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CHARACTERIZATION OF TMI-TYPE WASTES
AND SOLID PRODUCTS

QUARTERLY PROGRESS REPORT
JANUARY - MARCH 1982

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QUARTERLY PROGRESS REPORT
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ABSTRACT

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

Present results indicate a G value of 0.12 for radiolytic hydrogen generation from fully swollen H^+ form IRN-77 resin irradiated in a sealed air environment. Thus far there is no evidence that gas generation yields under these conditions depend sensitively on radiation dose rate, pH conditions or resin loading. Similarly, radiolytic attack on the functional group of IRN-77 resin in the sodium form is not particularly sensitive to local pH conditions or the uptake of corrosion products - corrosion will not "protect" the resin. Chemical aging and/or slow leaching have been observed to cause changes in the solution chemistry of irradiated resins once the irradiation is terminated. G values for $SO_4^=$ formation, determined from data on aged solutions of irradiated resins, decrease with increasing irrdiation dose. At this point, it is just possible that this reflects a radiation dose rate effect. Additional measurements have been initiated on solidification of irradiated resins in cement, and efforts to obtain field resin samples of irradiated resins are continuing.

CHARACTERIZATION OF TMI-TYPE WASTES AND SOLID PRODUCTS
QUARTERLY PROGRESS REPORT, JANUARY-MARCH 1982

1. INTRODUCTION

Brookhaven National Laboratory (BNL), under contract to the United States Nuclear Regulatory Commission (NRC), is presently carrying out a research program entitled, "Characterization of TMI-Type Wastes and Solid Products." The present document is the third progress report issued under this contract. Subsequent reports will be issued on a quarterly schedule.

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 ion exchange media subjected to high internal irradiation doses as a result of heavy radionuclide loadings. Previous experience in demineralization operations (for example at TMI-II) has indicated that in such materials, internal irradiation can produce effects of potential consequence in regard to licensing considerations. This program is aimed at generating information and developing test procedures which will permit characterization of the anticipated properties of ion-exchange waste products under field conditions. This involves four separate phases. First, a scoping study to determine the manner in which material properties of engineering interest might be altered by irradiation effects; second, an examination and delineation of those factors which govern the relationship between laboratory evaluations and field performance; third, a phenomenological/mechanistic description of the important radiation effects that may be anticipated for several generic materials under field conditions; and fourth, a specification of the type of tests which would adequately assess the radiation durability of a particular ion exchange waste product in a given licensing application.

The project has been reorganized as of January, 1981 into four separate tasks. Task 1 involves a characterization of field experience with heavily loaded ion exchange media. This is intended to provide a basis for comparison of laboratory and field results. Task 2 is a parametric study of the radiation induced degradation of organic ion exchange media. In Task 3 radiation effects on solidified forms or high integrity container materials for waste ion exchange media are to be characterized. Task 4 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.

A task defined previously (Swyler and Dayal, 1982) addressing irradiation effects in inorganic ion exchange media is no longer included in this project.

1.2 Scope of the Present Report

Early 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 vari-
ables on parameters which govern these phenomena. Effects of practical sig-
nificance 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, mois-
ture 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 (DVB)/sulfonic acid
cation resin and styrene-DVB/quartenary ammonium anion resin (MacKenzie, Lin,
and Barletta, 1981).

Later efforts (Swyler and Dayal, 1982) concentrated on characterizing
these various effects in terms of rates and yields, and on specifying the
effect of external variables on these yields. Most of this work falls under
Task 2. Major variables investigated are resin loading (H^+ form vs Na^+
form IRN-77 resin) and radiation dose rate; synergistic interaction between
corrosion and resin degradation were also examined. Experiments were carried
out under Task 4 investigating the role of irradiation-induced peroxides on
resin degradation, and self-buffering effects which could limit acid product
formation.

During the past report period, a major fraction of the effort was devoted
to completing the first phase of the radiation dose rate experiments on IRN-77
resin, under Task 2. Irradiation dose rate experiments on IRN-78 resin were
also initiated. In Task 3, experiments on solidification of irradiated resin
in cement were begun, in accordance with the program schedule. Experiments on
peroxide effects on radiation degradation continued in Task 4. In addition, a
series of corrosion experiments examined sulfuric acid attack and the trans-
port of corrosion products and acid species. A study of radiolytic oxygen up-
take by irradiated resins was also begun. In Task 1, negotiation continued
aimed at obtaining field samples of radionuclide loaded resins. Results of
these various activities are described below.

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 the Maine Yankee reactor site to explore the possibility of obtaining field resin samples. Inquiries were also made of personnel at the E.I. Hatch generating station. Communication continued between BNL and Battelle Columbus Laboratories, where Epicor II linear characterization experiments are underway. Results of these transactions are described below.

2.1 Visit to Maine Yankee Atomic Power Plant

D. R. MacKenzie and K. J. Swyler visited the Main Yankee plant in February, 1982 to obtain more detailed information on loading and availability of spent resins generated at this plant. MacKenzie's visit was sponsored by the NRC Technical Assistance Program (FIN A-3162).

It was established that, within the uncertainties of the sampling procedures, Maine Yankee had indeed shipped ion exchange resins with loadings as high as 125 Ci/ft^3, as reported in response to a survey conducted by BNL (MacKenzie, Lin, and Barletta, 1982). However, the bulk of the activity in these shipments was due to Co-58, whose half-life is 71 days. The large amounts of Co-58 were released into the reactor coolant prior to shut-downs for refueling, which occur roughly every 14 months. An oxidizing treatment of the coolant using peroxide caused release of the Co-58 from the interior surfaces of the reactor. The treatment was carried out to reduce the radiation level in the refueling operations area and thus reduce worker exposure. It succeeded very well in this, but considerable amounts of Co-58 were not removed by the reactor coolant cleanup beds and found their way into other parts of the system, where the Co-58 tended to plate out, thus increasing the radiation fields in other operations areas for several months and causing risk of increased worker exposure in those areas. The practice was eventually discontinued about 2 years ago since its overall benefit was debatable.

Maine Yankee personnel provided us with copies of analytical data sheets for reactor coolant samples taken just before addition of peroxide, and at intervals after addition, during the period in which the Co-58 level went through a maximum and began to decrease as it was removed by the coolant cleanup bed. After the Co-58 concentration in the coolant had levelled off, resins in the cleanup bed were transferred to a shipping container and dewatered for shipment.

Normally, between refuelings, the coolant cleanup resin would be changed every 2-3 months and the major long-lived activity normally was Cs-137. The shipping liners hold the equivalent of three coolant cleanup beds, but may contain material from other demineralizer systems, as well as from the coolant cleanup system. These shipments are more typical of what was shipped in the past and what is being shipped now than were those reported for the survey referred to above, and the curie loadings lately have been of the order of 1 Ci/ft^3 (of isotopes with $t_{1/2} > 5$ years).

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There is considerable uncertainty in the value obtained for the curie loading of the resins being shipped. This is due to the method of sampling the resins, not to the analytical methods used in determining their radioactivity content. Because of the high radiation field around the shipping liner, only one grab sample of 15-20 mL is taken. This is felt by the utility to be fairly representative, due to the mixing which occurs during transfer from the original beds to the spent resin holding tank and then to the shipping liners. Obviously, however, mixing may not be thorough enough to ensure a completely representative sample by simply dipping into the liner once. Analysis of the sample itself is straightforward. Several small portions are counted (10-20 mg portions because of the high activity level) to ensure that the resin within the grab sample is uniform.

It is clear that Maine Yankee correctly answered the question on the survey concerning maximum loading on resins for shipment. When questioned by phone, personnel at the plant stated that typical shipments were considerably below 125 Ci/ft^3, but did not give a figure. They also stated that the activity on the hot resins was due almost entirely to activation products rather than fission products, but did not specify Co-58. Considering the activation products to be largely Co-60, rather than Co-58, gives a misleading impression of the dose received by the resins. For example, Co-58 would deliver essentially all of its total dose, which is 1.4×10^7 rad for 125 Ci/ft^3, in a year. On the other hand, total dose from 125 Ci/ft^3 of Co-60 would be 9.1×10^8 rad, and in one year, the dose from Co-60 would be 1.15×10^8 rad. Thus, a loading of 125 Ci/ft^3 of Co-58 would not deliver a high enough dose to nuclear grade ion exchange resins to cause deleterious effects.

