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RECORDS ADMINISTRATION
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TO: E. L. ALBENESIUS

FROM: E. W. BAUMANN

EFFECTS OF GAMMA RADIATION ON INDIVIDUAL AND MIXED ION EXCHANGE RESINS

Introduction

The ion exchange resins that are used to deionize moderator in the reactor purification systems may accumulate sufficient radiation dose to damage the resins. This radiation damage would be manifested by the following:

- loss of useful exchange capacity of the bed, which is costly since resins from the reactor deionizers are not reused
- shrinking or swelling of the resins, which may have some effect on the hydraulic behavior of the beds
- release of resin degradation products into the process stream, which pollutes moderator with impurities and precursors of neutron-induced radioisotopes (e.g., ^{35}S and ^{32}P).

The present work is a laboratory study to determine the magnitude of these three effects by gamma irradiation of individual resins and their mixtures.

Summary

Individual cation and anion exchange resins and their mixtures were irradiated by gamma sources to a maximum dose of 2×10^8 rad. At this maximum dose, less than 10% of the cation resin exchange capacity was lost, but the loss in anion resin exchange capacity was about 50%. When individual resins were irradiated, resin degradation products could be leached out by water rinsing. These products were identified in part as sulfates or sulfonates and amines. Leachable material was almost eliminated when mixtures of anion and cation exchange resins were irradiated because one resin component absorbed the ionic degradation products of the other. The useful exchange capacity of the mixed resin was reduced substantially through this absorption of degradation products.

The volume of the irradiated cation resin increased to 110% of the original; that of the irradiated anion resin decreased to 87%. The volume of the irradiated mixed resins decreased still more, to 76%.

Li-OH mixed resins, which are used in the HWCTR, released more lithium than could be accounted for by the slight reduction in cation exchange capacity.

The macroreticular resin, "Amberlite" 200, claimed by the manufacturer to be more stable chemically and physically than the conventional gel resins, was slightly superior to "Amberlite" IR-120, which is currently used in the production reactors.

Discussion

Background

When ion exchange resins are used to process radioactive solutions, radiation damage to the resins results. Continued exposure will result in loss of exchange capacity, in volume changes, and, in some cases, in release of material from the resin into solution. Loss of exchange capacity is economically undesirable, shrinking or swelling of the resins may cause process problems, and the release of material from the resins may produce undesirable effects downstream of the resin beds.

A case in point is the ion exchange purification of water that is used as coolant in nuclear reactors. In this application, a dilute highly radioactive solution is passed through a bed of resin for a period of months. The major radiation dose comes from the short-lived radioactive materials collected while on-line. In addition, the longer-lived materials collected continue to irradiate the resin even if the resin is off-line. Because of the radiation problems, the resins are not regenerated. Hence reduction of exchange capacity through radiation damage to the resin is costly. Release of material from the resins into the coolant can result in the formation of activation products in the neutron flux of the reactor. The most objectionable element in this respect is sulfur, the precursor of two beta emitters, ^{35}S and ^{32}P, which have half lives long enough to merit concern if released to the environment.

Much of the work concerning radiation damage on individual resins was summarized by Marinsky[1]. Anion exchange resins were found to be generally more susceptible to radiation damage than cation exchange resins. In these investigations, the principal concern was the change in ion exchange capacity as a result of radiation, and only casual mention was made of the material that dissolves from the resins. The effects of radiation on mixed resins has not been previously reported.

In the present work, the amount and composition of soluble materials and the loss of exchange capacity as a result of gamma radiation were determined for cation, anion, and mixed resins. It was presumed that the degradation products are sulfates or sulfonates from the cation resin and amines from the anion resin, and that the following general reactions apply, where X and Y represent the cation and anion exchange resin matrices respectively, and R represents an organic group such as CH_3:

Degradation:

$$[X\text{-}SO_3]^- \ [H]^+ \overset{H_2O}{\rightsquigarrow} [X] + H_2SO_4 \tag{1}$$

$$[Y\text{-}NR_3]^+[OH]^- \rightsquigarrow \begin{array}{ll} \rightarrow [YOH] + NR_3 & (2a) \\ \rightarrow [Y\text{-}NR_2] + ROH & (2b) \end{array}$$

Absorption of Degradation Products in Mixed Bed:

$$[X\text{-}SO_3]^- \ [H]^+ + NR_3 \rightarrow [X\text{-}SO_3]^- \ [HNR_3]^+ \tag{3}$$

$$[Y\text{-}NR_3]^+ \ [OH]^- + H_2SO_4 \rightarrow [Y\text{-}NR_3]^+_2 \ [SO_4]^{2-} + 2H_2O \tag{4}$$

Thus, on irradiation of an individual resin, in addition to soluble nonionic material, soluble ionic materials that originate from the exchange groups will be released from the resins, rather than retained, because they are similar chemically to the exchange groups themselves. Beds of mixed resins that undergo radiation damage, on the other hand, would be expected to retain the ionic degradation products, and release only the nonionic products so that the pollution of a processed solution should be substantially reduced. However, radiation damage results in reduction of the available exchange capacity not only through destruction of exchange groups, but also through absorption of ionic degradation products.

Experimental Details

Degradation of mixed resin by radiation was studied in two experimental approaches, "column experiments" and "partitioned mixture experiments". "Column experiments", in which resin was subjected to several rinsing and irradiation cycles, provided a good measure of the amount of water-soluble material in the resin at successive stages of irradiation. However, accurate measurement of the exchange capacities in the mixed resin resulting from these cyclic treatments was difficult because non-uniform samples were obtained for analysis and because interactions occurred between eluted cations and anions during the analyses. The problems were eliminated in the "partitioned mixture experiments", from which supplemental data on exchange capacity losses in irradiated mixed resins were obtained. The cation and anion resins were maintained physically separate in these experiments, and contact between the resins was maintained through the water phase.

Column Experiments

A 250-ml sample of resin was rinsed exhaustively with water at 40°C according to the schedule given in footnote (b) of Table I. The flow rate through the one-inch diameter column was 8 to 9 ml/minute.

After rinsing, the moist resin was irradiated in a 10,000-curie Co^{60} source at dose rates from 6.4×10^5 to 1.7×10^6 rad/hour, as shown in Table I. The vented resin container was designed to minimize exposure to air. A given resin sample was subjected to the entire sequence of rinsing and irradiation cycles shown in Table I.

Each rinse was evaporated in an air stream at room temperature. Final drying of the residue was accomplished in a desiccator over anhydrous $CaSO_4$. Most of the residues attained constant weight. When the amount of residue was sufficiently large, analyses were made by a commercial microanalytical laboratory for the elements of interest: C, H, O, S, N, Cl, or Li. For those residues that had not dried to constant weight, free water was also determined.

