h are presently under way, to directly compare net corrosion at comparable doses.

The curves in Figures 3.5 and, particularly, 3.6 indicate that the initial effect of irradiation may be to promote the relatively rapid attack on a surface film. Further coupon characterization will be carried out to examine this effect. In any event, once this early stage is past, corrosion rates in Na^+ form and H^+ form resin at dose rate of 1.7×10^6 rad/h become more nearly comparable (Table 3.3).

At 3×10^8 rad, the ratio of net corrosion weight loss in H^+ form resin to that in Na^+ form at a dose rate of 1.7×10^6 rad/h. This is in reasonable agreement with previous results (Swyler and Weiss, 1981). There, however, substantial corrosion was also observed for coupons contacted with unirradiated Na^+ form resin. This is not observed in the present experiments, possibly due to differences in the initial pH of the Na^+ form samples. (See Section 3.4 also.)

Table 3.3

Mild Steel Corrosion Rates in Irradiated Resins

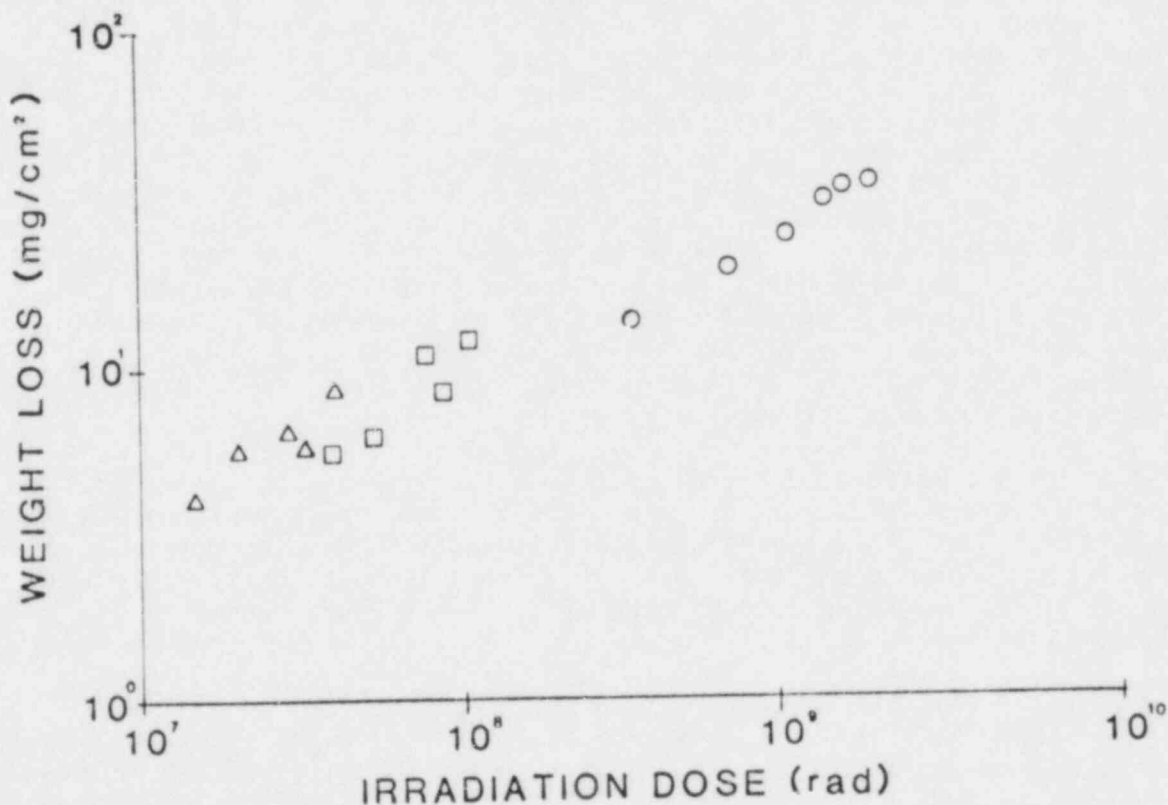| Resin Type	Radiation Dose Rate (rad/h)	Corrosion Rate $(g/cm^2)/h$		Total Corrosion Weight Loss (g)
		Initial (200 h)	Final (1000 h)	
H^+	0	7×10^{-2}	7×10^{-2}	0.282
	4×10^4	2×10^{-1}	4×10^{-2} a	0.394
	1×10^5	2×10^{-1}	4×10^{-2} a	0.401
	2×10^6	4×10^{-1}	3×10^{-2} a	0.452
Na^+	0	----	----	0.010
	4×10^4	5×10^{-3} =	5×10^{-3}	0.037
	1×10^5	1×10^{-2} =	1×10^{-2}	0.053
	2×10^6	7×10^{-2}	3×10^{-2} a	0.143

aCorrosion may be approaching saturation.