Since the doses presently being received by coolant cleanup resins at Maine Yankee are relatively low, they are not of interest from the point of view of radiation damage. However, it may be useful to obtain a sample for the purpose of characterizing a typical resin which has been used in the field. Ordinarily, spent resin samples are analyzed only for radionuclide content. Factors, such as pH, non-radioactive anion or cation loadings, exchange capacity, physical homogeniety, etc., may be of importance in solidification procedures or corrosion studies. A characterization of typical field resin samples would be useful in establishing the representativeness of various resin samples currently used in various programs at our laboratory. If desired, typical samples should be readily obtainable from the Maine Yankee plant.

2.2 Communication with E. I. Hatch Generating Station

In responding to a previous BNL questionnaire, Georgia Power Company personnel have indicated that spent resins with activites of roughly 60 Ci/ft^3 have been generated at the Hatch Reactor site; a major fraction of this activity was evidently due to long half-lived species - e.g. Cs^{137} (MacKenzie, Lin and Barletta, 1982). BNL is extremely interested in obtaining samples of such material and have inquired if any are in fact available. Under certain storage conditions, resins loaded at somewhat lower levels (approx. 10 Ci/ft^3 ^{137}Cs or ^{60}Co) would also be quite useful, and

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a detailed characterization of the chemical loading on typical spent resins might be of general interest. Telephone communications have not been completely successful in determining what spent resins (if any) might be conveniently available from this facility, and a written inquiry was forwarded in late March. We are awaiting a response.

2.3 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. This liner (PF-16) contains organic and inorganic ion exchange media. BCL personnel indicate that the mild steel liner wall will not be destructively tested, and that further core sampling of the liner content is no longer planned. Consequently, the BCL characterization experiments on this liner are essentially complete; results will be reviewed as they become available.

Since no further core sampling is planned the possibility of BNL obtaining portions of existing core samples was discussed. Availability is being determined at BCL; this presently appears promising. BCL personnel also indicated that characterization of an all organic resin Epicor-II liner is also being considered. They requested that part of this task might formally include providing field samples for BNL. Means of arranging this are presently being investigated.

2.4 Additional Field Experience at TMI-II

In addition to the loaded resins generated in the Epicor-II system, mixed-bed resins in the Let-down Demineralizer System (LDS) at TMI II may provide a useful field data base. These resins (IRN-154) have evidently been exposed to radiation doses estimated at 10^9 rad, under hydrothermal conditions. At present, scoping radiation durability tests on IRN-154 resin under similar conditions are contemplated in an NRC technical assistance program (FIN A-3162) at BNL. In the present project we will explore the possibility of obtaining field samples of LDS resins for comparative characterization.

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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. A series of six-week irradiations of Na^+ and H^+ form resin, at various dose rates, with and without corrosion coupons has now been completed. Certain results for the Na^+ form resins, with and without corrosion coupons, and the H^+ form resin with coupons, have been reported (Swyler and Weiss 1981; Swyler and Dayal, 1982). Results obtained during this report period are described below. These include gas generation and pH data for the H^+ form resin, and sulfate analysis data for the Na^+ form resin with and without corrosion coupons. In addition, measurements of the effect of irradiation on ion exchange capacity are reported here.

Long-term (> 6 months) irradiation of the various forms of IRN-77 resin at dose rates of approximately 4×10^6 rad/h and 10^5 rad/h are continuing. In addition, sealed tube irradiation on IRN-78 resin and vented tube IRN-77 resin were initiated. Results of these experiments, and additional spectroscopic and physical property (swelling, agglomeration, moisture retention) characterization of IRN-77 resins will be described in a future report.

3.1 Sample Preparation and Irradiation Procedures

The results presented here refer to samples of IRN-77 resin prepared and gamma irradiated in sealed Pyrex tubes, according to procedures described previously (Swyler and Dayal 1982, Section 3.1). The moisture content for the H^+ resin without corrosion coupons was determined both by oven drying, as described previously, and by thermogravitometric analysis (TGA).[*] The TGA technique and its applications to the study of irradiation effects on resin physical properties will be described more fully elsewhere. The initial moisture content of the H^+ form resin was determined to be 48-52%.

3.2 Gas Generation

Both the pressure and the composition of the gases generated (or taken up) during the irradiation of H^+ form IRN-77 resin were measured. The experimental techniques have been described previously (Swyler and Dayal, 1982, Section 3.2). An additional refinement was incorporated in that, prior to evacuating the large chamber into which the sample cell is broken, the chamber was first evacuated and then backfilled with helium. Thus any residual gas (He) present in the large chamber following final evacuation cannot be confused with air originally present in the sample cell. Further, prior to each series of measurements, a break-seal pressure test was carried out on a standard sample cell at atmospheric pressure. These refinements markedly improved the accuracy of the gas generation measurements.

The partial pressures of the various gases found in the atmosphere over irradiated IRN-77 H^+ resin have been calculated from the observed total

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[*]Perkin-Elmer Model TGS-2.

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pressure and compositional analysis. The total pressure and various partial pressures are shown in Table 3.1 for different times and at different irradiation dose rates.

Table 3.1

Partial Gas Pressures in the Atmosphere Over Irradiated H$^+$ Form IRN-77 Resin

Dose Rate (rad/h)	Time (h)	Pressure (psi)						
		H_2	CO	CO_2	N_2	O_2	Ar	Total
0	0	0	0	0	11.5	3.08	0.14	14.7$^+$
"	165	0	0.37	2.10	10.4	1.95	0.13	15.3
"	340	0	0.08	0.08	11.0	3.09	0.14	14.4
"	508	0.02	0.12	1.98	10.9	2.20	0.14	15.4
"	675	---	---	---	---	---	---	14.6
"	845	0.01	0.74	2.26	9.84	1.52	0.12	14.6
"	1018	---	---	---	---	---	---	14.4
4×10^4	0	0	0	0	11.5	3.08	0.14	14.7$^+$
"	165	0.11	0.15	2.31	11.2	0.52	0.14	14.4
"	340	0.24	0.08	2.51	11.0	0.01	0.14	14.0
"	508	0.38	0.50	2.02	10.7	0.07	0.14	13.8
"	675*	0.02	0.35	1.98	9.80	1.89	0.12	14.2
"	845*	0.05	0	0.04	10.6	2.55	0.13	13.4
"	1018	0.69	0.13	1.62	10.7	0.01	0.13	13.3
1×10^5	0	0	0	0	11.5	3.08	0.14	14.7$^+$
"	165	0.25	0.40	1.87	10.7	0.09	0.13	13.5
"	340	0.63	0	2.83	11.2	0.01	0.14	14.9
"	508	---	---	---	---	---	---	14.1
"	675	1.03	0.60	1.65	10.5	0.01	0.13	14.1
"	845	1.17	0.19	1.94	10.5	0.01	0.13	13.9
"	1018	1.40	0.26	1.74	10.5	0.01	0.13	14.1
1.7×10^6	0	0	0	0	11.5	3.08	0.14	14.7$^+$
"	165	4.83	0.86	2.87	10.1	0.01	0.14	18.9
"	340	9.62	0	4.43	10.0	0.01	0.12	24.3
"	508	15.8	0.24	6.41	9.74	0.02	0.13	32.4
"	675	---	---	---	---	---	---	38.2
"	845	28.9	0.43	8.88	9.66	0.01	0.13	48.2
"	1018	35.6	0.52	8.71	9.90	0.21	0.13	55.1

--- = Gas composition not analyzed.
* = Compositional analysis suspect.
$^+$ = Assumes initial composition of standard air at 1 atmosphere.