The resin from these experiments was analyzed by methods described in a later section.

Partitioned Mixture Experiments

The "partitioned mixtures" were prepared by encapsulating the anion resin, leaving the cation resin loose in the container, and adding enough water to cover the mixture. The capsule was made of 100-mesh stainless steel screen[2]. These mixtures were sealed in short sections of 1-inch stainless steel pipe and irradiated in the gamma field produced by mixed fission products from spent reactor fuel, at a dose rate of 2.5×10^6 rep/hour. After irradiation, the individual resins were analyzed for residual and total regenerable capacities. Unirradiated individual resins were also analyzed. In addition to the mixtures, encapsulated anion resins were also irradiated, to furnish more detailed information with regard to the effect of radiation dose on exchange capacity.

Analysis of Mixed Resins

The individual resins were analyzed by the standard methods of elution, but the mixed resins were analyzed by the special scheme shown in Figure 1, which was devised to obtain as much information as possible from each sample. An extra elution sequence for the Li-OH resin was required (Step 1) so that the Li^+ could be determined in a medium free from alkali metals; other analyses were also performed on this sample to permit normalization of these data to those from Step 2.

Resins Examined

All resins were of the strong-acid or strong-base type, and were composed of a polystyrene matrix, with either sulfonic acid or quaternary ammonium exchange groups attached. The range in size of the resin beads was nominally 16 to 50 mesh (U.S. Standard Sieves), and the crosslinking was equivalent to 8% divinylbenzene. The commercial designations for the resins are as follows:

Cation Exchange Resins (H^+)

Amberlite® IR-120
"Amberlite" XE-77, nuclear grade Amberlite IR-120; resin has been washed with organic solvents and exhaustively regenerated.
"Amberlite" 200, a resin reported to have exceptional chemical and physical stability.
Dowex® 50W-X8

Anion Exchange Resin (OH^-)

"Amberlite" IRA-400

Mixed Cation and Anion Exchange Resins

"Amberlite" XE-150, a 1:1 equivalent mixture of the nuclear grade resins Amberlite XE-77 (H^+) and Amberlite XE-78 (OH^-)
Illco® TM-1, a 1:1 equivalent mixture of Dowex 50W-X8 (H^+) and Dowex 1-X8 (OH^-)
"Illco" NR-7, a 1:1 equivalent mixture of Amberlite IR-120 (Li^+) and Amberlite IRA-400 (OH^-)

Results

Leachable Materials

Table I presents weights and elemental compositions of residues from the column experiments. The residues are considered fairly representative of material released from the resins, with the exception of certain volatile constituents, such as low molecular weight amines and other organic compounds, which undoubtedly were lost during the evaporation.

®"Amberlite" is a Trademark of Rohm and Haas Company, Philadelphia, Pennsylvania.

"Dowex" is a Trademark of Dow Chemical Company, Midland, Michigan.

"Illco" designates resins processed and marketed by Illinois Water Treatment Company, Rockfort, Illinois.

In Table II, the results from Table I for C, S, N, and Li are expressed as values relative to the amount of resin. The total quantity of the element that will be released on irradiation of a known amount of resin is indicated by expressing the results on a weight basis. Tabulation of data in terms of g-atoms per equivalent of resin capacity provides a means of comparing the apparent exchange capacity loss indicated from the composition of the residue with that found from the exchange capacity determination made on the irradiated resin (Tables IV and V). The sulfur content of the residues corresponds rather well with loss of exchange capacity (sulfonic acid groups) from individual cation resin, but the nitrogen content does not shown a similar correspondence to loss of exchange capacity (amine groups) for individual anion resins. This is probably due to loss of volatile amines from the residue during evaporation. A comparison of similar data for mixed resins is not conclusive because degradation products were absorbed by the resin rather than rinsed out.

Cation Exchange Resins

The preliminary wash of each unirradiated cation resin produced a straw-colored solution; rinses of the irradiated resins were variously straw-colored to brown and murky as if suspended gelatinous material was present. This suspended material was not retained by the 1/2-inch plug of glass wool at the bottom of the resin column.

For "Amberlite" IR-120, "Amberlite" XE-77, and "Dowex" 50W-X8, all of which are similar to composition, the residue from the first rinse after irradiation contained a large proportion of sulfur and a small proportion of carbon, as shown in Table I. The residue from further rinsing contained a larger proportion of carbon. "Amberlite" 200 released material of essentially the same composition during both the initial rinse after irradiation and on further rinsing.

Table II shows that less than 10% of the sulfur was released from any of the resins up to the maximum radiation dose of 2.2 x 10^8 rad. The amount of carbon released, in terms of g-atoms per equivalent of resin, was less than that of the sulfur for all the resins except "Amberlite" 200.

Anion Exchange Resins

The only anion exchange resin that was examined for leachable material was "Amberlite" IRA-400. The leach water from the irradiated resin was yellow, and the resin had a strong ammonia-like odor after irradiation.

The quaternary ammonium groups on the resin probably decompose by a Hofmann-type degradation to produce an alcohol and an amine, as shown by Equation 2a-b. These products would have volatilized during the evaporation step. Therefore the amount of residue and the elemental content of the residue represent only the minimum release expected.

Mixed Resins

The data in Table I show that the amount of material released from the mixed H-OH resins was consistently small; even the rinses of irradiated resin were colorless. Elemental analyses were obtained only on the residue from the final irradiation and rinsing step, when the resin had received a total dose of 2 x 10^8 rad. The fraction of carbon was much larger than in residues from individual resins. Small fractions of sulfur and nitrogen were found.

The Li-OH mixed resin released more material than the H-OH resins. The residues were greenish-white. Even the residue from the preliminary rinse was unusually large, perhaps becuase of hydrolysis of the lithium resin. All the residues contained large proportions of lithium, which probably originated as LiOH. This hydroxide would have been converted to the carbonate by absorption of CO_2 from the air during evaporation to produce a high carbon content not representative of the material dissolved from the resin. The presence of carbonate in the residue was confirmed qualitatively by effervescence on acidification.

The residue from the Li-OH resin contained little sulfur, probably because the sulfate (sulfonate) released from the cation resin was absorbed by the anion resin. The nitrogen content of the leached material was higher than from the H-OH mixture since, as shown in Table V, amines (volatile base) were not retained on the cation exchange resin. Still, the nitrogen content of the leached material, as with the individual anion resin above, was probably reduced by volatilization of amines during evaporation.