Figure 3.7 Corrosion weight loss vs radiation dose at different dose rates for mild steel coupons contacted with Na^+ form IRN-77 resin. Dose rate (rad/h). o - 1.7×10^6; □ - 1×10^5; △ - 4×10^4.

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3.4 Acid Product Formation

Following irradiation, two grams of the various resin samples were contacted with 10 mL of deionized water. The pH of the supernate was determined in a manner described previously (Swyler and Weiss, 1981). In a separate series of measurements, pH is being determined on 5-mL aliquots withdrawn from the supernate. The objective is to determine which method provides a better measure of the yield of acidic species and other decomposition products. Thus far, there does not appear to be any gross difference in the results obtained with the two techniques.

The evolution of supernatant pH with irradiation time at various dose rates is shown in Figure 3.8 for sodium and hydrogen form resins containing corrosion coupons, and for the sodium form resin alone. Irradiation decreases the supernatant pH in accord with previous observations. The pH, however, is strongly influenced by the corrosion process. In samples with corrosion coupons, the pH tends to steady values which are substantially higher than those measured in the absence of corrosion. Data on H^+ form resin have been reported previously (Swyler and Weiss, 1981); there a pH approaching 1.0 was observed for samples irradiated to 10^9 rad without corrosion coupons. In the presence of corrosion, the steady value of supernate pH is roughly 3. In the sodium form resin without a corrosion coupon, the pH approaches 2 in heavily irradiated samples. With corrosion coupons, Figure 3.8 suggests a steady pH value near 4 which is approached more rapidly at higher dose rates.

To the extent that supernate pH values reflect actual conditions in the resin, corrosion evidently tends to stabilize the H^+ ion concentration as the irradiation proceeds. This may occur 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. Iron is known to provide such a protective effect (Egorov and Novokov, 1967). 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. Further insight may be gained by examining the formation of soluble sulfate, which reflects radiation damage at the exchange sites (Section 3.4) and the nature and spatial extent of corrosion product uptake (Sections 3.2, 3.5, and 6.2).

For the Na^+ form resin without corrosion coupons, hydrogen ion can be well fitted to an expression of the form

$$[H^+] = C\phi + [H^+]^0 \tag{2}$$

where ϕ is the radiation dose and C is a constant, independent of dose rate over the range of approximately 10^4-10^6 rad/h. This behavior is shown in Figure 3.9. C is approximately 5×10^{-12} moles/liter-rad giving a hydrogen "yield" of 2.5×10^{-2} H^+ ions/100 eV for the Na^+ form resin. This is about 50 times smaller than the yield found earlier (Swyler and Weiss, 1981) for the H^+ form resin irradiated in vented vessels. It should also be noted

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that expression (2) differs from that previously proposed for irradiation of Na$^+$ form resin in vented vessels. There, preliminary analysis suggested that $[H^+] \sim \phi^{3/2}$.
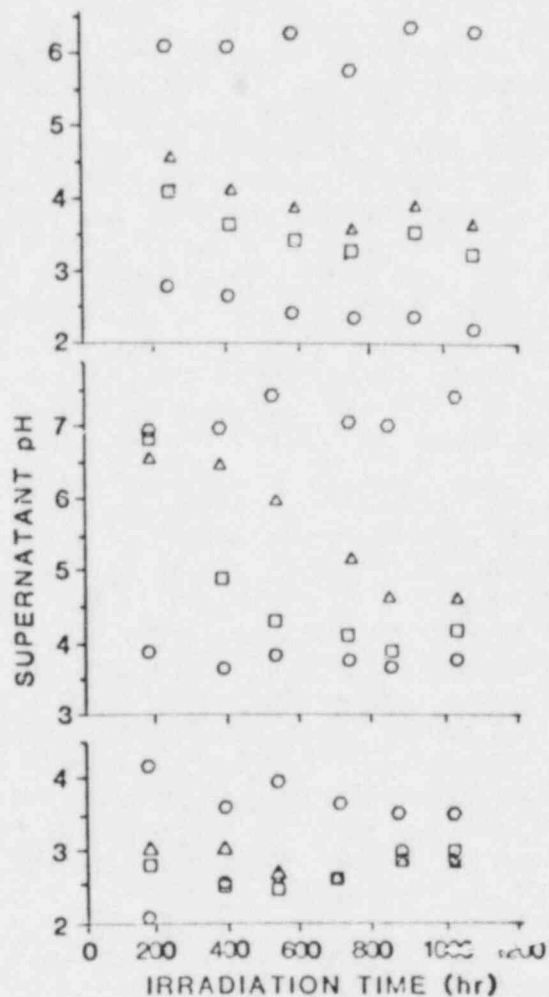
Figure 3.8   Supernatant pH vs irradiation time for various forms of IRN-77 irradiated at different dose rates. Upper: Na$^+$ form resin; Middle: Na$^+$ form resin + corrosion coupon; Lower: H$^+$ form resin + corrosion coupon. Dose rates (rad/h). o - 1.7 x 10^6; □ - 1 x 10^5; △ - 4 x 10^4; ⬡ - unirradiated.

