

# Effect of Cobalt-60 Gamma Radiation on Ion Exchange Resin\*

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The effect of gamma radiation on commercial ion exchanger was studied. The air dried samples conditioned were sealed in polyethylene pouch and exposed to radiation from cobalt-60 (2000 curie, dose rate  $2 \cdot 10^5$  r/hr) for a given period ranging from 1 to 177 hrs. The total ion exchange capacity of the sample was determined.

Gamma irradiation up to 20 hrs., do not prohibitively decrease the capacity of cation exchangers. When exposed for 177 hrs., carboxylic cation exchanger was most resistant to radiation damage. It was proved that phenolic base cation exchanger was more stable than sulfonated styrene-divinyl benzene cation exchanger, anion exchanger lost the capacity more three times than cation exchanger with exposure for 177 hr., and for the strong basic quarternary ammonium anion exchanger, chloride form was somewhat more stable than hydroxyl form.

## INTRODUCTION

The ion exchange methods have been used successfully in radiochemical process for the separation of ions having closely similar properties such as lanthanides, actinides and fission products, for the removal of radioactive substances from solution, etc.. The early ion exchange resins were mainly phenol type, but the polymer of styrenes has been used recently, in order to improve the exchange capacity and physical chemical stability of resins. Cationic and anionic exchangers which are made of styrene divinyl benzene copolymer having an reacting group, are the most widely used in various industrial process. When the resin are reused repeatedly, important troubles occurred are rock out of its net structure with colloidal particles, oxidation by oxidants and decreases of exchange capacity by degradation. It has been found that those troubles rarely occur on cation exchanger, but strongly basic quarternary ammonium exchangers are decompose to lower amines and lose several tens per cent of its original capacity. When the ion exchange resin was used for the separation of radioactive substance, besides the above mentioned troubles, the radiation damage of resin should be considered as an important problem.

The effect of  $\alpha$ -,  $\beta$ - or  $\gamma$ - radiation upon resin is mainly concerned with the intensity of radiation field and the period of irradiation time. However, effects of physical and chemical conditions such as environment, exchange procedure etc., should be taken into consideration. In this paper results of the radiation damage study on several ion exchange resins are presented. Ion

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\* Studies on the treatment of radioactive nuclides by ion exchange (Part 12).

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exchange resins were irradiated with a cobalt-60 gamma source, without consideration about the effect of physical, chemical conditions, and the loss of capacity was measured.

### EXPERIMENTAL

The radiation work was carried out with a cobalt-60 gamma source (2,000 curie, dose rate  $2 \times 10^6$  r/hr.)

The ion exchange resin samples were prepared as follows: commercial exchangers (16~60 mesh) were conditioned by treating with hydrochloric acid and sodium hydroxide solution.

A solution of 5% sodium chloride solution was passed through the cation exchanger, and followed by a 10% hydrochloric acid solution. After this Na-H exchange treatment was repeated two or three times, the resin was converted to the hydrogen form or sodium form, washed with water until the effluent was free from acid or chloride ion and then dried at 60°C.

A solution of 5% sodium hydroxide was used for weakly acidic cation exchanger in stead of sodium chloride solution.

The anion exchanger was conditioned by treating with 5% sodium hydroxide solution at 40°C and then with 5% sodium chloride solution (or 5% hydrochloric acid for weakly basic anion exchange resin). The resin was converted to the hydroxide or chloride form, and washed with water until the effluent become free from chloride or hydroxide ion, respectively, by using silver nitrate or phenolphthalein as indicator.

The solution of sodium hydroxide used was free from carbon dioxide, and the washing of anion exchanger was carried out with CO<sub>2</sub> free water.

A 5g of the sample sealed in polyethylene pouch was exposed to the cobalt-60 source for a given period ranging from 1 to 177 hours. Taking a 1g portion of the irradiated resin, capacity loss was measured by following column procedure.

Strongly acidic cation exchanger was filled in a column of 5 mm. diameter, converted to hydrogen form by treating with 1 *N* hydrochloric acid, and then 1 *N* solution of calcium chloride was passed through the column. Effluent was titrated with 1/10 *N* sodium hydroxide solution.

Weakly acidic cation exchanger was conditioned as above, a solution of 1/10 *N* sodium hydroxide was passed through the column, and the effluent was titrated with 1/10 *N* hydrochloric acid solution.