Exchange Capacity of Individual Resins

Exchange capacities of individual resins from both column experiments and partitioned mixture experiments are shown in Table IV. For column experiments, results are reported on the weight basis of oven-dry resin that remained after the entire irradiation and leaching sequence shown in Table I. Results for partitioned mixture experiments are reported on the weight basis of the air-dry unirradiated resin; treated resins underwent only a single irradiation and no rinsing steps.

Results in Table IV demonstrate that anion resin is much more susceptible to radiation damage than is cation resin. Ultimate capacity measurements for anion resin show that less than 10% of the total (salt-splitting) exchange capacity was converted to weak-base groups, and that decomposition with loss of amine groups (Equation 2a) is the primary reaction.

Exchange Capacity of Mixed Resins

Column Experiments

Mixed resins, rather than separate components, were analyzed because the resins could not be satisfactorily separated, especially after irradiation. Because the principal error encountered in analyzing mixed resin was that of obtaining a uniform sample, the sequential schemes described in Figure 1 were devised to obtain as much information as possible from each sample. Final interpretation of data through the use of ratios reduced the sampling error.

Measurement of residual alkalinity or acidity in the individual resins was obscured by the neutralization reaction that occurred on elution of the mixed resin. Therefore, residual values were calculated by subtracting measured sulfate or volatile base content from the total exchange capacity as shown in Table V.

To obtain a value for the total exchange capacity that the resin in this particular sample would have had prior to irradiation, it was assumed that all degradation products related to exchange capacity losses were absorbed by the companion resin. Then the original total exchange capacity, T°, would be the total exchange capacity measured on the irradiated sample, T, plus the appropriate degradation product, V or S. Since these degradation products were held by the companion resin, the quantity found by analysis was proportional to the amount of the companion resin in the sample. Only in a 1:1 equivalent mixture would the measured V or S be applicable to both resins. The V and S were added to the total exchange capacity without correction for the calculation of T°, however, since the accuracy of the experimental results did not warrant further refinement.

In Table V, buildup of volatile base and sulfate within the mixed resins is evident. Even in the unirradiated mixed resin a small amount of sulfate and volatile base were found. This indicates that a small loss in exchange capacity of individual resins is sustained by absorption of degradation products when the resins are mixed. A mixed H-OH resin does not have the strong amine odor that is associated with the anion resin alone, probably because the amine has been absorbed by the cation resin.

The amounts of volatile base and sulfate were notably less for the irradiated Li-OH mixture than for the H-OH counterparts, although the fractional exchange capacity loss was similar. The Li-OH mixture is as susceptible to radiation damage as the H-OH mixture, yet it is less able to retain degradation products, particularly the volatile base and lithium.

Results in Table II and Table V suggest that some of the lithium in the original resin was contained elsewhere than on the strong acid exchange groups of the original resin. This is evident in the discrepancy between the lithium content and the total (salt-splitting) capacity of the unirradiated resin. The presence of excess lithium was confirmed independently by the high lithium content of the residue, where the lithium released is much greater than the measured loss of salt-splitting capacity of the resin. The lithium content of the resin after irradiation is in good agreement with the measured salt-splitting capacity.

Partitioned Mixture Experiments

The partitioned mixture experiments were designed to overcome the uncertainties inherent in the analysis of mixed resin from the leaching experiments. As described in the experimental section, the resins were maintained physically separate, and contact was maintained through the water phase. Thus there was no problem of separating the resins prior to analysis, and all results could be expressed relative to the original resin.

Only exchange capacity measurements were made on these resins; results are given in Table VI. Determination of the residual acidity of the irradiated cation resin was not possible because these resins reacted with the steel container in which they were irradiated. The anion exchange resins were not affected, however, and their analyses are considered reliable.

In the last column of Table VI, these data are corrected to correspond to a 1:1 anion-to-cation equivalent mixture, so that these results can be compared with those from the leaching experiments, in which the 1:1 mixture was used.

Production of Carbon Dioxide

Additional exhaustion of the anion resin occurs through absorption of carbon dioxide that is produced from radiolysis of organic material. Tables IV and V and Figure 2 show that in general CO_2 contributed less than 10% to resin exhaustion in the dose range used in this work. Furthermore, for the resins from the column experiments, at least, no effect on the CO_2 production was evident when a cation resin was mixed with the anion resin. This provides indirect evidence that the precursor of this CO_2 comes primarily from the anion exchange resin.

The mixed resins that were irradiated in the sealed tubes during the partitioned mixture experiments showed a much higher CO_2 production than those from the other experiments. The differences in the experimental conditions, namely, the closed system in which the irradiations were made and the fact that these resins were not rinsed before irradiation, may account for the higher results.

Volume Changes

Table I shows that shrinkage of the mixed resins on irradiation was significantly greater than that of either individual component. This was determined from the height of the wet packed column during the leaching experiments. Because shrinking occurred with both the H-OH and the Li-OH resins, it is attributed primarily to shrinking of the anion resin. This was qualitatively confirmed by microscopic examination of the resin, which showed the anion exchange resin beads in the wet swollen state were perceptibly smaller in the irradiated sample.

Shrinking of the anion resin bead on irradiation would be caused by loss of hydrophilic exchange groups and by partial conversion of the highly swollen hydroxyl form to the less highly swollen sulfate and carbonate forms. The cation resin may also have shrunk, rather than swelled as it did when irradiated alone, through partial conversion of the sulfonic acid group to a less hydrophilic salt form by absorption of the volatile base from the anion resin.

Further, part of the shrinking may be accounted for by a reduction on irradiation of the tendency of mixed resins to agglomerate. Shrinking of the resin bed would result in an increase in pressure drop across columns during service.

Discussion

To illustrate the effect of mixing on exchange capacity of irradiated resins, data from Tables IV, V, and VI are plotted as a function of dose in Figures 3 and 4. Capacities are expressed as the fraction of the original residual or total exchange capacity that remained after irradiation. Values for mixed resins from column experiments were obtained from the following expressions:

$$(R/R^\circ) = \frac{(R/T^\circ)\text{irradiated}}{(R/T^\circ)\text{unirradiated}}$$

$$(T/T^\circ) = \frac{(T/T^\circ)\text{irradiated}}{(T/T^\circ)\text{unirradiated}}$$

Loss in total exchange capacity is independent of whether the resin is irradiated alone or in a mixture. However, the residual exchange capacity, which is the titratable acidity or alkalinity in the resin, is reduced in resin mixtures compared to individual resins. The residual capacity of the cation resin is more greatly affected in the H-OH mixture than in the Li-OH mixture. Removal of amine degradation products by the hydrogen form of the resin is promoted by the neutralization reaction that accompanies this step; removal by the lithium form involves only simple exchange.