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SUPERNATANT pH

5

4

3

2

1

10^7   10^8   10^9   10^10

IRRADIATION DOSE (rad)
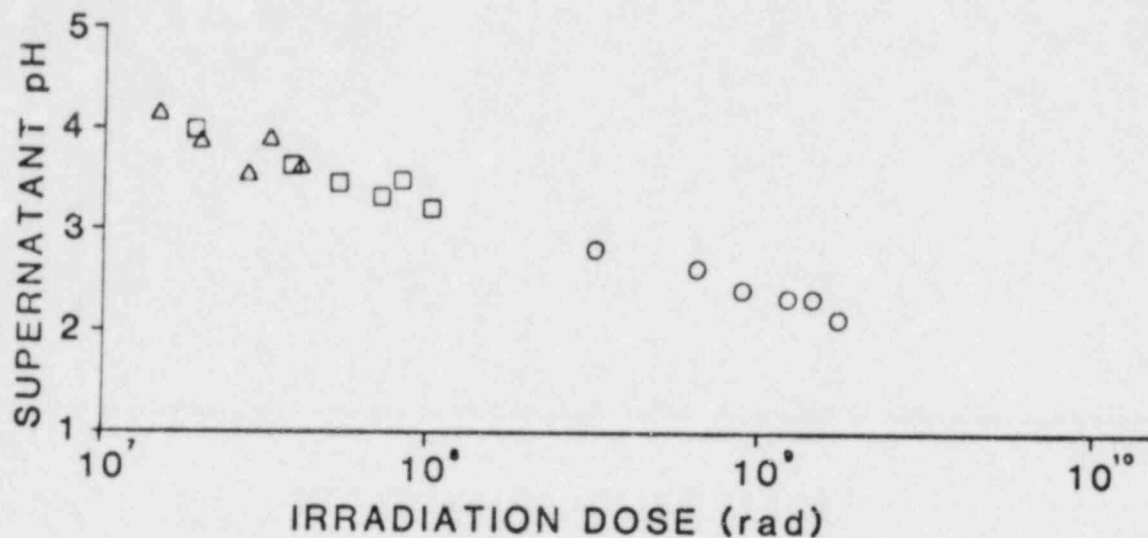
Figure 3.9   Supernatant pH vs radiation dose at different dose rates in
Na$^+$ form IRN-77 resin. Dose rate (rad/h) o - 1.7 x 10^6;
□ - 1 x 10^5: △ - 4 x 10^4.

3.5   Sulfate and Soluble Iron Analysis

The supernatant solutions over H$^+$ form resins containing corrosion cou-
pons were analyzed for sulfate and iron. The sulfate analysis techniques have
been described previously (Swyler and Weiss, 1981). Iron was detected by
atomic absorption. The toal amount of each species present in solution was
determined (in moles) from the measured solution concentration and the total
volume of supernate (10 mL) in contact with the resin.

Table 3.4 indicates that increasing amounts of free sulfate are present
in the unirradiated samples. Most of this, however, is stoichiometrically
balanced by radiation dose. The highest levels correspond to approximately
25% of the sulfate and soluble iron levels become more nearly balanced. This
suggests that, as the irradiation proceeds, the pH is stabilized by the forma-
tion of iron sulfates; the iron effectively replaces hydrogen ions generated
in the radiolytic decomposition of sulfonic functional groups.