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For the unirradiated control samples, the pressure does not vary systematically with time. The pressure averaged over all control samples is 14.8 psi and the r.m.s deviation is ±0.41 psi. These values should be taken to reflect, respectively, the average initial pressure for these experiments, and the experimental uncertainty (±3%) in a given pressure determination.

The compositional analyses are subject to additional uncertainty. In particular, air may be introduced in the sample transfer processes. This seemed to have happened in the samples indicated by an asterisk (*) in Table 3.1.

Table 3.1 indicates that the principal gas generated is hydrogen. 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 3.1. A least squares power-law fit to the data indicate that pressure varies as $(dose)^{1.03}$. While this dependence is not strictly linear, the departure from linearity lies within present experimental uncertainty. Between 10^6 and 10^9 rad, the G value derived from the fit is $0.12 \pm .011$. Both the G-value and total pressure correspond reasonably well to those found earlier for Na^+ form resin (Swyler and Dayal, 1982). In contrast, the maximum hydrogen pressure is less than one third of that found earlier in H^+ resin contacted with mild steel corrosion coupons.
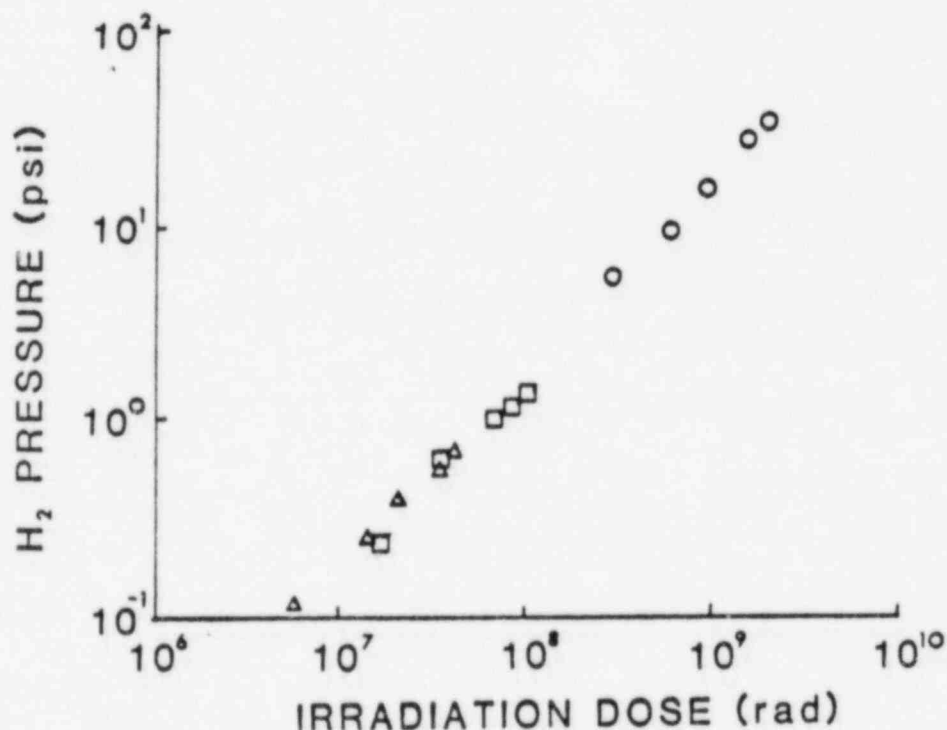

Figure 3.1 Hydrogen pressure over irradiated IRN-77 H^+ form resin. Dose rates (rad/h): 0 - 1.7×10^6; □ - 1×10^5; Δ = 4×10^4.

A second major radiolytic gaseous component is carbon dioxide. As indicated earlier, this seems to appear in two stages. In irradiated control samples and in samples irradiated at 4×10^4 and 10^5 rad/h, CO_2 data indicate a level of roughly 2 psi which, once achieved, remains fairly stable with time. For irradiation at 1.7×10^6 rad/h, a second stage of generation is evident after atmospheric oxygen has been scavenged; CO_2 concentration continue to increase with irradiation dose. It is noteworthy that, initially, the oxygen uptake is not quite completely accounted for by CO and CO_2 generation. The table also indicates that some oxidation (or possibly biodegradation) of the resin may be occurring even in unirradiated samples.

3.3 Acid Product Formation

Following irradiation, two grams of the various H^+ 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 and sulfate concentration was determined on 5-mL aliquots withdrawn from the supernate.

The evolution of supernatant pH with irradiation time at various dose rates is shown in Table 3.2 for hydrogen form resins without corrosion coupons. For the H^+ form resin without corrosion coupons, hydrogen concentration can be fitted to an expression of the form

$$[H^+] = C\phi^{0.75} + [H^+]^0$$

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 3.2. C is approximately 7.7×10^{-9} moles/liter-(rad)$^{3/4}$ and $[H^+]^0$ is approximately 1×10^{-3} moles/liter. It should also be noted that this expression differs from that previously proposed for irradiation of H^+ form resin in vented vessels. There, preliminary analysis suggested that $[H^+] \sim \phi$. Actually, if sulfuric acid is being generated linearly with irradiation dose, one expects a sublinear dependence of $[H^+]$ on radiation dose, since, at low pH, sulfuric acid is not completely dissociated.

Table 3.2

Supernate pH of Irradiated H^+ Form IRN-77 Resin

Dose Rate (rad/h)	Irradiation Time (h)	Dose (rad)	pH[a]	pH[b]
0	0	0	3.4	
	165	0	3.3	3.8
	340	0	3.4	3.9
	508	0	3.7	3.8
	675	0	3.7	3.9
	845	0	3.3	3.4
	1018	0	3.1	3.9
4×10^4	0	0	3.4	
	165	6.6×10^6	2.8	2.3
	340	1.36×10^7	2.6	2.1
	508	2.03×10^7	2.6	2.1
	675	2.70×10^7	2.5	2.0
	845	3.38×10^7	2.0	1.9
	1018	4.07×10^7	1.9	1.8
1×10^5	0	0	3.4	
	165	1.65×10^7	2.6	2.1
	340	3.40×10^7	2.5	1.9
	508	5.08×10^7	2.4	1.8
	675	6.75×10^7	2.1	1.7
	845	8.45×10^7	2.1	1.7
	1018	1.02×10^8	2.0	1.6
1.7×10^6	0	0	3.4	
	165	2.8×10^8	1.7	1.4
	340	5.78×10^8	1.6	1.1
	508	8.63×10^8	1.3	1.0
	675	1.14×10^9	1.3	1.0
	845	1.44×10^9	1.2	0.9
	1018	1.73×10^9	1.1	0.9

[a]Measured in supernate, 12 hours after preparation.
[b]Measured in aliquot of supernate, 2-8 weeks after preparation.