These data, then, confirm that the useful capacity of mixed resin is reduced on irradiation not only through loss of exchange groups but also through mutual absorption of the ionic products that result. This phenomenon might prove of significance in the ion exchange purification systems for water used in nuclear reactors, where ionic concentrations are low and the resins are used with radioactive solutions for long periods of time. Here resin degradation may prove to be the factor that limits resin lifetime.

Impurities are released from the individual cation and anion exchange resins on irradiation, but irradiated mixed H-OH resins produce pure water because of their ability to absorb ionic degradation products. Mixed resin in the Li-OH form will cause a greater pollution of water on irradiation than the H-OH mixture because the cation resin in the lithium form does not quantitatively retain the volatile base and the anion resin cannot retain the lithium.

The presence of volatile base and sulfate that can be eluted from mixed resins identifies these as resin degradation products. The results for loss of exchange capacity of individual resins are in general agreement with those previously reported[1].

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TABLE I

WATER-SOLUBLE MATERIAL FROM ION EXCHANGE RESINS BEFORE AND AFTER IRRADIATION

(Column Experiments)

Resin	Weight of 250 ml Resin Sample Treated, g		Cumulative Radiation Dose[a], 10^8 rad	Wet-Packed Volume of Resin, % of Original	Treat-ment[b]	Weight of Dissolved Solids from Treatment, mg	Elemental Composition of Solids, wt %						
	As-Received	Oven-Dry					C	S	H	O	N	Cl	Li
Cation Exchange Resins (H^+ Form)													
"Amberlite" IR-120	180	104	0	100	A	6	37		4.9				
					B	<1	-						
			1.1	nd	A	3902	2.5	15	7.0	63			
					C	20	15	14	6.2	42			
			2.2	nd	A	2152	2.5	25	3.1	54			
					C	82	5.2	15	6.7	58			
					Total	6162							
"Amberlite" XE-77	192	101	0	100	A	79	27	12	6.1	43			
					B	3	-	-	-	-			
			0.51	106	A	926	0.6	22	3.4	54			
					C	11	15	14	6.1	-			
			1.01	110	A	940	7.9	25	2.9	56			
					C	23	25	12	5.9	16*			
			1.51	110	A	1093	4.3	23	4.2	27*			
					C	22	22	12	5.7	15*			
			1.93	106	A	914	3.2	26	3.8	33*			
					C	19	19	13	6.0	30*			
					Total	4030							
"Amberlite" 200	200	120	0	100	A	2							
					B	5							
			1.1[c]	101	A	2273	16	18	4.6	60			
					C	330	20	23	3.7	52			
			2.2[d]	101	A	1447	20	18	4.7	56			
					C	251	21	19	4.7	55			
					Total	4308							
"Dowex" 50W-X8	128	91.5	0	100	A	104	30	11	6.0	44			
					B	32	36	12	5.5	29			
			1.1	100	A	4145	0.4	16	7.2	59			
					C	12	15	14	6.1	36			
			2.2	104	A	2117	3.7	27	3.2	59			
					C	14	18	13	6.1	-			
					Total	6424							
Anion Exchange Resin (OH^- Form)													
"Amberlite" IRA-400	181	90.5	0	100	A	145	46	-	9.4	27	6.3	-	
					B	55	58	-	9.9	23	4.7	0.3	
			0.57[d]	100	A	39	41	-	9.6	24	10.9	0	
					C	11	42	-	9.6	-	10.1	0.4	
			1.21[c]	95	A	37	37	-	9.0	25	10.8	Trace	
					C	3	45	-	8.5	-	4.2	0.4	
			1.80[d]	87	A	32	38	-	9.0	25	10.4	Trace	
					C	9	40	-	8.9	-	3.3	0.5	
					Total	331							
Mixed Cation and Anion Exchange Resins													
"Amberlite" XE-150 (H-OH)	127	66	0	100	A	1							
					B	1							
			1.1	85	A	1							
					C	<1							
			2.3	76	A	9	32	-	5	26	1		
					C	3		0.2			4		
					Total	15							
"Illco" TM-1, #1 (H-OH)	177	88	0	100	A	1	No analyses - Insufficient sample						
					B	2							
			1.1	86	A	2							
					C	1							
					Total	6							
"Illco" TM-1, #2 (H-OH)	172	88	0	100	A	2							
					B	2							
			1.1	88	A	2							
					C	<1							
			2.1	76	A	9	46	0.8	6.0		3.9	0.4	
					C	2		2.6			4.7		
					Total	17							
"Illco" NR-7 (Li-OH)	171	82	0	100	A	90	43		7.3	31	5.9	Trace	-
					B	51	32		4.5	38	3.1	0	3.4
			1.1	85	A	653	18		0.1	37	0	0	16
					C	212	18		1.3	40	1.5	0	15
			2.3[c]	77	A	532	15		1.6	39	1.2	0.5	13
					C	232	15	10.1	4.1	40	3.2	2.5	8.5
					Total	1770							

(a) Dose rate was 1.7 x 10^6 rad/hr except as noted.

(b) Treatments were as follows:
A = 1 column volume (250 ml) passed once through column.
B = Composite of 3 successive treatments: 1 column volume recycled 10 times each treatment.
C = 1 column volume recycled 10 times.

(c) Dose rate was 7.2 x 10^5 rad/hr.

(d) Dose rate was 6.4 x 10^6 rad/hr.

nd = not determined.

* O analysis suspect; material balance poor.

TABLE II

Elements Released from Resins Before and After Irradiation
(Column Experiments)

	Cumulative Radiation Dose, 10^8 rad.	Cumulative Amount of Element Released mg-atoms/g dry resin (g-atoms/g-eq. of resin)			
		C	S	N	Li
Cation Exchange Resins (H^+ Form)					
"Amberlite" IR-120	0	0.002	- -		
	1.1	0.08	0.18 (0.037)		
	2.2	0.13	0.35 (0.071)		
"Amberlite" XE-77	0	0.02	0.003 (0.0006)		
	0.51	0.03	0.06 (0.014)		
	1.01	0.10	0.13 (0.030)		
	1.51	0.13	0.21 (0.046)		
	1.93	0.16	0.28 (0.062)		
"Amberlite" 200	0	-	- -		
	1.1	0.29	0.13 (0.028)		
	2.2	0.52	0.21 (0.045)		
"Dowex" 50W-X8	0	0.045	0.004 (0.0008)		
	1.1	0.059	0.22 (0.048)		
	2.2	0.132	0.41 (0.089)		
Anion Exchange Resin (OH^- Form)					
"Amberlite" IRA-400	0	0.091		0.010 (0.0028)	
	0.57	0.110		0.014 (0.0040)	
	1.21	0.124		0.017 (0.0049)	
	1.80	0.138		0.020 (0.0058)	
Mixed Cation and Anion Exchange Resins					
"Amberlite" XE-150 (H-OH)	0	-	-	-	
	1.1	-	-	-	
	2.3	0.004	-	0.0001 (0.00005)	
"Illco" TM-1, #2 (H-OH)	0	-	-	-	
	1.1	-	-	-	
	2.1	0.004	-	0.0004 (0.00021)	
"Illco" NR-7 (Li-OH)	0	0.06	-	0.006 (0.0027)	0.005 (0.0014)
	1.1	0.22	-	0.009 (0.0040)	0.24 (0.109)
	2.3	0.34	0.009 (0.005)	0.021 (0.0095)	0.39 (0.179)