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Table 3.4

Sulfate and Soluble Iron Levels in the
Supernate of Irradiated H^+ Form Resin

Dose Rate (rad/h)	Contact/ Irradiation Time (h)	Dose (rad)	Moles[a] $SO_4^=$	Moles[a] Soluble Fe	Moles[b] Insoluble Fe
0	191	0	4.2×10^{-7}	----	5.7×10^{-4}
	372	0	3.6×10^{-6}	----	2.7×10^{-3}
	533	0	1.8×10^{-6}	----	2.0×10^{-3}
	698	0	3.9×10^{-6}	----	3.2×10^{-3}
	871	0	5.7×10^{-6}	10^{-7}	5.7×10^{-3}
	1018	0	1.1×10^{-5}	2×10^{-7}	5.0×10^{-3}
3.87×10^4	191	7.4×10^6	1.1×10^{-5}	----	3.4×10^{-3}
	372	1.4×10^7	1.7×10^{-5}	10^{-7}	5.6×10^{-3}
	533	2.1×10^7	3.4×10^{-5}	10^{-5}	5.4×10^{-3}
	698	2.7×10^7	3.8×10^{-5}	10^{-5}	6.2×10^{-3}
	871	3.4×10^7	3.8×10^{-5}	2×10^{-5}	8.1×10^{-3}
	1018	4.0×10^7	3.6×10^{-5}	2×10^{-5}	7.0×10^{-3}
1.0×10^5	191	1.9×10^7	1.8×10^{-5}	----	3.6×10^{-3}
	372	3.7×10^7	3.5×10^{-5}	10^{-7}	5.4×10^{-3}
	533	5.3×10^7	7.3×10^{-5}	2×10^{-5}	5.3×10^{-3}
	698	7.0×10^7	6.9×10^{-5}	4×10^{-5}	6.4×10^{-3}
	871	8.7×10^7	7.1×10^{-5}	4×10^{-5}	7.2×10^{-3}
	1018	1.1×10^8	8.2×10^{-5}	5×10^{-5}	7.1×10^{-3}
1.7×10^6	191	3.3×10^8	3.2×10^{-5}	1×10^{-4}	5.5×10^{-3}
	372	6.3×10^8	2.6×10^{-4}	1×10^{-4}	6.5×10^{-3}
	533	9.1×10^8	3.9×10^{-4}	2×10^{-4}	6.7×10^{-3}
	698	1.2×10^9	3.9×10^{-4}	2×10^{-4}	6.8×10^{-3}
	871	1.5×10^9	7.8×10^{-4}	4×10^{-4}	6.5×10^{-3}
	1018	1.7×10^9	8.5×10^{-4}	5×10^{-4}	7.6×10^{-3}

[a]Total amount present in (10 mL) supernatant solution over (2 g) resin.
[b]Insoluble iron was determined as the difference between corrosion coupon
weight loss and soluble iron, assuming the coupon is 100% iron.

Where comparison is possible, sulfate levels indicated in Table 3.4 are
somewhat lower than those found earlier under somewhat different irradiation
conditions (Swyler and Weiss, 1981, Tables 3.3 and 5.1). G-values have been
estimated from linear fits to the data in Table 3.4 at 1.0×10^5 rad/h and
1.7×10^6 rad/h. The respective values are 0.4 and 0.3, roughly half those
found earlier. Possibly some of the difference could reflect either the dif-
ference in irradiation atmosphere (sealed vs vented conditions) or a protec-
tive effect due to coupon corrosion. (More importantly, however, the prelimi-
nary G-values do not indicate a significant dose rate effect in sulfate
formation.)

Examining the correlation between pH (Figure 3.8) and sulfate formation
(Table 3.4) for H^+ form resin contacted with corrosion coupons provides
further evidence for loss of hydrogen in the corrosion process. Based on
earlier work indicating that the dominant acidic species is H_2SO_4, the pH
for a net $SO_4^=$ generation of 8.5×10^{-4} moles of should be approximately
1. Instead, a value of approximately 3 is measured. Evidently, the fate of

hydrogen ion formed in attack on exchange sites depends strongly on corrosion mechanisms.

3.6 Visual Examination and Absorption Spectroscopy

Both corrosion and irradiation produce color changes in IRN 77 resin. A pronounced darkening of the resin takes place in the immediate vicinity of a mild steel coupon which is undergoing corrosion. This effect occurs in both irradiated and unirradiated samples, in both sealed and vented atmospheres, and is almost certainly associated with the uptake of corrosion products by the resin. Consequently, the spatial _ _ent of the darkened region (Figure 3.10) may provide a measure of the effective (transport-limited) resin volume which contributes to corrosion in a given geometry.

Mild steel corrosion alone does not produce visible coloring of the supernate formed by contacting deionized water (D.I.W.) with H^+ form resin. Soluble species which absorb visible light appear to be uniquely associated with irradiation induced degradation. Optical absorption measurements have been carried out on supernates formed from D.I.W. and H^+ form resin after irradiation as described above. Absorption spectra are also given for unirradiated control samples. The present data refer entirely to the samples contacted with corrosion coupons for 1018 hours (Figure 3.11).

In the visible region, the spectra are relatively featureless. For unirradiated samples, the U.V. spectrum shows peaks at approximately 250 and 285 μm, and a U.V. edge at 190 μm (lower curve). Results are essentially similar for samples irradiated at 4×10^4 rad/h during contact (not shown). However, irradiation leads to changes in the spectra (upper curve). These include a growth and shift of the absorption band near 285 μm and emergence of a broad feature which fills in the region between the 250 μm band and the U.V. edge. The new features become quite intense with increasing radiation dose; the long wavelength tail of the 285 μm band accounts for most of the visible coloring. As discussed below, efforts are under way to correlate these spectral features with particular decomposition products.