The pH values in Table 3.2 are substantially lower than those found for H^+ resin contacted with mild steel corrosion compounds. This confirms the uptake of H^+ ion in the corrosion process and indicates that in the corrosion mechanism, the acidic species is not completely regenerated.
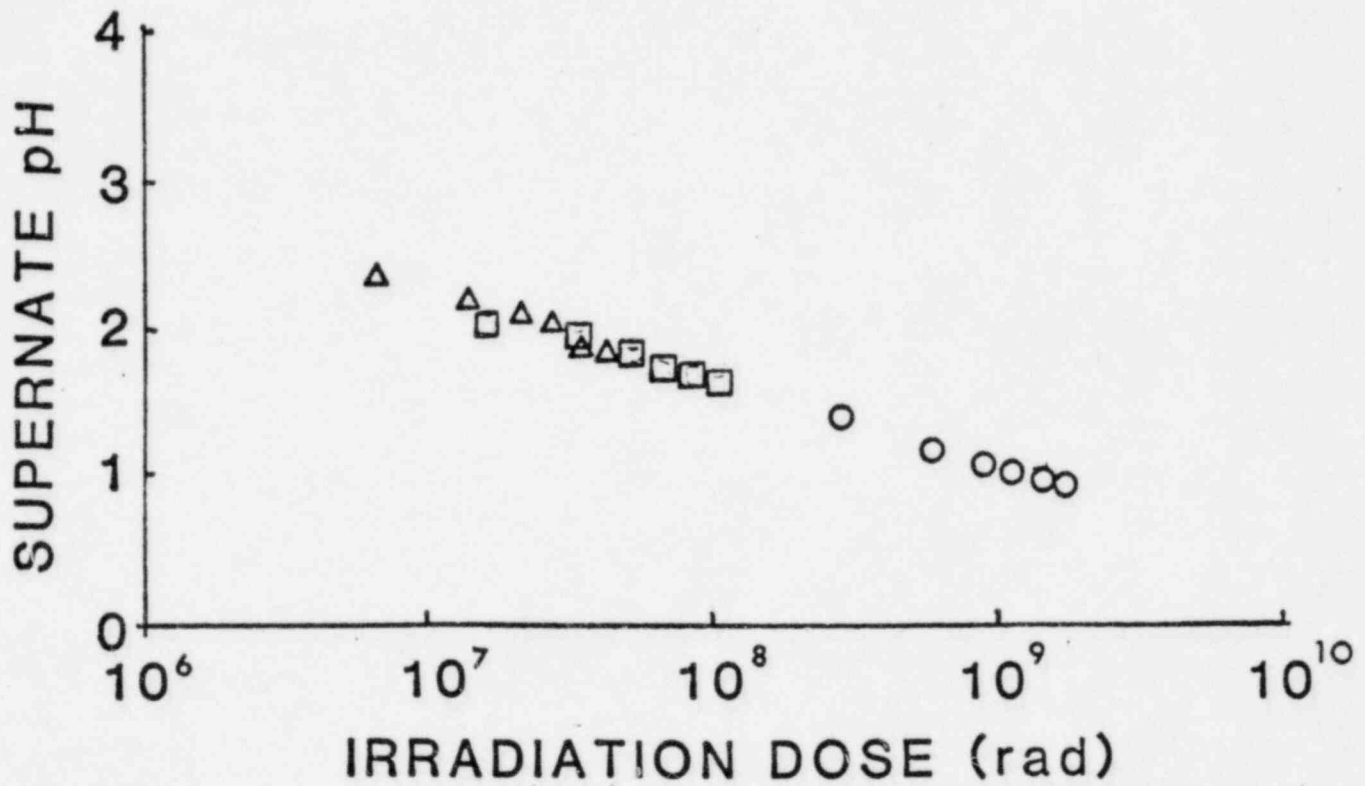
Figure 3.2 Supernate pH vs irradiation dose for irradiated IRN-77
H^+ form resin. Dose rates (rad/h): $O - 1.7 \times 10^6$;
$\square - 1 \times 10^5$; $\triangle - 4 \times 10^4$.

3.4 Sulfate and Soluble Iron Analysis

The supernate solutions over Na^+ form resins with and without corrosion coupons have now been analyzed for sulfate. Techniques have been described previously (Swyler and Weiss, 1981). Results are shown in Table 3.3.

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Table 3.3

Sulfate Content and pH of Supernatant[a]
Over Irradiated Na$^+$ Form IRN-77 Resin

Sample	Dose Rate (rad/h)	Total Dose (rad)	pH[b]	[SO$_4^=$][c]
IRN 77	0	0	4.09	1.48×10^{-5}
Na$^+$	"	0	4.35	1.04×10^{-5}
without	"	0	4.57	7.57×10^{-6}
corrosion	"	0	4.75	6.53×10^{-6}
coupons	"	0	---	---
	"	0	4.98	4.67×10^{-6}
	4×10^4	9.28×10^6	4.40	3.93×10^{-5}
	"	1.57×10^7	3.92	6.80×10^{-5}
	"	2.22×10^7	3.66	8.23×10^{-5}
	"	2.87×10^7	3.47	1.03×10^{-4}
	"	3.52×10^7	3.30	6.64×10^{-5}
	"	4.17×10^7	3.28	6.26×10^{-5}
	1×10^5	2.31×10^7	3.75	6.64×10^{-5}
	"	3.93×10^7	3.33	1.06×10^{-4}
	"	5.55×10^7	3.15	1.27×10^{-4}
	"	7.17×10^7	2.94	2.00×10^{-4}
	"	8.80×10^7	2.87	2.20×10^{-4}
	"	1.04×10^8	---	---
	1.7×10^6	3.79×10^8	2.34	6.09×10^{-4}
	"	6.44×10^8	2.28	7.27×10^{-4}
	"	9.10×10^8	2.15	9.23×10^{-4}
	"	1.17×10^9	2.13	1.10×10^{-3}
	"	1.44×10^9	2.05	1.26×10^{-3}
	"	1.70×10^9	2.07	1.18×10^{-3}
IRN 77	0	0	5.06	6.62×10^{-6}
NA$^+$	"	0	5.48	3.40×10^{-6}
with	"	0	5.67	3.94×10^{-6}
corrosion	"	0	5.50	3.23×10^{-6}
coupons	"	0	---	---
	"	0	5.93	3.38×10^{-6}
	4×10^4	6.50×10^6	5.13	2.46×10^{-5}
	"	1.30×10^7	4.74	5.80×10^{-5}
	"	1.95×10^7	4.48	7.40×10^{-5}
	"	2.60×10^7	4.14	1.11×10^{-4}
	"	3.25×10^7	4.15	1.29×10^{-4}
	"	3.92×10^7	3.97	1.71×10^{-4}
	1×10^5	1.62×10^7	4.56	5.93×10^{-5}
	"	3.24×10^7	4.40	1.02×10^{-4}
	"	4.86×10^7	4.15	1.59×10^{-4}
	"	6.48×10^7	3.75	2.08×10^{-4}
	"	8.10×10^7	3.90	2.70×10^{-4}
	"	9.77×10^7	3.78	3.19×10^{-4}
	1.7×10^6	2.65×10^8	3.33	6.48×10^{-4}
	"	5.30×10^8	3.06	9.23×10^{-4}
	"	7.96×10^8	2.90	1.03×10^{-3}
	"	1.06×10^9	2.78	1.63×10^{-3}
	"	1.37×10^9	2.72	2.08×10^{-3}
	"	1.60×10^9	2.79	1.71×10^{-3}

[a]Two grams resin in 10 mL D.I.W.
[b]Measured in aliquots of the supernate prepared from resin stored after irradiation. See Section 5.
[c]Total amount (moles) in solution.

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In Figure 3.3, sulfate concentrations are plotted vs irradiation dose. There is no evidence that sulfate yields are significantly different in samples with and without corrosion coupons; nor is there yet any clear evidence of a radiation dose rate effect. "G"-values obtained from this data are 0.5 near 10^9 rad, and 0.9 near 10^8 rad. The "G" value near 10^8 rad is in reasonable agreement with previous estimates obtained in measurements on vented samples (Swyler and Weiss, 1981). A decrease in G value at higher total doses has been noted earlier for H^+ resin with corrosion coupons (Swyler and Dayal, 1982).
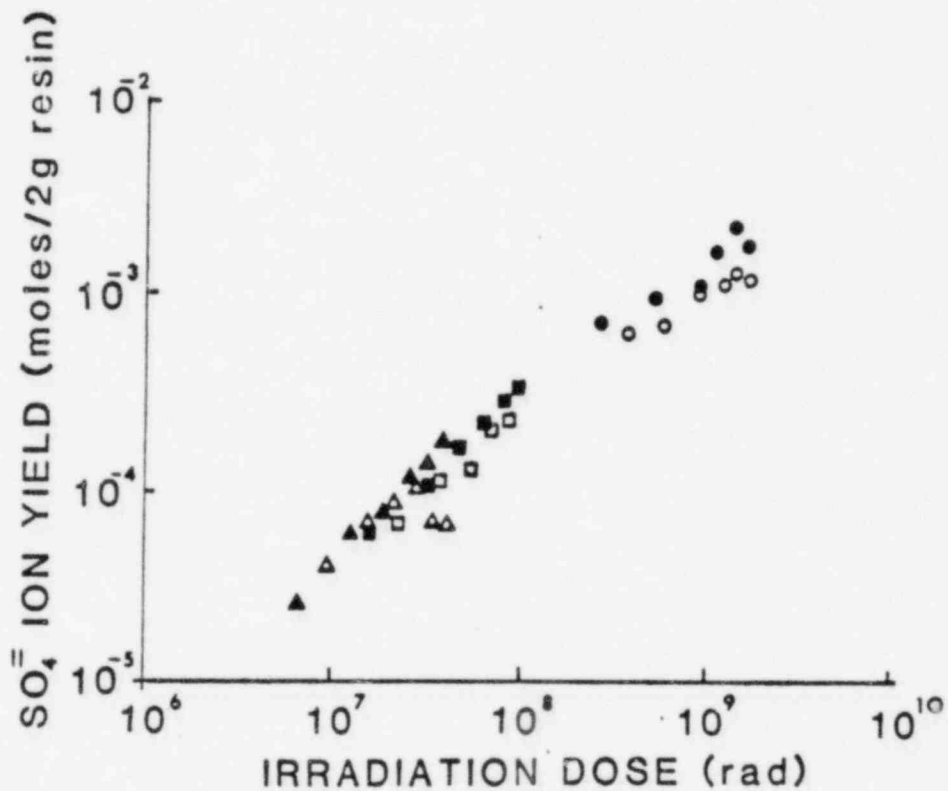

