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RADIATION EFFECTS ON ION-EXCHANGE RESINS

Part II: Gamma Irradiation of Dowex 1.

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U. S. ENERGY RESEARCH AND
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Fabrication Engineering and Testing
PRODUCT AND SURVEILLANCE GROUP

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Radiation Effects
Ion Exchange Resins

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RADIATION EFFECTS ON ION-EXCHANGE RESINS

Part II: Gamma Irradiation of Dowex 1.

Armen R. Kazanjian and David R. Horrell

Abstract. The effects have been determined of gamma radiation on the anion exchange resin, Dowex 1. Part I on Dowex® 50W was reported May 10, 1974. The exchange capacity (both strong and weak base), moisture content, radiolysis products, and physical deterioration of the resin were analyzed after irradiation with doses up to 6.9×10^8 rads. The resin capacity decreased approximately 50 percent after a radiation dose of 4×10^8 rads. Resin irradiated, when air dried in the nitrate form, showed more stability than resin irradiated in 7N nitric acid (HNO_3), which in turn showed more stability than resin irradiated when air dried in the chloride form. Radiation decreased the strong base capacity to a greater extent than the total capacity. The result indicates that some of the quarternary ammonium groups were transformed to secondary and tertiary amine groups that have weak base ion-exchange capability.

INTRODUCTION

Dowex®-1 anion exchange resin is used to separate plutonium in the Rocky Flats Plant plutonium recovery operations. The alpha radiation from plutonium slowly deteriorates the resin, which must be replaced periodically. The current study was undertaken to determine the effects of high energy radiation on Dowex-1 resin (trademark of Dow Chemical U.S.A.). The experiments involved gamma radiation of the resin in both the air-dried form and in 7N HNO_3 (nitric acid), and subsequent analyses of the resin for exchange capacity, moisture content, physical deterioration, and radiolysis products. This work is part of a larger effort which includes the gamma- and alpha-radiation effects on Dowex-1 anion exchange resin and Dowex-50 cation exchange resin. The gamma radiation effects on Dowex-50

have previously been reported by the authors (1).¹ Related information on this subject is given in the references (2 through 7).

DISCUSSION

Experimental:

Dowex-1, has the following structural formula:

In the formula, R and A represent alkyl groups and anions, respectively. The cross-linking agent (divinylbenzene) and the quarternary ammonium groups are attached at the ortho- and meta-positions, as well as the para-position. The resin used was 50-100 mesh Dowex 1-X4, Baker analyzed reagent. The X4 indicates that the resin was 4 percent cross-linked.

Irradiations were carried out with a cobalt-60 gamma source that delivered a dose rate of 1.20×10^6 rads per hour. Doses up to 6.9×10^8 rads were administered to resin that was either air-dried or in 7N HNO_3 , the medium in which plutonium is loaded on a resin column. The air-dried resin was irradiated in both the nitrate and chloride form.

¹Numerals in parentheses relate to references listed at end of text.

The irradiated resins were analyzed for exchange capacity, moisture content, trimethylamine concentration, and physical deterioration. The procedure for determining the capacity is included in Appendix I, Page 11. Both the strong base (or quarternary) capacity and total capacity were determined in units of milliequivalents per millilitre (ml) of wet-tapped resin, per gram of air-dried resin, and per gram of oven dried (110°C) resin. The moisture content is the difference in weight between the air-dried and oven-dried resin.

The quarternary ammonium groups on Dowex-1 are primarily trimethylamine groups, which were analyzed by washing the irradiated resin with dilute hydrochloric acid (HCl), and using a gas chromatograph and a mass spectrometer in tandem. The physical deterioration or appearance of the irradiated resin beads was examined with a scanning electron microscope.

Results:

The exchange capacity and moisture content results are shown in Table I and Figures 1 to 3. Radiation-induced changes can occur in both the insoluble polymer matrix and the attached quarternary ammonium groups. Changes in the polymer would be primarily manifested in the moisture content, whereas changes in the attached groups are directly related to the exchange capacity. Effects in these two areas will be discussed separately.