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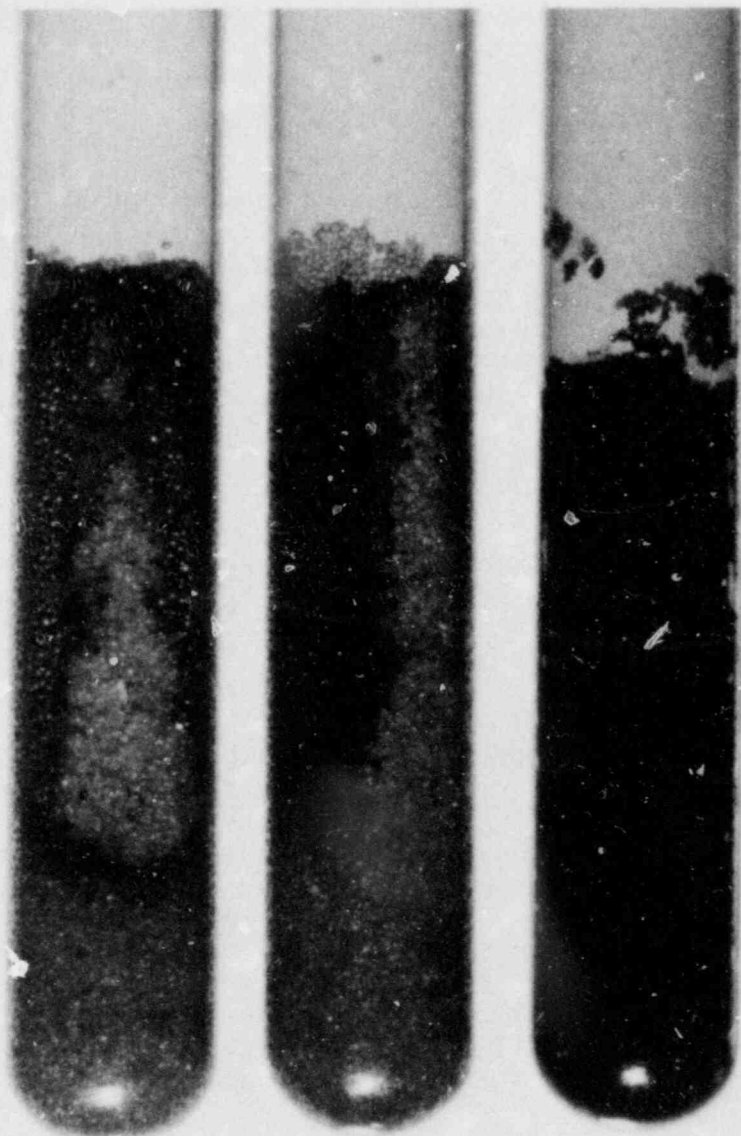
Figure 3.10 Resin blackening in irradiated Na+ form resin containing mild steel corrosion coupons. Dose rates: left, 4×10^4 rad/h; center, 1×10^5 rad/h; right, 1.7×10^6 rad/h. Irradiation time 2189 h. The light vertical regions in the left and center samples match the edges on the coupons.

Figure 3.11   U.V. absorption spectra of the supernates formed from H⁺ IRN-77 resin containing corrosion coupons. Upper curve: irradiated at 1.7×10^6 rad/h; lower curve-unirradiated. Contact times - 1018 h.

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4.   CHARACTERIZATION OF IRRADIATION EFFECTS ?! INORGANIC ION-EXCHANGE MEDIA*

