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Citation
Bulletin of the Institute for Chemical Research, Kyoto University (1959), 37(5-6): 349-352

Issue Date
1959-12-25

URL
http://hdl.handle.net/2433/75741

Type
Departmental Bulletin Paper
Effect of Cobalt-60 Gamma Radiation
on Ion Exchange Resin*

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(Received August 10, 1959)

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 2·10⁵ 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 lantanides, 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 styrens has been used recently, in order to
improve the exchange capacity and physical chemical stability of resins. Ca-
tionic 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
occured 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 rearly 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 α-, β- or γ- 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 $2 \times 10^5$ 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 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 CO₂ free water.

A 5 g 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 1 g 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 1N sodium hydroxide solution converting the resin to the hydroxide form, and washed with water to methyl orange neutral. Add a solution of 1N sodium sulphate through the column, and sodium hydroxide formed in effluent was titrated.

Weakly baseic anion exchanger converted to hydroxide form was treated with 1N hydrochloric acid, converted to chloride form. A solution of 1N 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>
<thead>
<tr>
<th>Type of resins</th>
<th>Form</th>
<th>Capacity (meq/gr. of dry resin) for irradiation time (hr)</th>
<th>Capacity loss (%) for 177 hr. (3.5 x 10^7 r)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Strong acid nuclear sulfonic acid type</td>
<td>Dowex 50 Na</td>
<td>3.55</td>
<td>3.57</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>3.66</td>
<td>3.58</td>
</tr>
<tr>
<td>acid type</td>
<td>Zeollex SA H</td>
<td>3.48</td>
<td>3.46</td>
</tr>
<tr>
<td>(styrene base)</td>
<td>Dianion SK #1 H</td>
<td>3.52</td>
<td>3.60</td>
</tr>
<tr>
<td>Strong acid sulfonic acid type</td>
<td>ZeoRex H</td>
<td>1.96</td>
<td>2.06</td>
</tr>
<tr>
<td>(phenolic base)</td>
<td>Duolite C3 H</td>
<td>2.06</td>
<td>2.17</td>
</tr>
<tr>
<td>Weak acid carboxylic</td>
<td>Duolite CS101 H</td>
<td>7.85</td>
<td>8.02</td>
</tr>
<tr>
<td>Carbonaceous exchanger</td>
<td>Sulfonated coal H</td>
<td>0.50</td>
<td>0.48</td>
</tr>
<tr>
<td>Strong base quaternary ammonium</td>
<td>Dowex 2 Cl</td>
<td>2.10</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>1.88</td>
<td>1.81</td>
</tr>
<tr>
<td>(styrene base)</td>
<td>Dianion SA #100 Cl</td>
<td>2.06</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>1.98</td>
<td>1.93</td>
</tr>
<tr>
<td>Weak base</td>
<td>Dowex 3 Cl</td>
<td>2.45</td>
<td>2.47</td>
</tr>
</tbody>
</table>

The values of capacity loss shown in Table 1 is rather high, comparing with the previous works, 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 x 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 x 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%. 

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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


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