Moisture Content

The topmost curves in the Figures 1, 2, and 3 show that resin irradiated in 7N HNO_3 exhibits different behavior than resin irradiated in the air-dried form. The water content increases greatly with absorbed dose in 7N HNO_3 , whereas it decreases relatively slower with the absorbed dose in air-dried resin. The water content varies with the porosity of the resin beads and the porosity is inversely related to the degree of cross-linking. Irradiation of an ion exchange resin (or any organic polymer) produces both cross-linking and degradation (or fragmentation). Determining the water content indicates

which of the two effects is predominant. Irradiating air-dried Dowex-1 resin results in a predominance of cross-linking, although the effect is not striking. On the other hand, irradiating Dowex-1 in 7N HNO_3 results in considerable degradation of the polymer. Doses greater than 4×10^8 rads produced a gelled material in which the individual resin beads were no longer discernible. The phenomenon can be explained on the basis of the indirect effect. Approximately 70 percent of the radiation energy impinging on resin in 7N HNO_3 is absorbed by the HNO_3 solution. The primary effect of radiation on HNO_3 solutions is the formation of nitrite ions, which exist as undissociated HNO_2 in acid solution (8). The nitrite yield in 7N HNO_3 is about 2.2 molecules per 100 electron volts (eV) of absorbed energy (8). The increased degradation of the polymer can be attributed to attack by HNO_2 or its free radical predecessors and may not be due to the direct attack of radiation on the polymer matrix.

Exchange Capacity

The loss in exchange capacity upon irradiation is shown in Figures 1, 2, and 3. The resin irradiated when air dried in the nitrate form showed more stability than resin irradiated in 7N HNO_3 , which in turn showed more stability than resin irradiated when air dried in the chloride form. The rate of capacity loss in Dowex-1 decreases with absorbed dose. After a decrease to somewhat less than half the original value, the capacity changes at a slow rate. This increased stability can be attributed to a number of causes. The most obvious cause is the increase in cross-linking brought about by radiation. Cross-linking increases the radiation stability of polystyrene ion exchange resins, up to a point; and this appears to occur in the resin irradiated in the air-dried form (see Figures 2 and 3). In contrast, resin irradiated in HNO_3 exhibited relatively little cross-linking; consequently, there was almost a constant decrease in capacity with dose. Other causes for increased stability include the formation of new exchange sites and the increase in accessibility to existing exchange

TABLE I. Capacity and Moisture Content of Dowex-1 Resin.

Hours	Rads $\times 10^{-8}$	Percent H ₂ O	Total (milliequivalents per oven-dried gram)	Quarternary (milliequivalents per oven-dried gram)	Total (milliequivalents per air-dried gram)	Quarternary (milliequivalents per air-dried gram)	Total (milliequivalents per millilitre)	Quarternary (milliequivalents per millilitre)
<i>Air Dried, Nitrate Form:</i>								
0	0	48.3	4.40	4.30	2.28	2.22	1.50	1.46
65	0.81	47.4	3.87	3.67	1.89	1.80	1.35	1.22
89	1.11	49.3	3.89	3.80	1.97	1.89	1.25	1.26
113	1.41	47.1	3.30	3.30	1.75	1.75	1.26	1.19
121	1.52	42.3	3.31	2.96	1.91	1.71	1.33	1.06
137	1.71	48.2	3.53	3.36	1.83	1.63	1.18	1.10
161	2.01	49.6	3.50	3.49	1.77	1.67	1.18	1.08
199	2.49	48.6	3.42	2.97	1.75	1.52	1.21	1.01
294	3.68	46.6	3.08	2.77	1.65	1.28	1.10	0.85
348	4.35	46.5	4.06	2.15	2.17	1.14	1.23	0.70
480	6.00	42.6	2.53	1.60	1.45	0.92	0.94	0.62
552	6.90	41.2	2.40	1.52	1.41	0.90	0.88	0.54
<i>Air Dried, Chloride Form:</i>								
0	0	48.3	4.40	4.30	2.28	2.22	1.50	1.46
73	0.91	46.9	2.60	2.28	1.38	1.21	0.77	0.68
96	1.20	46.6	1.70	1.60	0.91	0.86	0.58	0.52
137	1.71	42.3	2.20	2.20	1.33	1.30	0.76	0.69
173	2.16	38.7	1.70	1.69	1.05	1.04	0.70	0.62
216	2.70	45.7	1.79	0.92	0.97	0.50	0.60	0.35
240	3.00	37.1	1.51	1.49	1.00	0.94	0.70	0.48
<i>7N Nitric Acid, Nitrate Form:</i>								
0	0	48.3	4.40	4.30	2.28	2.22	1.50	1.46
65	0.81	52.0	3.82	3.63	1.83	1.74	1.24	1.17
89	1.11	56.5	3.75	3.54	1.63	1.54	1.17	1.08
113	1.41	59.0	3.35	3.15	1.37	1.29	0.94	0.84
121	1.52	60.7	3.72	3.17	1.46	1.24	0.95	0.83
137	1.71	61.5	2.76	2.48	1.06	0.95	0.71	0.59
161	2.01	65.9	3.19	2.84	1.09	0.97	0.72	0.63
199	2.49	71.2	2.80	2.40	0.80	0.76	0.54	0.51
294	3.68	79.6	2.35	1.74	0.48	0.36	0.34	0.24
348	4.35	91.4	—	1.84	1.44	0.14	0.70	0.07