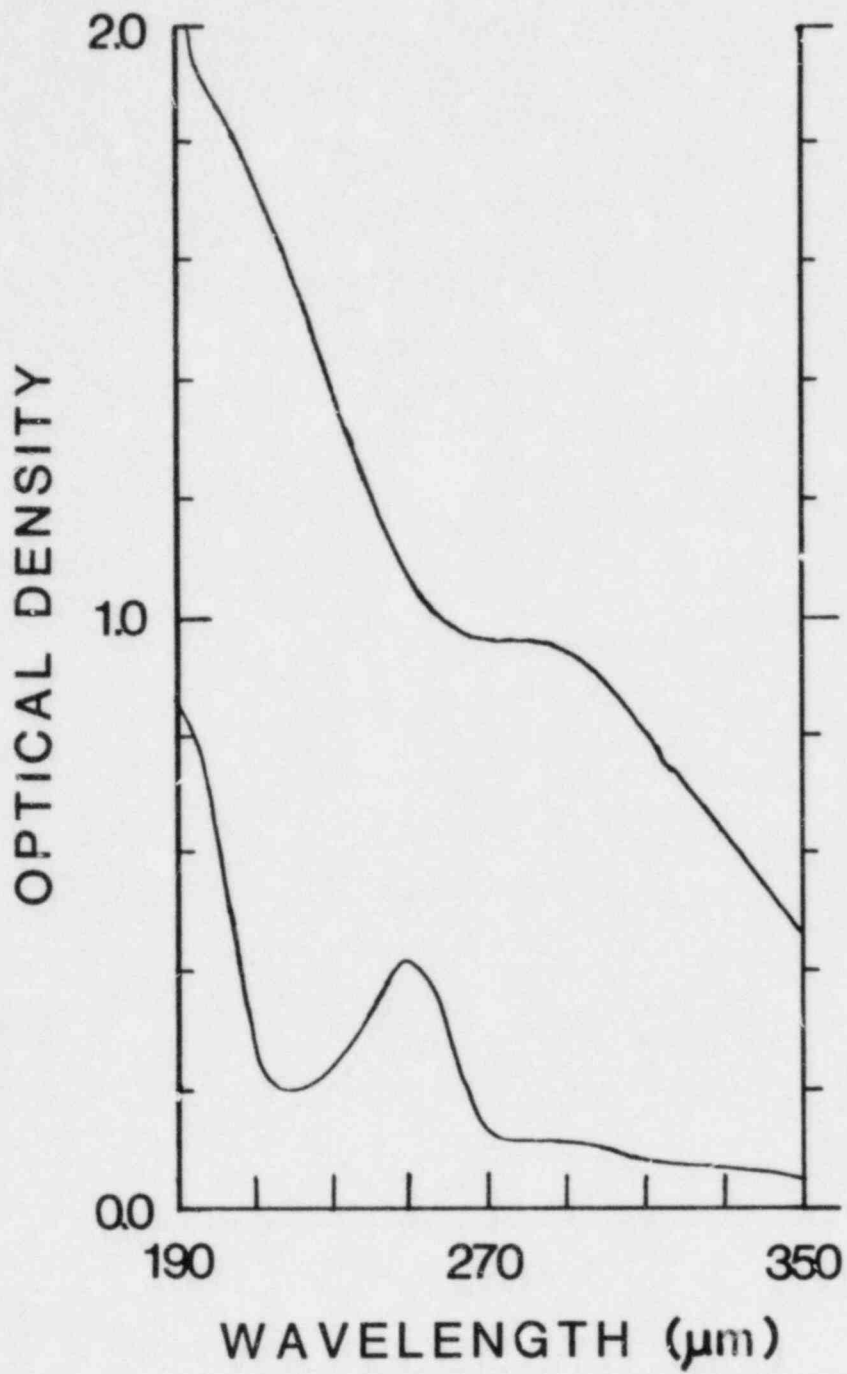Recently, the NRC has been sponsoring a technical assistance task in our laboratory (FIN A-3162, Task 6C) to investigate the effects of irradiation on a chabazite zeolite. The particular material (Linde IE-95) and experimental parameters were chosen to simulate conditions anticipated in decontaminating water in the TMI-II containment building. This task was completed and a draft report issued in the first quarter of FY 1982 (Swyler and Barletta, 1981).

The results of this study have a direct bearing on the scope of the present research task. Present indications are that the ion exchange and structural properties of zeolites specifically chabazite are not particularly sensitive to ionizing radiation. Consequently, only a limited amount of work is contemplated to establish a threshold radiation dose at which damage effects become observable in zeolite materials. Present plans involve a more detailed characterization of those factors which govern radiolytic gas generation from incorporated water.

Given that zeolites will probably play an important role in any future decontamination operation: resulting from off-normal operations, we are presently attempting to identify other areas where the existing data base may be inadequate to support detailed licensing assessments. These may include, for example, the possibility of synergistic or catalytic effects with other waste stream components, and compatibility with processing steps such as solidification, etc.

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*Noted added in proof: as of the second quarter of FY 1982, this task is to be dropped from the project (see page 2).

5.   CHARACTERIZATION of IRRADIATION EFFECTS ON SOLIDIFIED FORMS

This task is not scheduled to begin until the second quarter of FY 1982. In view of recent suggestions that disposal of highly loaded spent resins in a high-integrity container may be a preferable alternative to solidification, we are considering some reduction of the present task. Current plans are to begin experimental solidification studies with heavily irradiated resins using water/Portland cement mixtures (Morcos and Weiss, 1981). Initial emphasis will be placed on determining how resin irradiation affects solidification process latitude.