TABLE III

Identification of Symbols

R_C = Residual Cation Exchange Capacity:

(a) For H^+ resins, this is the titratable acidity eluted from a resin by a neutral salt solution; for new resins this was assumed to be the same as T_C, below.

(b) For Li^+ resins, this is the lithium content of the resin.

T_C = Total Cation Exchange (Salt-Splitting) Capacity:

The titratable acidity eluted by a neutral salt solution from a resin after exhaustive regeneration with acid.

R_A = Residual Anion Exchange Capacity:

The total titratable alkalinity (to pH 4.0) eluted from a resin by a neutral salt solution. There are generally two well-defined inflection points in the titration curve, so that R_A is defined as the sum of: (OH^-) and (HCO_3^-):

(OH^-) -- determined by the titration to pH 7.2
(HCO_3^-) -- determined by the titration from pH 7.2 to pH 4.0

The assignment of (OH^-) and (HCO_3^-) was made for simplicity.

T_A = Total Anion Exchange (Salt-Splitting) Capacity:

The strong-base exchange groups on the resin. These were determined by converting the resin to the desired anionic form by a salt solution, then eluting the anion held by the resin by another salt solution, and determining the concentration of the eluted anion.

$T_A + W$ = Ultimate Anion Exchange Capacity:

The strong-base plus the weak-base exchange groups on the resin. This was determined in a manner similar to T_A, except that the resin was converted to the desired anionic form by treatment with an acid, rather than a salt as above.

S = Sulfate content of the anion resin in the mixed resin (Equation 4).

V = Volatile base (NR_3) content of the cation resin in the mixed resin (Equation 3).

Superscript "o" indicates the unirradiated resin.

TABLE IV

Exchange Capacity of Individual Resins Before and After Irradiation

(See Table III for identification of symbols)

		Results of Analysis (meq/g dry resin)					Interpretation of Results			
			R_A							
	Dose, 10^8 rad	$R_C \equiv T_C$ (c)	(OH^-)	(HCO_3^-)	T_A	T_A+W	$T_C/T_C°$	$(OH^-)/R_A°$	$(HCO_3^-)/R_A°$	$T_A/T_A°$
Cation Exchange Resins (H^+ Form)										
"Amberlite" IR-120 (a)	0	4.75					1.0			
	2.2	4.33					0.91			
"Amberlite" XE-77 (a)	0	4.78					1.0			
	1.9	4.46					0.93			
"Amberlite" 200 (a)	0	4.64					1.0			
	2.2	4.44					0.96			
"Dowex" 50W-X8 (a)	0	4.78					1.0			
	2.2	4.43					0.93			
Anion Exchange Resins (OH^- Form)										
"Amberlite" IRA-400 (a)	0		3.12	0.17	3.41	3.35		0.88	0.12	1.0
	1.8		1.74	0.62	2.31	2.41		0.53	0.19	0.68
			(meq/g moist resin)							
"Amberlite" IRA-400 (b)	0		1.36	0.08	1.78	1.90		0.94	0.06	1.0
	0.014		1.35	0.10	-	-		0.94	0.07	-
	0.20		1.28	0.13	-	-		0.89	0.09	-
	0.49		1.13	0.14	1.37	1.51		0.78	0.10	0.77
	1.4		0.70	0.21	0.98	1.13		0.49	0.15	0.55
"Amberlite" IRA-400 (b)	0		1.54	0.18	1.82	1.91		0.90	0.10	1.0
	0.71		1.18	0.26	1.40	1.52		0.69	0.15	0.77
"Amberlite" XE-78 (b)	0		1.44	0.14	1.61	1.67		0.91	0.09	1.0
	0.49		1.16	0.19	1.32	1.39		0.73	0.12	0.82
	0.71		1.08	0.21	-	-		0.68	0.13	-
	1.4		0.76	0.28	0.89	0.99		0.48	0.18	0.55

(a) Column experiments.
(b) Partitioned mixture experiments.
(c) Residual and total exchange capacity of the cation exchange resin are considered the same.

TABLE V

Analysis of Mixed Resins from Column Experiments
(See Table III for identification of symbols)