Figure 3.3   Soluble sulfate generation vs irradiation dose for IRN-77 Na^+ form resin (2 g) with and without corrosion coupons. Dose rates (rad/h): o - 1.7×10^6; □ - 1×10^5; △ - 4×10^4. Solid points - sample with corrosion coupon; open points - sample without corrosion coupon.

3.5 Cation Exchange Capacity Determination

Radiation damage is known to affect ion exchange capacity (Egorov and Novokov, 1967; Gangwer, Goldstein, and Pillay, 1977). The mechanism of radiation damage at functional groups in the resin can be studied by examining the correlation between changes in exchange capacity and formations of functional group decomposition products (i.e. sulfates). During this report period, initial cation exchange capacity measurements were carried out on various samples of IRN-77 resin in H^+ and Na^+ forms. These samples had been irradiated and/or contacted with corrosion coupons under conditions described previously.

The measure of exchange capacity is performed using the procedure outlined by Fisher and Kunin (1955). Approximately 5 g of resin is placed in a funnel with Whatman #1 filter paper and positioned above a 1-L Erlenmeyer flask. One liter of 1 Molar HNO_3 is put in the separatory funnel and slowly run over and through the resin converting it to the hydrogen form. The resin is then rinsed free of acid and placed into a Buchner funnel and air is drawn over it with suction until all gross water is removed (approx. 5 minutes).

One gram of the resin (weighed to nearest mg) is placed into a 250-mL Erlenmeyer flask and covered with 200 mL 0.1 N NaOH/10% NaCl solution. The remaining resin is weighed and dried at 110°C to determine the solid content. The sample in the Erlenmeyer flask is stoppered and allowed to stand overnight. Fifty-mL aliquots of the supernatant liquid are then back titrated with 0.1 N HCl Acculute solution to the phenolphthalein endpoint. The cation exchange capacity is calculated as follows:

$$\frac{(200 \times N_{NaOH}) - 4(\text{mL acid} \times N_{acid})}{\text{Sample weight} \times \% \text{ solids}/100}$$

$$= \frac{\text{meq cation exchange capacity}}{\text{gram of dry } H^+ \text{ form resin}}$$

% moisture is calculated as follows:

$$= \frac{\text{weight resin before drying} - \text{weight resin after drying}}{\text{weight of resin before drying}} \times 100$$

The results are shown in Table 3.4

Table 3.4

Exchange Capacity of Irradiated[a] IRN-77 Resins

Resin Type	Irradiation Dose Rate rad/h	Irradiation Dose (rad)	% Moisture	Dry Exchange Capacity (meq/g)
H^+ with coupon	0	0	54.6	5.83
	0	0	56.7	5.94
	4×10^4	2.0×10^7	56.2	5.57
	4×10^4	4.1×10^7	54.2	5.69
	1×10^5	5.6×10^7	55.2	5.58
	1×10^5	1.1×10^8	55.3	5.60
	1.7×10^6	8.0×10^8	57.1	5.46
	1.7×10^6	1.6×10^9	55.0	4.85
Na^+ with coupon	0	0	55.2	5.53
	0	0	54.5	5.46
	4×10^9	1.9×10^7	55.6	5.57
	4×10^9	3.9×10^7	55.0	5.56
	1×10^5	4.8×10^7	55.0	5.46
	1×10^5	9.9×10^7	55.2	5.42
	1.7×10^6	8.0×10^8	55.4	4.93
	1.7×10^6	1.6×10^9	51.8	4.45
Na^+	0	0	55.4	5.49
	0	0	55.0	5.50
	4×10^4	2.2×10^7	55.5	5.67
	4×10^4	4.2×10^7	55.6	5.42
	1×10^5	5.5×10^7	57.8	5.66
	1×10^5	8.8×10^7	56.5	5.56
	1.7×10^6	9.1×10^8	56.0	5.47
	1.7×10^6	1.7×10^9	52.2	4.90

[a]All irradiations carried out in Pyrex tubes as described in Swyler and Weiss (1981).

The correlation between exchange capacity and sulfate formation is shown in Figure 3.4. The figure also shows a hypothetical curve (solid line) which would result if the exchange capacity decreased by one equivalent for each mole of $SO_4^=$ (i.e. if the only effect on exchange capacity was due to the scission of the $-SO_3^+$ functional group). The data points lie somewhat above the hypothetical curve – this may indicate that, while functional groups are certainly removed by the irradiation, other exchange groups (e.g., carboxylic acid) are formed as well by radiolytic attack on the polymer backbone (Egorov and Novokov, 1967). It has been found that radiolytic oxygen attack on polymers may be relatively enhanced at low dose rates (Clough and Gillen, 1981). The present data, however, do not yet indicate a relatively greater exchange capacity for a given dose at low radiation dose rates.
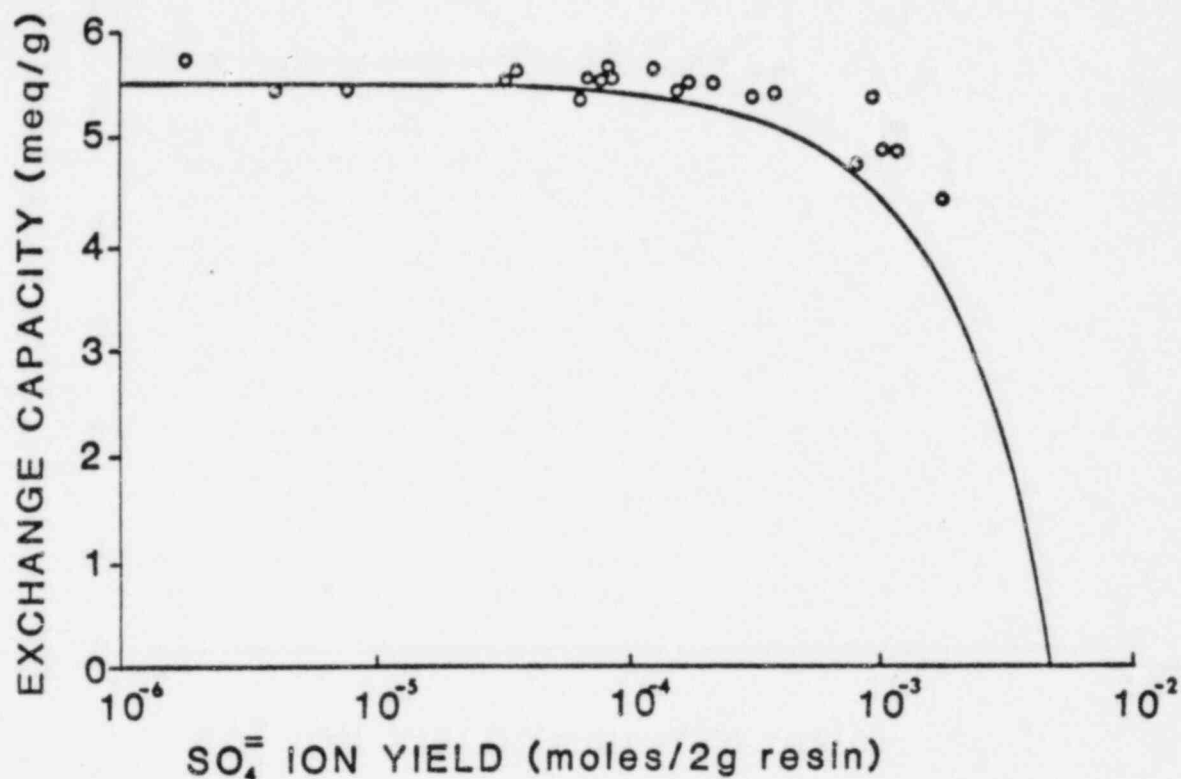
Figure 3.4   Cation exchange capacity vs soluble sulfate yields for irradiated IRN-77 resin. Solid line: Hypothetical curve assuming 1 mole of SO_4 represents a decrease in total exchange capacity of 1 meq.