Strongly basic anion exchanger was treated with 1 *N* sodium hydroxide solution converting the resin to the hydroxide form, and washed with water to methyl orange neutral. Add a solution of 1 *N* sodium sulphate through the column, and sodium hydroxide formed in effluent was titrated.

Weakly basic anion exchanger converted to hydroxide form was treated with 1 *N* hydrochloric acid, converted to chloride form. A solution of 1 *N* sodium sulphate was passed through the column, and the chloride ion in effluent was titrated with 1/10 *N* silver nitrate solution.

## RESULTS

The results are summarized in Table 1.

Table 1. Capacity loss of resins as a result of gamma irradiation.

Type of resins	Form	Capacity (meq/gr. of dry resin) irradiation time (hr)					Capacity loss (%), irradi. for 177 hr. ( $3.5 \times 10^7$ r)	
		0	1	15	20	177		
Strong acid nuclear sulfonic acid type	Dowex 50	Na	3.55	3.57	3.47	3.49	3.32	6.5
		H	—	3.66	3.58	3.48	3.18	10.4
	Zeollex SA	H	3.48	3.46	3.48	3.45	3.31	4.9
(styrene base)	Diaion SK #1	H	3.52	3.60	3.50	3.47	3.20	9.1
Strong acid sulfonic acid type	ZeoRex	H	1.96	2.06	2.06	2.04	1.91	2.5
(phenolic base)	Duolite C3	H	2.06	2.17	2.15	2.10	2.05	0.5
Weak acid carboxylic	Duolite CS101	H	7.85	8.02	7.74	7.77	8.00	-1.9
Carbonaceous exchanger	Sulfonated coal	H	0.50	0.48	0.49	0.46	0.45	10.0
Strong base quarternary ammonium	Dowex 2	Cl	2.10	1.96	2.00	1.99	1.61	23.3
		OH	—	1.88	1.81	1.74	1.40	33.3
(styrene base)	Diaion SA#100	Cl	2.06	2.02	1.99	1.94	1.77	14.1
		OH	—	1.98	1.93	1.90	1.53	25.8
Weak base	Dowex 3	Cl	2.45	2.47	2.40	2.40	2.08	16.1

The values of capacity loss shown in table 1 is rather high, comparing with the previous works<sup>1)</sup>, but this may be attributed to the difference of the field strength of gamma source.

All cation exchangers show only a small loss of the capacity for gamma irradiation up to 20 hrs. ( $4 \times 10^6$  r), but carboxylic type resin increased its swelling property and the effluent on regeneration of phenolic resin became more darkened. For anion exchangers, they were found that exchange capacity decreased distinctly, appearance of resins turned to brownish from pale yellow, color of regeneration effluent deepened and amine-like odor was extensive.

However, when exposed for 177 hrs. ( $3.5 \times 10^7$  r), the exchange capacity of any resin but carboxylic resins decreased. Among of strongly acidic exchangers, capacity loss of styrene type resins (4.9~10.4%) is larger than that of phenol type resins (0.5~2.5%), and this shows that the capacity loss is inversely dependent on the chemical stability of cationic resin in free form. But it agreed with the order of stability (e.g. solubility) of resin that the capacity loss of free form resins is larger than that of sodium forms.

Anion exchange resins lost the capacity more three times than cation exchange resins. Weakly basic resin lost 16% of its capacity. For strongly basic anion exchangers, the capacity loss of chloride form was 14.1~23.3%, and of hydroxide form was 25.8~33.3%.

The loss of exchange capacity under irradiation may be caused by decomposition of base resin, or by oxidation decomposition of base resin and functional group\* with oxidatives resulted from radiation effect on water. However, if dehydrogenation or dehydration occurred in base resin under irradiation, it may be caused the gain of exchange capacity per unit weight of resin.

#### REFERENCES

- (1) I. R. Higgins, *USAEC, ORNL-1352* (1953) ; S. A. Fisher, *USAEC, RMO-2528* (1954) ; G. I. Cathers, "Progress in Nuclear Energy, III, Process Chemistry," Vol. 1. p. 68 (1956) ; J. L. Ryan, E. J. Wheelwright, *Ind. Eng. Chem.*, **51**, 60 (1959).

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\* Decomposition of functional groups was checked by detection of sulphate ion in wash solution of irradiated cation exchangers, and by appearance of amine-like odor in irradiated anion exchangers.