		Results of Analysis(a) (meq/g of dry mixed resin)									Interpretation of Results							
Resin	Dose, 10^8 rad	T_C	T_A	T_A+W	S	V	CO_2(b)	R_A (OH^-)	R_A (HCO_3^-)	R_C (Li^+)	$R_C=T_C-V$	$R_A=T_A-S$	$T_C^\circ=T_C+S/2$	$T_A^\circ=T_A+V$	R_C/T_C°	T_C/T_C°	R_A/T_A°	T_A/T_A°
"Amberlite" XE-150 (H-OH)	0	1.90	1.89	1.94	0.05	0.16	-				1.74	1.84	1.92	2.05	0.91	0.99	0.90	0.92
	0	1.87	1.91	2.12	0.02	0.11	-				1.76	1.89	1.88	2.02	0.94	0.99	0.94	0.95
	0	-	-	-	-	-	0.31											
	2.2	1.72	1.20	1.25	0.41	1.07	-				0.66	0.79	1.92	2.27	0.34	0.90	0.35	0.53
	2.2	1.79	1.01	0.90	0.22	1.11	-				0.68	0.79	1.90	2.12	0.36	0.94	0.37	0.48
	2.2	-	-	-	-	-	0.36											
"Illco" TM-1 (H-OH)	0	1.94	2.22	2.46	0.15	0.06	-				1.88	2.07	2.01	2.28	0.94	0.97	0.91	0.97
	0	1.96	2.21	2.43	0.15	0.05	-				1.91	2.07	2.03	2.26	0.94	0.97	0.92	0.98
	0	-	-	-	-	-	0.06											
	1.1	1.58	1.41	1.74	0.36	0.76	-				0.82	1.05	1.86	2.17	0.44	0.85	0.48	0.65
	1.1	2.08	1.31	1.24	0.28	0.89	-				1.19	1.03	2.22	2.20	0.54	0.94	0.47	0.60
	1.1	-	-	-	-	-	0.13											
"Illco" TM-1 (H-OH)	0	1.85	2.02	2.67	0.15	0.04	-				1.81	1.87	1.93	2.06	0.94	0.96	0.91	0.98
	0	1.87	2.02	2.64	0.16	0.07	-				1.80	1.86	1.95	2.09	0.92	0.96	0.89	0.97
	0	-	-	-	-	-	0.06											
	2.2	2.01	0.89	1.20	0.52	1.32	-				0.69	0.36	2.27	2.21	0.30	0.89	0.16	0.40
	2.2	1.76	0.94	1.20	0.50	1.19	-				0.57	0.44	2.01	2.13	0.28	0.88	0.21	0.44
	2.2	-	-	-	-	-	0.19											
"Illco" NR-7 (LiOH)	0	1.77	2.23	2.38	0.01	0.09	-	1.95	0.20		1.68	2.22	1.78(c)	2.32(c)	0.94	0.99	0.96	0.96
	0	1.77	2.24	2.29	0.01	0.06	-	1.97	0.20		1.71	2.23	1.78	2.30	0.96	0.99	0.97	0.97
	0	1.77		2.25			-			1.91								
	0	1.72		2.22			-			1.91								
	0						0.17											
	2.3	1.48	0.85	0.82	0.23	0.26	-	0.30	0.26		1.22	0.62			0.69	0.83	0.27	0.37
	2.3	1.57	0.86	0.95	0.23	0.27	-	0.28	0.24		1.30	0.63			0.73	0.88	0.27	0.37
	2.3	2.17	-	0.62	-		-			2.06								
	2.3	1.41	-	0.95	-		-			1.37								
	2.3						0.29											

(a) Results from a single sampling of mixed resin are tabulated in each row.
(b) Millimoles of CO_2 per g. of dry mixed resin.
(c) These values were used for calculation of the ratios; T_C° and T_A° cannot be calculated for the irradiated Li-OH resins, since V and S were not quantitatively retained.

TABLE VI

Analysis of Mixed Resins from Partitioned Mixture Experiments

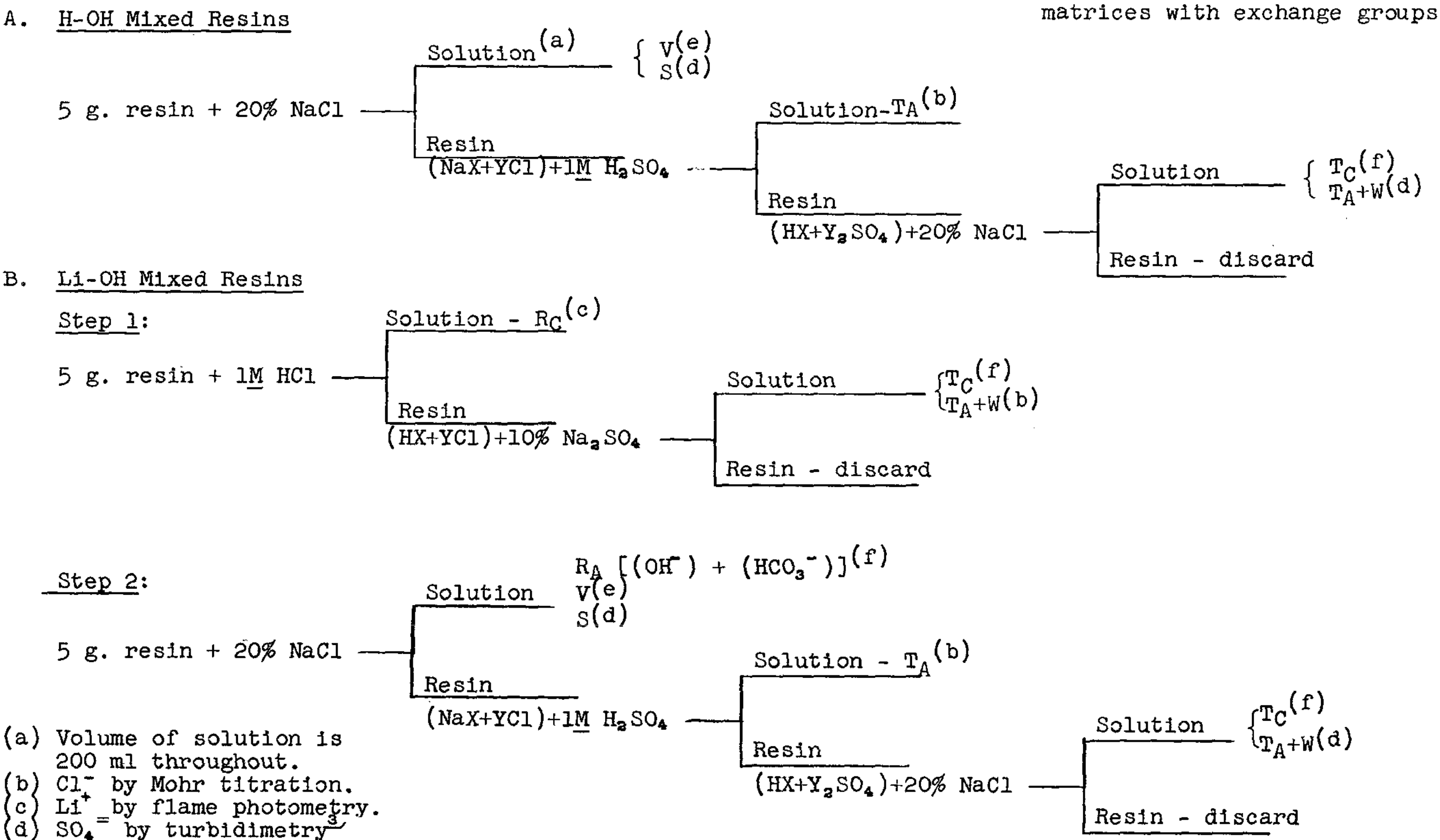
(See Table III for identification of symbols)