There are certain problems affecting the sensitivity of the exchange capacity and the moisture content determinations. For the exchange capacity it was noticed that if 2 grams of irradiated resin are weighed out and then put into water, weight loss due to dissolution of the resin can be up to 20% of the total resin weight. Therefore, when a capacity determination is done, it only reflects the exchange capacity of the remaining resin. There are also soluble fractions which produce intense absorption bands in the ultra-violet. Finally, there are insoluble components of the resin which are obviously from the resin but have no bulk morphological similarity to the resin. These are flaky suspended particles.

During moisture determinations the method calls for suctioning of the resin for five minutes to remove gross amounts of water before weighing. This also is not highly precise because the amount of moisture retained by the resin is proportional to packing of resin in funnel, humidity of the ambient air, porosity of filter, etc. A more reproducible and accurate way of determining moisture content would be to centrifuge the resin in a closed system. The resin is then weighed and dried in a vacuum oven overnight at 70°C.

In order to more fully characterize the resin breakdown the following analytical scheme is proposed.

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After irradiation, 2 grams of the resin should be placed in a weighing vial and 10 mL of deionized water added. The bottle should then be weighed (to nearest mg) so that moisture loss and sample extraction can be accounted for. Samples should be allowed to sit for at least a week to equilibrate with the water. pH should be taken in the bottle right before $SO_4^=$ analysis is done. This will permit better correlation of acidity species. Soluble Fe should also be analyzed if a coupon was used. If the resin is in the Na^+ form, then this element should be analyzed. A known volume of the supernatant should be withdrawn and dried overnight. The dried weight will give soluble fraction of resin as a percentage of total. The remaining supernatant should be withdrawn and the resin washed from the bottle onto a mesh screen, which will pass insoluble fragments but leave the bulk resin beads. After removal of insoluble fragments these should be dried and weighed. The resin remaining on the screen should then be treated as per Fisher and Kunin for moisture content and exchange capacity. Using this procedure, a more detailed picture of the resin decomposition will emerge to aid in distinguishing between the mechanisms involved. Also, if practical, insoluble and soluble fractions should be characterized.

4. CHARACTERIZATION OF IRRADIATION EFFECTS ON SOLIDIFIED FORMS

This task began late in the second quarter of FY 1982. Experimental solidification studies are currently under way, using a mixture of water, Portland Cement and irradiated IRN-77 resin. The initial objective is to determine how resin irradiation affects solidification process latitude.

Several parametric studies (Manaktala and Weiss, 1980; Weiss and Morcos, 1981) have been carried out on solidification of unirradiated resins in cement. These studies have served to define regions on the water-cement-resin tertiary composition diagram where acceptable forms can be produced. The size and shape of this acceptable region will, almost certainly, depend upon the chemical (pH, resin loading, soluble decomposition products) physical (moisture retention, swelling; mean size) and ion exchange properties of the resin. All of these properties may be modified by irradiation. In fact, it is just these properties which are being characterized in Task 2.

In our initial experiments, a number of small (2 in. diameter x 4 in. long) cylindrical forms have been cast from irradiated (9×10^8 rad) and un-irradiated IRN-77 resin in the sodium form. Resin-cement-water ratios of 27.5:137.5:55.0 and 37.5:137.5:55.0 were chosen for initial tests. The first formulation represents an optimal mixture from previous studies; the second is to provide a measure of process latitude. Following curing, the forms will be tested mechanically and chemically. Results on forms using irradiated and un-irradiated resin will be compared to determine the effect of resin irradiation on solidified form properties. When possible, such effects will be correlated with irradiation effects on resin properties, as determined in Task 2.

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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 ion exchange 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.

5.1 Corrosion Studies

Experiments to investigate the mechanism of mild steel corrosion in IRN-77 resin continued during this report period. In one series of measurements, mild steel corrosion in mixtures of resin and sulfuric acid is being studied. Two grams of IRN-77 resin are contacted with 10-mL solutions of sulfuric acid of various strengths until a pH is obtained which is similar to that found in the supernate over irradiated resins. In this process, it is observed that addition of Na^+ form resin raises the acid solution pH, while addition of H^+ form resin does not. This agrees with previous observations on the 'self-buffering' effect in Na^+ form resin. Next, the resin is either held immersed in solution or drip-dried to approximately 50% moisture content. Both immersed and drip-dry samples are then contacted with mild steel corrosion coupons. Immersion simulates conditions which might occur if free liquid collects in a container. Immersion may in principle modify the transport of corrosive species within the resin bed, atmospheric oxygen scavenging and atmospheric effects on corrosion. Subsequently, the sample is either irradiated or held as a control. Corrosion and other properties are then observed as a function of contact time.

In a second series of measurements, drip-dry IRN-77 resins are contacted with corrosion coupons in a "column" configuration: The coupon is a metal disc (12.4 mm diam x 3 mm thick) which fits snugly in the bottom of a flat bottomed Pyrex tube. A column of resin (H^+ or Na^+ form) is then loaded over the corrosion coupon. The column height is variable; intital lengths range from 13 to 50 mm. The tube is then closed (stoppered) and gamma-irradiated to different doses. Unirradiated control specimens are stored for a period of time consistent with the irradiaton time. Following irradiation the tube is usually examined. A dark zone appears in the resin over the corrosion coupon as observed earlier (Swyler and Weiss, 1981; Swyler and Dayal, 1982). The height of this dark zone is measured as a function of contact time. Next, the resin sample is removed as a 'core', by breaking the bottom of the tube. The moisture content, pH and sulfate content are then characterized for material at different heights within the column. The objective is to observe the concentration gradient of corrosive products, moisture content and acidic species within the bed in the vicinity of the coupon specimen and to relate this with corrosion rate behavior.

Results of these corrosion experiments will be described in detail in the future. Initial sulfuric acid contact experiments without irradiation have not reproduced the pitting type of corrosion which is found in samples

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contacted with drip-dry resins and irradiated. This is probably because of the extremely low local pH which occurs in individual irradiated resin beads. A simple volumetric calculatio indicates that in drip-dry resins which give a 2 g/10 mL supernate pH of 2, the pH within individual beads before mixing with water could be as low as 1. (This suggests that if pitting corrosion is a problem it might actually be beneficial to immerse the resin in water. However, this presents other difficulties.) Initial data from the corrosion zone studies suggest that resin at least as far as 25 mm from the coupon is contributing to the corrosion process. This is consistent with earlier observations from Task 2, that, while corrosion tends to raise the pH of irradiated resin, the pH was not particularly sensitive to where the resin is sampled. This is discussed further in Section 6.