5. MECHANISTIC STUDIES AND DEVELOPMENT OF TEST PROCEDURES

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

Earlier measurements described (Swyler and Weiss) have addressed the role of peroxides in the irradiation-induced degradation of ion-exchange media, and considered the equivalence of electron and gamma irradiation in prompting radiation damage. These measurements are continuing. Samples have been prepared to determine if degradation is enhanced when resin is irradiated in the presence of peroxide. The accelerator used in the electron irradiation experiments is presently being upgraded; experiments will resume during the next quarter. In addition, other measurements were initiated to study the protective effect (in terms of acid product formation) observed with Na^+ form resins, and to spectroscopically examine the corrosion products taken up by resin contacted with corrosion coupons.

6.1 Self-Buffering Effects in Sodium Form Resins

Earlier, based on the correlation between pH change and $SO_4^=$ formation in irradiated resins, it was speculated that hydrogen ions produced by radiolytic attack on exchange groups could be exchanged at undamaged sites. This would account for the protective effect, relative to radiolytic acid product formation, observed with Na^+ form resin (Section 3.3). One attractive feature of this mechanism is that it does not require that Na^+ protect the exchange groups against intrinsic damage. This would be contrary to experience (Egorov and Novokov, 1967).

To determine if this mechanism is plausible, measurements were carried out to determine the ability of Na^+ form resin to take up H^+ ion from H_2SO_4 solution. In what is sensibly a titration technique, 2-g samples of IRN-77 resin in the sodium form were added to 10-mL solutions of sulfuric acid in various molarities. The pH of the H_2SO_4 solution was measured with a glass electrode before and after the resin addition allowing time (17 hr) for the system to equilibrate. Results are given in Table 6.1.

A significant H^+ uptake by the resin is clearly evident. Moreover, the magnitude of the pH elevation is about what would be required to account for the relatively low (1:10) ratios of $[H^+]$ to $[SO_4^=]$ previously observed. It appears then, that the mechanism is at least a plausible means of accounting for the protection effect of Na^+ loading. If the protection mechanism does in fact depend on the ability of the resin to uptake its own decomposition products, then radiation effects on exchange capacity which do not involve scission of functional groups (Egorov and Novokov, 1967) may be important in the protection mechanism. Possibly, such effects could account for the different functional relations observed for acid formation in Na^+ form resin.

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To maintain a critical perspective, however, it is not yet clear that the hypothetical protection mechanism would lead to a linear relationship of the type shown in Figure 3.9.

Table 6.1

pH Elevation of H_2SO_4 Solutions (10 mL) by
Sodium Form IRN-77 Resin (2 g)

H_2SO_4 Solution Molarity[a]	0.0	0.005	0.005	0.5	2.5
Solution pH	5.6	2.7	2.1	1.0	0.8
Solution + Resin pH	4.0	3.7	2.8	1.4	1.0

[a]All molarities are approximate.

6.2 Investigations of the Interactions Between Resin and Corrosion Products

Corrosion effects on resin chemical loading may be of particular mechanistic interest, since Fe ion is said to improve resin radiation resistance. It has been mentioned by Egorov and Novikov that when H^+ ions of the irradiated resin are exchanged for Fe^{+3} ions, the resin turns black. This effect is said to be an indirect confirmation of the presence of carboxylic and phenolic groups in the irradiated resin, since sulfosalicylic acid, which contains these groups, is known to form a dark colored complex with Fe^{+3} ions. The sulfosalicylic acid would presumably result from radiolytic attack on the resin backbone.

In order to determine if this effect was responsible for darkening of resins contacted with corrosion coupons, irradiated and unirradiated H^+ form resins were contacted with Fe^{+2} and Fe^{+3} ions in solution to see if dark regions were formed. The following experiment was set up:

0.1 g of $FeSO_4$ was made up to 25 mL with $0.1MH_2SO_4$.

0.1 g of $Fe_2(SO_4)_3$ was made up to 25 mL with $0.1MH_2SO_4$.

0.1 g of sulfosalicylic acid was made up to 25 mL with $0.1MH_2SO_4$.

Approximately 1 g portions of irradiated (3×10^8 rad) and nonirradiated IRN-77 H^+ form resin were put into separate containers. Fe^{+2}/H_2SO_4 was added to one set and Fe^{+3}/H_2SO_4 was added to another set of irradiated and nonirradiated resins. After three days, the irradiated resin turned black in the presence of Fe^{+2} and Fe^{+3} solutions while the nonirradiated resin showed no color change. Next, Fe^{+2}/H_2SO_4 solutions were added to the sulfosalicylic acid (SSA) solution in the ratio 1:1. The Fe^{+2} and SSA remained clear while the Fe^{+3} solution with SSA turned pink. This experiment effectively rules out the formation of sulfosalicylic acid as the final form of the irradiated species, because the Fe^{+2} turned the irradiated resin black, but not the SSA solution. In other words, no color change would be affected between Fe^{+2} and SSA produced in the radiated resin. Ultraviolet absorption spectrum was also run with SSA. These did not agree at all with the spectra of the supernate above the resin.