		Results of Analysis (meq/g moist anion or cation resin)						Interpretation of Results (Corrected to 1:1 equivalent mixture)			
		Cation Resin		Anion Resin							
				R_A							
Resin	Dose, 10^8 rad	R_C	T_C	OH^-	HCO_3^-	T_A	T_A+W	T_C/T_C°	T_A/T_A°	R_C/R_C°	R_A/R_A
'Amberlite" IR-120 (H^+)	0	2.63	~2.63	1.59	0.22	1.82	1.91	1.0	1.0	1.0	1.0
and	0.53	2.22	2.46	0.79	0.40	1.49	1.64	0.94	0.82	0.80	0.72
'Amberlite" IRA-400 (OH^-)	1.0	1.49	2.32	0.33	0.57	1.29	1.44	0.88	0.71	0.43	0.62
'Amberlite" XE-77 (H^+)	0	2.59	~2.59	1.44	0.14	1.61	1.67	1.0	1.0	1.0	1.0
and	0.53	2.13	2.39	0.77	0.36	1.31	1.37	0.92	0.81	0.76	0.78
'Amberlite" XE-78 (OH^-)	1.0	1.72	2.33	0.35	0.49	1.12	1.20	0.90	0.70	0.52	0.63

FIGURE 1

Scheme for Analysis of Mixed Resins
(See Table III for identification of symbols)

X and Y are the respective cation and anion resin matrices with exchange groups



(a) Volume of solution is 200 ml throughout.
(b) Cl^- by Mohr titration.
(c) Li^+ by flame photometry.
(d) $SO_4^=$ by turbidimetry[3]
(e) Volatile base distilled from caustic solution.
(f) Acid-base titration.