5.2 Aging and Dilution Studies on Aqueous Supernates of Irradiated Resins

Thus far, pH results (Swyler and Weiss, 1981; Swyler and Dayal, 1982) on the supernates of irradiated resins in de.onized water solutions, have largely referred to measurements carried out on 'fresh' solutions - i.e., 12 hours after the solution was made. As indicated earlier, these measurements were made by inserting a pH electrode into the supernatant in contact with resin; stable readings were obtained after 5 min. In conjunction with the sulfate measurements carried out during this report period, additional resin water solutions were prepared from resin which had been stored (aged) in corked tubes following irradiation. For these samples, pH was determined for 1-mL aliquots taken from the supernatant one week after preparation. A comparison between the pH values obtained in the supernate of 'fresh' resin and that obtained with aliquots taken from the supernate over "aged" resin is given in Table 5.1. The pH values in the "aged" resin are generally lower. This most probably indicates a continuing degradation or leaching of the irradiated resin during storage. The equivalence of pH measurements made on the supernate in contact with the resin and pH measurements made on aliquots of the supernate has been investigated. There is no significant difference in the results, provided that the measurements are made at the same time. It is noteworthy that aging apparently occurs in unirradiated resins.

Aging effects also occur when the irradiated resins are contacted with water for extended periods. Table 5.2 shows a decrease in supernatant pH with aging time; the effect is most pronounced in samples which contain corrosion coupons. The table also shows the effect of a 10:1 solution on aged supernate pH at higher pH, the dilution increase is approximately 1 pH unit; for lower pH values (approx. 2.25) the increase is smaller (0.6 to 0.7 pH units) indicating that some acid is not fully dissociated at low pH.

Aging and dilution effects have also been investigated for $SO_4^=$ concentration (Table 5.3). There is an aging effect in which $SO_4^=$ concentration increases. Interestingly, the increase is greatest for samples with the longest contact time with corrosion coupons. A part of the increase may be the slow dissolution of sulfate corrosion products. The increase in $SO_4^=$ is less than the increase in H^+ as indicated by pH drop.

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Table 5.1

pH of Supernates Formed With "Fresh" and "Aged" Irradiated Resins

Resin Type	Dose Rate (rad/h)	Irradiation Time (weeks)	Fresh[a] Resin pH	Resin[b] Aging (weeks)	Aged[c] Resin pH
H$^+$ with coupon	0	1	4.2	16	3.7
	"	2	3.6	15	2.9
	"	3	3.9	14	3.2
	"	4	3.7	13	2.8
	"	5	3.6	12	2.8
	"	6	3.6	11	2.6
	4×10^4	1	3.04	16	2.60
	"	2	3.10	15	2.40
	"	3	2.72	14	2.24
	"	4	2.61	13	2.38
	"	5	3.07	12	2.71
	"	6	2.93	11	2.72
	1×10^5	1	2.82	16	2.42
	"	2	2.55	15	2.21
	"	3	2.49	14	2.28
	"	4	2.66	13	2.62
	"	5	2.90	12	2.59
	"	6	2.87	11	2.62
	1.7×10^6	1	2.04	16	1.78
	"	2	2.58	15	2.24
	"	3	2.71	14	2.26
	"	4	2.67	13	2.17
	"	5	2.94	12	2.37
	"	6	3.05	11	2.40
Na$^+$ with coupon	0	1	6.97	16	5.06
	"	2	6.96	15	5.48
	"	3	7.48	14	5.67
	"	4	7.07	13	5.50
	"	5	7.01	12	---
	"	6	7.46	11	5.50
	4×10^4	1	6.58	16	5.13
	"	2	6.44	15	4.74
	"	3	5.98	14	4.48
	"	4	5.15	13	4.14
	"	5	4.60	12	4.15
	"	6	4.61	11	3.97
	1×10^5	1	6.87	16	4.56
	"	2	4.91	15	4.40
	"	3	4.29	14	4.15

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Table 5.1 (Continued)

pH of Supernates Formed With "Fresh" and "Aged" Irradiated Resins

Resin Type	Dose Rate (rad/h)	Irradiation Time (weeks)	Fresh[a] Resin pH	Resin[b] Aging (weeks)	Aged[c] Resin pH
Na$^+$ with coupon	"	4	4.09	13	3.75
	"	5	3.96	12	3.98
	"	6	4.21	11	3.78
	1.7×10^6	1	3.98	16	3.33
	"	2	3.63	15	3.06
	"	3	3.90	14	2.90
	"	4	3.78	13	2.78
	"	5	3.69	12	2.72
	"	6	3.79	11	2.79
Na$^+$ without coupon	0	1	6.10	16	4.99
	"	2	6.08	15	4.35
	"	3	6.26	14	4.57
	"	4	5.74	13	4.75
	"	5	6.39	12	---
	"	6	6.25	11	4.98
	4×10^4	1	4.55	16	4.40
	"	2	4.11	15	3.96
	"	3	3.86	14	3.66
	"	4	3.64	13	3.47
	"	5	3.92	12	3.30
	"	6	3.61	11	3.28
	1×10^5	1	4.09	16	3.75
	"	2	3.64	15	3.33
	"	3	3.46	14	3.15
	"	4	3.28	13	2.94
	"	5	3.56	12	2.87
	"	6	3.23	11	---
	1.7×10^6	1	2.77	16	2.34
	"	2	2.62	15	2.28
	"	3	2.39	14	2.15
	"	4	2.35	13	2.13
	"	5	2.34	12	2.05
	"	6	2.17	11	2.07

[a] pH measured in supernate made from resin 12 h after irradiation.
[b] Resin aged in stoppered tubes following irradiation for time indicated.
[c] pH of 1 mL aliquot taken from supernate made with aged resin, sampled one week after preparation.

Table 5.2

Aging and Dilution Effects on the Aqueous Supernate pH
on Irradiated IRN-77 Resins

Sample	Dose Rate (rad/h)	Irradia- tion Time (wks)	Fresh[a] pH	Aging Time (wks)	Aged[a] pH	Aged pH After 10:1 Dilution[b] 12 h	96 h
H^+ resin	0	6	3.58	18	2.69	3.57	3.69
with	4×10^4	6	2.92	18	2.72	3.50	3.56
coupon	1×10^5	6	2.89	18	2.66	3.36	3.38
	1.7×10^6	6	3.04	18	2.26	2.93	2.93
Na^+ resin	0	6	7.46	11	4.83	5.32	5.75
with	4×10^4	6	4.62	11	4.29	4.83	5.25
coupon	1×10^5	6	4.21	11	3.95	4.70	4.99
	1.7×10^6	6	3.79	11	2.91	3.51	3.54
Na^+ resin	0	6	6.25	11	4.50	5.01	5.08
	4×10^4	6	3.61	11	3.19	3.79	4.18
	1×10^5	6	3.23	11	2.87	3.58	3.83
	1.7×10^6	6	2.17	11	2.22	2.81	2.82

[a]Dilution = 2 g resin + 10 mL DIW.
[b]Dilution = 2 g resin + 110 mL DIW.

Table 5.3

Aging Effects on the pH and Sulfate Ion Content
of Aqueous Supernate of IRN-77 H^+ Resin[a]

Resin Aging Time (Weeks)	Aged Resin Supernate pH	Moles $SO_4^=$	Supernate Aging Time (Weeks)	Aged Supernate pH	Moles $SO_4^=$	$\dfrac{\Delta[SO_4^=]}{\Delta[H^+]}$
1	3.68	4.1×10^{-7}	6	2.73	6.8×10^{-7}	.016
2	2.91	3.4×10^{-6}	6	2.66	6.7×10^{-6}	.29
3	3.16	1.7×10^{-6}	6	2.90	3.2×10^{-6}	.27
4	2.84	3.7×10^{-6}	6	2.67	6.8×10^{-6}	.45
5	2.79	5.4×10^{-6}	6	2.63	9.3×10^{-6}	.54
6	2.60	1.0×10^{-5}	6	2.40	1.84×10^{-5}	.57

[a]Unirradiated control samples contacted with mild steel corrosion coupons
and aged in sealed Pyrex vessel.