It is interesting that a mild steel coupon placed in contact with an unirradiated resin will turn the resin black, but a solution of Fe^{+2} or Fe^{+3} ions added to unirradiated resin has no effect. The corrosion induced blackening of an unirradiated resin evidently does not involve simple uptake of Fe^{+2} or Fe^{+3}. For irradiated resins, the present data does not rule out corrosion induced blackening by simple iron uptake. The sites at which the uptake occurs, however, cannot be equivalent to those in unirradiated resins.

7. SUMMARY AND CONCLUSIONS

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

Thus far, there is no evidence for a pronounced radiation dose rate effect in the radiation-induced decomposition of (fully swollen) IRN-77 resin, irradiated in closed systems.

In other words, a given radiation dose appears to produce a given amount of damage (in terms of acidic species and sulfate formation) which does not strongly depend on a radiation dose rate. Additional data are required to confirm this early trend. Also dose rate effects, presumably involving the formation of hydroperoxides, have been observed when certain polymers are irradiated in open systems containing atmospheric oxygen (Gillen and Clough, 1981). The present results, however, support the validity of accelerated testing at high dose rates, as proposed in current NRC Technical Assistance Documents (MacKenzie, Lin, and Barletta, 1981).

There is a substantial interaction between mild steel coupons and acidic species produced in the irradiation-induced decomposition of IRN-77 resin.

The interaction is such that initial corrosion rates are substantially increased by irradiation, and local pH values tend to steady concentrations independent of dose rate. The results of this interaction are as follows: Initially, corrosion rates are greatest 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, and do not depend strongly on dose rate. For others (Na^+ form resin) although corrosion rates are lower, this asymptotic behavior has not yet been observed.

One may speculate that a rate limiting process in radiation enhanced corrosion may be the mechanism by which steady pH conditions are achieved. Once this occurs, additional radiolytic H^+ ion is either taken up in this corrosion process or generated at greatly reduced rates. To examine this possibility in detail will require an examination of the correlation between pH change, corrosion weight loss, H_2 gas generation and damage to the resin exchange sites. In any event, the practical implications are as follows.

- First, for a given radiation dose, experiments at accelerated dose rates may tend to underestimate the net corrosion which will occur at low dose rates under field conditions.

- Second, in terms of corrosion weight loss, a conservative estimate can probably be obtained by extrapolating initial data determined in accelerated testing (i.e., at high dose rate) to long contact times.

- Third, since the present data indicate that corrosion may tend to saturate with increasing contact time, a preferable alternative would

be to determine how the saturation levels scale with radiation dose rate. However, saturation levels may be vastly more sensitive to external conditions than initial corrosion rates. For example, comparison of the present data with previous results for H^+ form resin (Swyler and Weiss, 1981) suggests that saturation weight loss depends sensitively on venting conditions (and presumably, moisture loss) during contact.

Substantial amounts of hydrogen gas can be generated in the corrosion of mild steel in IRN-77 resin. At the same time, oxygen is unquestionably removed from the environment of irradiated resins. This scavenging is quite effective at low dose rates and total doses.

The magnitude of this effect depends on resin loading as does corrosion, and may be also connected with the "steady" pH value. Initial data indicate roughly one mole of H_2 generated for every mole of Fe contained in corrosion.

Initial data suggest that the O_2 scavenging effect may partly involve a radiolytic conversion of O_2 to CO_2. If this is in fact the case, the ultimate oxidized species (i.e., CO_2) is sufficiently stable as to sensibly eliminate licensing concern over formation of an explosive mixture of oxygen and radiolytic hydrogen in sealed containers in vented (or leaky) storage containers. It is also possible that hydroperoxides or stable peroxides are involved as intermediate or final species (Egorov and Novokov, 1967, Gillen and Clough, 1981). In any event, the amount of oxygen present will depend, among other factors, on the specific O_2 oxygen uptake capacity or uptake rate for the resins. Measurements in this area are currently under way.

The "protective effect" (or low pH yield) encountered in Na^+ form resin is at least qualitatively consistent with an uptake of radiolytic H^+ ion by the resin itself.

This mechanistic observation, if confirmed by future experiments, holds several practical implications. First, the protective effect should be directly related to the capacity of an irradiated resin to take up H^+, which is a parameter which can be directly measured and, in some cases, controlled. Second, it indicates that the resin chemical loading may be modified by irradiation - conceivably, resin which begins as Na^+ form may be partially converted to H^+ form by irradiation. Such a conversion, if it is in fact effective, would have implications for subsequent processing and solidification.

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