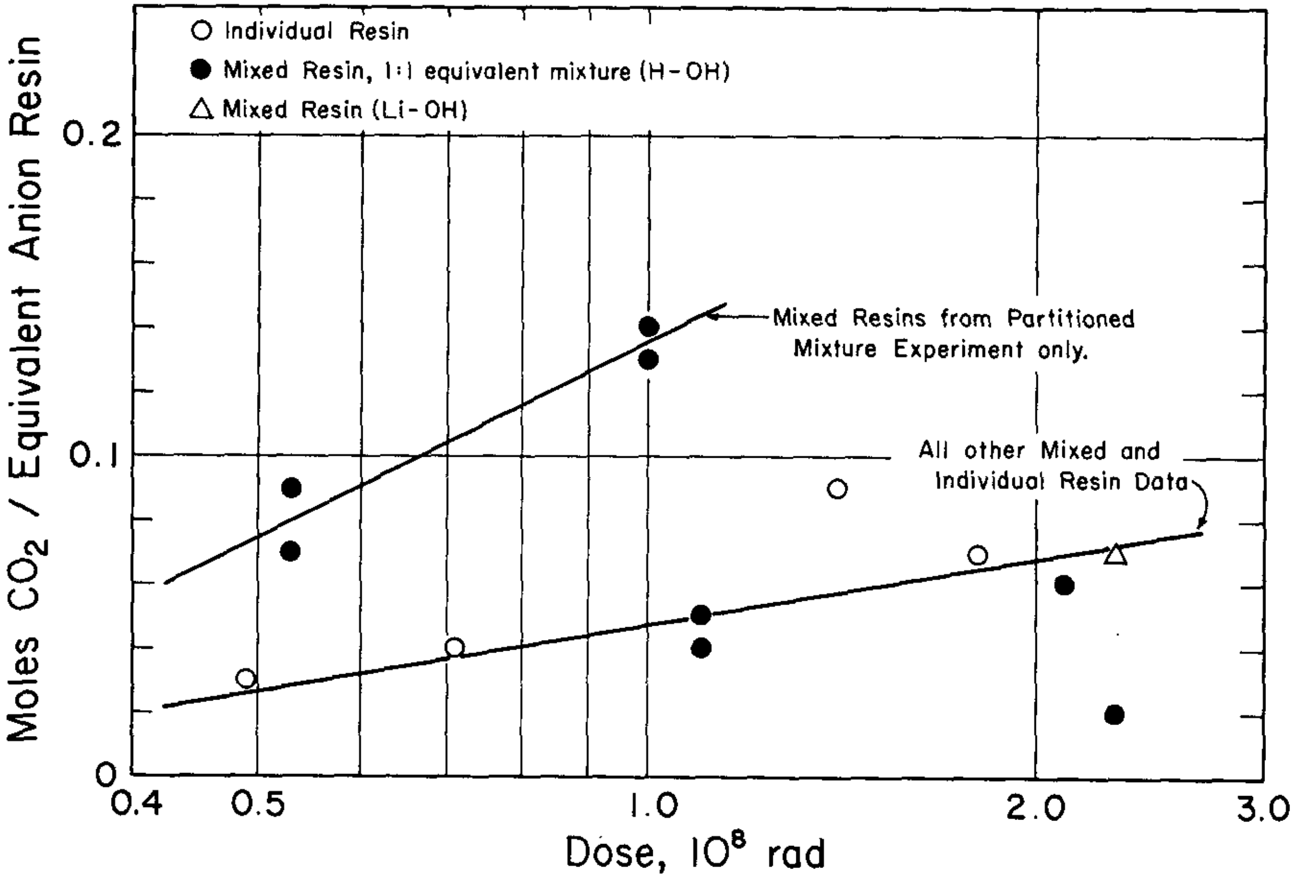


FIG. 2 PRODUCTION OF CARBON DIOXIDE DURING GAMMA IRRADIATION OF RESINS

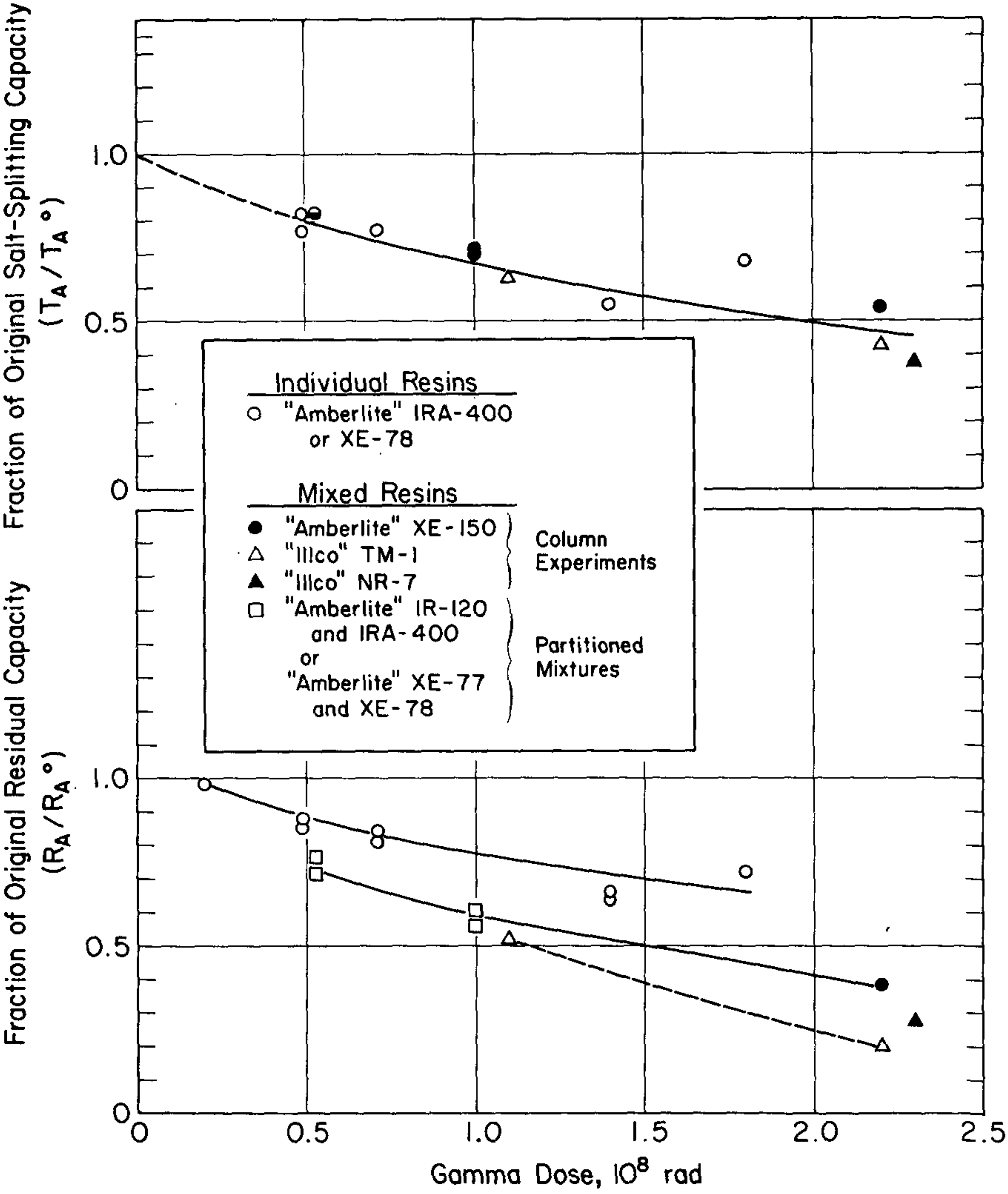


FIG. 3 EFFECT OF GAMMA RADIATION ON EXCHANGE CAPACITIES OF ANION EXCHANGE RESIN ALONE AND MIXED WITH CATION EXCHANGE RESIN

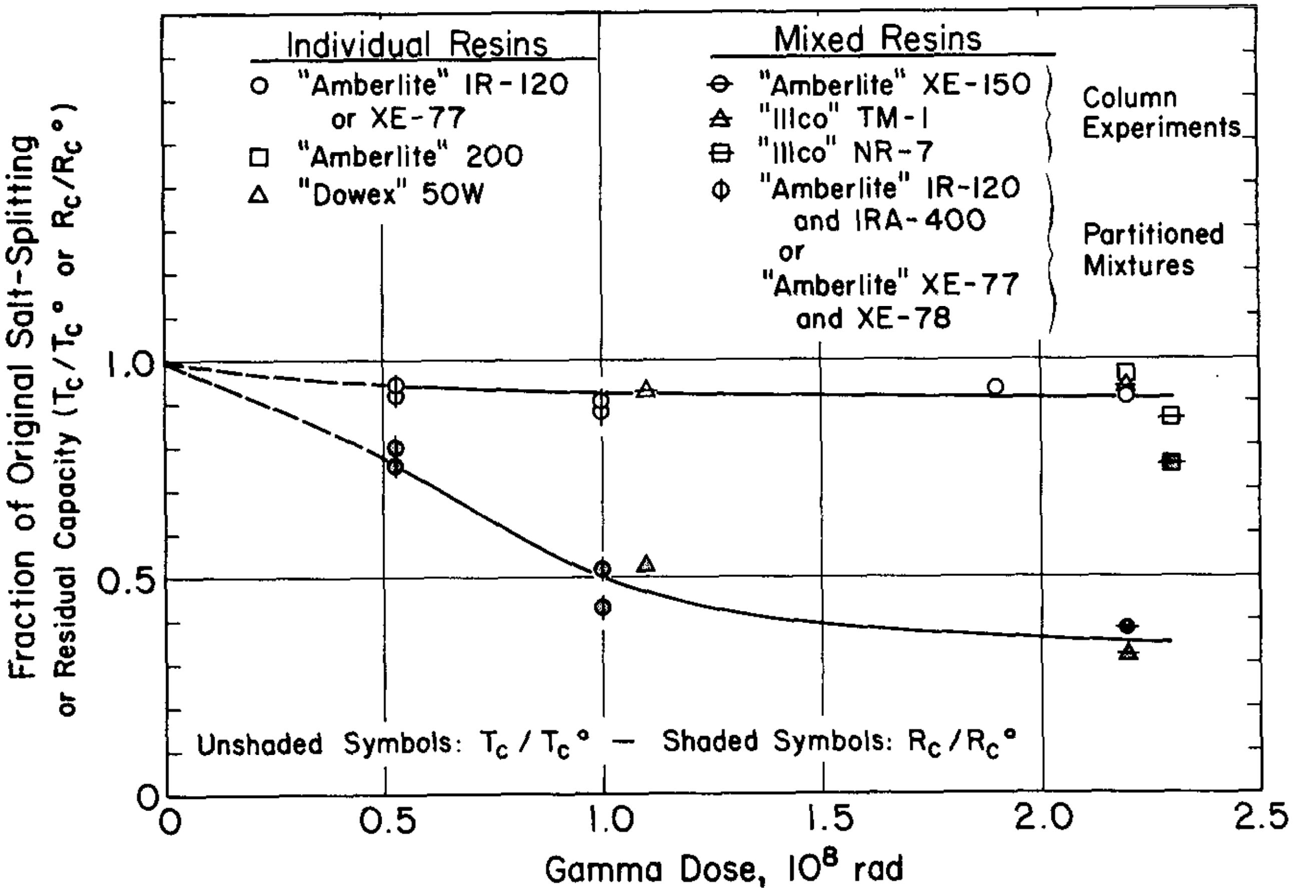


FIG. 4 EFFECT OF GAMMA RADIATION ON EXCHANGE CAPACITIES OF CATION EXCHANGE RESIN ALONE AND MIXED WITH ANION EXCHANGE RESIN