Lastly, dilution measurements were carried out to investigate whether the total $SO_4^=$ levels in the supernate are dependent on the ionic strength of the solution or other concentration dependent factors. Total sulfate levels in the supernate were determined for a solution of 2 g resin in 10 mL D.I.W. The solution was then diluted to 2 g resin in 100 mL D.I.W. and total $SO_4^=$ in the supernate determined again. For total sulfate levels between 5 x 10^{-6} to 1 x 10^{-3} moles, the two methods give the same results to within about 20%. Agreement is better for high total sulfate levels; in general total sulfate values determined from dilute solutions are systematically lower than those indicated in the original solution.

pH levels for aliquots from the aqueous supernates of aged resins are plotted vs irradiation dose in Figure 5.1 for Na^+ form resin. The functional dependence is somewhat different from that found earlier for fresh resin supernates (Swyler and Dayal, 1982). The present data indicate a decrease in the $[H^+]$ formation rate with increasing radiation dose, assuming that data at different dose rates are equivalent. Again, one might expect lower yields of free H^+ at lower pH if dissociation effects are involved. Further, if the relatively low H^+ yield in Na^+ form resin is due to uptake of H^+ ion by the resin, it is reasonable that this effect becomes more pronounced at lower pH. This is particularly true if additional exchange sites are created by the irradiation (Section 3). The correlation between H^+ (Fig. 5.1) and $SO_4^=$ yields (Fig. 3.3) is presently being examined to provide additional mechanistic insight. It is just possible that yields fall off at higher dose rates.
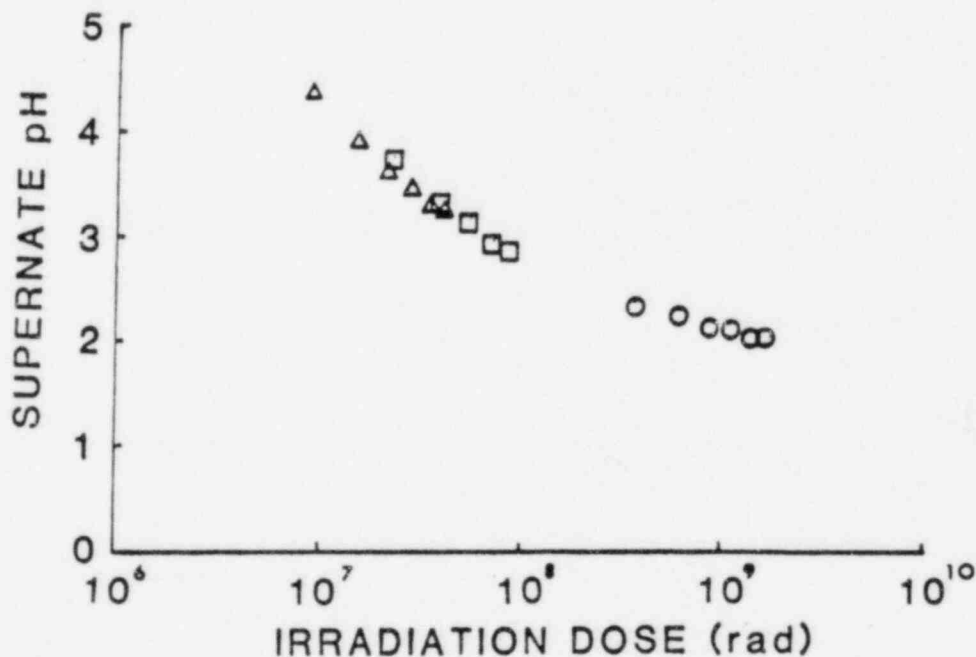

Figure 5.1 Supernatant pH vs irradiation dose rate for irradiated Na^+ form resin, aged 11-16 weeks before measurement. Dose rates (rad/h): o - 1.7x10^6; □ - 1x10^5; △ - 4x10^4.

5.3 Other Experiments

Experiments are continuing on the effect of radiolytic peroxide formation and an irradiation-induced oxygen scavenging and resin oxidation. Results in these areas will be described in future reports.

6.   DISCUSSIONS AND CONCLUSIONS

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

As yet, there is no evidence of a radiation dose rate effect in radiolytic hydrogen generation from fully swollen IRN-77 resin irradiated in a sealed environment.

In other words, initial data suggest that the amount of hydrogen produced depends only on radiation dose, and not on the rate at which the dose is administered. Data on H^+ form IRN-77 resin lead to a G-value of 0.12 for hydrogen generation.

Initial data give roughly similar G-values and total pressure for Na^+ form IRN-77 resin, indicating that hydrogen generation does not depend sensitively on resin loading. This implies that hydrogen generation is not particularly sensitive to local pH conditions, and suggests that hydrogen gas generation involves mechanisms other than (bulk) water radiolysis. This question falls naturally within the scope of future studies on the effect of resin moisture content and bead size.

Oxygen is removed from the atmosphere over irradiated resins by an efficient radiation-induced oxidation process.

The data on H^+ form resin support those for sodium form resins: a radiation dose of approximately 10^7 rad is sufficient to promote consumption of at least 1×10^{-3} moles of O_2 per gram of resin. Some, but not all of this oxygen may reappear in carbon dioxide.

Carbon dioxide generation continues once atmospheric oxygen is depleted. This second stage generation is less efficient, however, and is not easily detected for doses below 10^8 rad in the present experiments. Subsequently, the ratio of CO_2 to H_2 generation is about 1:4. This ratio (Barletta, Swyler, Chan, and Davis, 1981) may be useful in characterizing the radiolytic decomposition process from field data.

There are chemical aging and/or slow leaching effects which cause slow changes in the solution chemistry of irradiated resins after the irradiation is terminated.

The present data are not yet able to clearly distinguish between slow chemical reactions and slow leaching effects. Data on unirradiated resins suggest that slow chemical reactions may in part involve an oxidation process that begins once the Pyrex tubes are broken and the samples exposed to fresh oxygen in stoppered storage tubes. In any event, the effect is to decrease the pH and increase the $SO_4^=$ levels in supernatants. More importantly, this effect may cause post irradiation results, at least as far as determined by the present techniques, to become time dependent. This has implications for test development and interpretation which are not always recognized (Egorov and Novokov, 1967).

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If oxidation effects are in fact involved in post-irradiation aging, there is reason to believe that irradiation effects in an open or oxygen rich atmosphere may be dose rate dependent (Gillen and Clough, 1981). This is currently being investigated by direct measurement. For the present, we note that the pH values for aged resin supernates vs irradiation dose differ somewhat (and in fact appear more regular) from those reported earlier (Swyler and Dayal, 1981) for fresh supernates. In particular, the relationship between $[H^+]$ and irradiation dose for the Na^+ form departs from linearity. The qualitative features of earlier observations are preserved however and, in particular there is as yet no clear evidence for a dose rate effect. Other test methods will be investigated (rinsing, titration), which, while probably less representative of field conditions than static leaching of decomposition products, may provide an improved measure of resin degredation.

Thus far, there is no evidence that radiolytic attack on the functional group of IRN-77 resin is affected by pH conditions or by the uptake of corrosion products.

Taking soluble $SO_4^=$ levels as a measure of functional group attack, and recalling that the pH is elevated for samples containing corrosion coupons, the observation above follows directly from Figure 3.3.

This behavior has both mechanistic and practical implications. The lack of pH dependence suggests that radiolytic effects in incorporated water do not enhance attack on the functional group. The relative insensitivity of the $SO_4^=$ yields to external conditions indicates that this parameter may be extremely useful in comparative evaluations of resin degradation.

G values for $SO_4^=$ formation, determined from the data in Figure 3.3, decrease with increasing radiation dose. At this point, it is just possible that the apparent decrease in G values with increasing dose actually reflects a situation in which G values are greater at low radiation dose rates. Long-term irradiation experiments at low dose rate, as well as correlation of H^+ and $SO_4^=$ yield data, are presently under way to examine this possibility.

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