NOTE: Average values of duplicate results.

FIGURE 1. Air-Dried Resin, Nitrate Form.

sites. These last two postulates have been made without any particular experimental support.

Resin irradiated in the nitrate form (either in 7N HNO₃ or air dried) is much more stable than resin irradiated in the chloride form. Two reasons for this difference can be offered. The first is based on the fact that nitrate ion is a good scavenger for hydrated electrons. Hydrated electrons, formed in aqueous solution by high energy radiation, are partly responsible for the loss in capacity by reacting with exchange groups (9). The nitrate ions thereby protect

the exchange groups (quarternary ammonium) by reacting with hydrated electrons. The second reason is the formation of the strong oxidizing radical, chlorine (Cl[•]). The chlorine atom, formed in chloride solutions by the following reaction, may be strongly reactive toward the quarternary ammonium group:

Both the strong base (or quarternary) capacity and the total capacity were determined in these tests (see Appendix I, Page 11). The quarternary

Legend

- $\circ$ — Right-hand Coordinate for water content.
- Milliequivalents per oven-dried gram:
- $\square$ — Total capacity.
- $\blacksquare$ — Strong-base capacity.
- Milliequivalents per air-dried gram:
- $\diamond$ — Total capacity.
- $\bullet$ — Strong-base capacity.
- Milliequivalents per millilitre.
- $\blacktriangle$ — Total capacity.
- $\triangle$ — Strong-base capacity.

FIGURE 2. Air-Dried Resin, Chloride Form.

ammonium groups are strongly basic and are able to exchange anions in neutral solutions. Weakly basic groups, consisting of secondary and tertiary amines, are also present in the resin. Strong acid solutions are necessary for anion exchange on these weak base groups. Almost all of the original Dowex-1 exchange capacity is the strong base type. Upon irradiation, the resin loses its strong base capacity at a faster rate than its total capacity. Obviously, there has been an increase in the number of weak base groups (4).

It appears that the radiolytic attack does not eliminate the entire quarternary group in all cases but merely reduces it to a secondary or tertiary amine group.

Trimethylamine Yields

The quarternary ammonium groups consist primarily of trimethylamine (see formula in Experimental Section), so that trimethylamine

FIGURE 3. Resin Irradiated in 7N HNO₃ (nitric acid).

(TMA) would be expected to be a major radiolysis product. Analysis of the wash solutions showed this to be true. Resin samples irradiated for various times produced TMA concentrations on the order of 0.1 millimoles TMA per ml of wet-tapped resin. Unfortunately, the results were scattered and did not show a regular increase in concentration with absorbed dose. The TMA yields were about one half the decrease in exchange capacity. This is in contrast to the results with Dowex-50 (1), where the sulfate ion yield from the sulfonic acid exchange groups increased with absorbed dose and was equivalent to the loss in exchange capacity. These results with Dowex 1, however, add confirmation to

the explanation given for the difference in loss of strong-base and weak-base exchange capacity; i.e., radiation does not eliminate the entire quarternary group in all cases but merely reduces it to a secondary or tertiary amine group. Analysis of the resin-wash solutions by gas chromatography-mass spectrometry showed only insignificant amounts of volatile products other than TMA.

Gaseous Products

Low-boiling point gaseous products from irradiated air-dried resin, resin in 7N HNO₃, and 7N HNO₃

FIGURE 4 Unirradiated Resin (air-dried nitrate form). Magnification 60X.

TABLE II. Radiolytic Gaseous Products.

Species	Air-Dried Resin	Resin in 7N HNO ₃ (nitric acid)	7N HNO ₃ (nitric acid)
Hydrogen (H ₂)	*0.09	0.02	0.02
Nitrous Oxide (N ₂ O)	0.03	0.2	—
Carbon Dioxide (CO ₂)	—	0.6	—
Carbon Monoxide (CO)	0.02	—	—
Nitrogen (N ₂)	—	0.2	—
Nitric Oxide (NO)	—	0.2	—

*Molecules produced per 100 electron volts of absorbed energy. Yields of other products less than 0.01

eV of absorbed energy, are presented in Table II. No hypothesis for the origins of these gases has been made.

Microscopic Analysis

Resin irradiated when air dried in the nitrate form at doses of 3.68×10^8 rads (294 hours) and 6.00×10^8 rads (480 hours) was examined with a scanning electron microscope at a magnification of 60X and 240X. Figures 4 through 9 show the physical damage. The resin is gouged, pitted, and cracked unlike Dowex-50 which showed no physical deterioration at these radiation doses. About the same amount of damage appeared in the resins irradiated for 294 and 480 hours. Additional tests showed that a temperature of 45 °C and 7N HNO₃ (the temperature and medium in which some of the resin was irradiated) do not damage the resin in any way.

were analyzed by mass spectrometry. The yields, expressed in terms of molecules produced per 100

FIGURE 5. Unirradiated Resin (air-dried nitrate form). Magnification 240X.

FIGURE 6. Air-Dried Nitrate Form Resin Irradiated with 3.68×10^8 Rads Magnification 60X

FIGURE 7. Air-Dried Nitrate Form Resin Irradiated with 3.68×10^8 Rads. Magnification 240X.

FIGURE 8. Air-Dried Nitrate Form Resin Irradiated with 6.00×10^8 Rads. Magnification 60X.

FIGURE 9. Air-Dried Nitrate Form Resin Irradiated with 6.00×10^8 Rads. Magnification 240X.

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APPENDIX I. Quarternary Ammonium Anion Exchangers (strongly basic).

Procedure*

1. Place about 10 millilitres (ml) of wet swollen sample in a 0.5-inch inside diameter (ID) column.
2. Pass 170 ml of 4 percent sodium hydroxide through the resin at a relatively constant flow rate for a half hour.
3. Rinse the resin with deionized or distilled water at the same flow rate for one hour.
4. Pass 100 ml of 1N sodium chloride through the resin at a relatively constant flow rate for a half hour.
5. Rinse the resin with deionized or distilled water until a chloride free effluent is obtained (about 15 minutes).
6. Remove the sample from the column and tap, and settle two 2-ml aliquots of the resin. Record the exact number of ml in each aliquot, then filter and get weights.
7. Transfer the samples to 400-ml beakers with minimum flush water.
8. Add two ml of CP sulfuric acid to each beaker.
9. Dilute each sample to approximately 200 ml with deionized or distilled water preheated to 80 °C. Allow each sample to cool to room temperature.
10. Titrate by Volhard method.
11. Calculate the wet volume quarternary capacity of the resin:

$$\text{Capacity, Cl}^- = \frac{\text{ml AgNO}_3 \text{ (silver nitrate)} \times \text{normality AgNO}_3}{\text{ml sample}} = \text{milliequivalents per millilitre.}$$

12. Replace the remaining resin in the column and pass 100 ml of 1N hydrochloric acid through the resin at a relatively constant flow rate for a half hour.
13. Rinse the resin with deionized or distilled water at the same flow rate until the effluent tests neutral to pH paper.
14. Repeat Steps 6 through 10.
15. Calculate the wet volume total capacity of the resin:

$$\text{Capacity, Cl}^- = \frac{\text{ml AgNO}_3 \times \text{normality AgNO}_3}{\text{ml sample}} = \text{milliequivalents per millilitre.}$$

16. Get percent of water (H₂O) on separate samples.
17. Attach the vacuum flask with sintered glass filter to a vacuum and wash one sample into the filter.
18. Place each sample in a previously tared weighing bottle, reweigh and place in an oven overnight at 105 to 115 °C. Be sure to vent the weighing bottles.
19. Cool each sample in a desiccator and reweigh.
20. Calculate the moisture content as follows:

$$\text{Percent Moisture, Cl}^- = \frac{(\text{gram wet sample} - \text{gram dry sample}) \times 100}{\text{gram wet sample}}$$

*Dowex: Ion Exchange, The Dow Chemical Company, Midland, Michigan. 1964. Page 35.