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RADIATION EFFECTS ON DOWEX MSC-1, AMBERLITE 252, AND DUOLITE C-264 ION EXCHANGE RESINS

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DISCLAIMER

SUBJECT DESCRIPTORS
Ion Exchange Materials
Radiation Effects

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ABSTRACT

The radiation effects on three new cation exchange resins were investigated. The resins were Dowex MSC-1, Amberlite 252, and Duolite C-264. The properties examined were ion exchange capacity, moisture content, plutonium loading and elution characteristics, thermal stability, and gas generation. There were some differences in the radiation effects on these properties but the overall radiation stability was considered to be about the same. The resins were relatively radiation stable, indicative of cation resins of this type.

INTRODUCTION

Ion exchange resins are used extensively in the nuclear industry for the separation and purification of actinides. To fulfill this function, the resins, which are primarily organic polymers, must have acceptable radiation stability. Many studies of the effects of high energy radiation on ion exchange materials have been made. The results from most of these studies have been summarized in Reference 1. Investigators at Rocky Flats have also contributed to this literature as part of their evaluation of new and improved resins.[2-5] Three new cation exchange resins have been evaluated and the results of the radiation study are presented in this report.

The three resins are Dowex MSC-1, Amberlite 252, and Duolite C-264. Radiation effects on five properties of these resins were examined. The five properties are ion exchange capacity, moisture content, plutonium loading and elution characteristics, thermal stability, and gas generation. Because of experimental facility, the irradiations were made using gamma radiation rather than the alpha radiation from americium 241 that would actually be encountered in Rocky Flats operations. The use of gamma radiation is further justified because previous work has shown that the effects of gamma and alpha radiation on ion exchange resins are comparable.[2,4] In any case, gamma irradiations suffice to determine the relative radiation stabilities of similar materials such as the three resins examined.

EXPERIMENTAL

The irradiations were performed in a commercial cobalt 60 gamma source (Gammacell-220). The dose rate was determined by Fricke dosimetry to be 3.48×10^5 rads per hour. The samples were irradiated in glass vials for periods up to 165 days (1.38×10^9 rads). The resins were barely covered with $0.5N$ HCl during irradiation since this is the medium in which the resin would be in contact with americium 241 in Rocky Flats operations.

Samples of the three resins were obtained from the manufacturers. Amberlite 252 was obtained from the Rohm and Haas Co., Dowex MSC-1 from the Dow Chemical Co., and Duolite C-264 from Diamond Shamrock. The three resins consisted of a styrene-divinylbenzene copolymer matrix with sulfonic acid functional groups. The plutonium loading and elution measurements were made on 20-50 mesh size resin. The other measurements were made on un-sieved, as-received resin.

The procedure for measuring the ion exchange capacity is outlined in the Appendix. The plutonium loading and elution measurements were made on 50 mℓ resin batches placed in columns after irradiation. Plutonium was loaded to 10% breakthrough with a $0.5N$ HCl feed solution containing 9 g/ℓ of plutonium. Ten percent breakthrough is the point at which the plutonium concentration in the effluent is 10% of that in the feed. Both the feed solution and the $0.35N$ HNO_3 that follows it were passed up through the column.

The 7*N* HNO_3 eluent was then passed down through the column. The measure of elution efficiency was the volume of eluent required to elute 90% of the plutonium loaded on the column.

Differential Scanning Calorimetry (DSC) was used to measure the thermal stability of resins in contact with 0.5*N* HCl and Differential Thermal Analysis (DTA) was used to measure the thermal stability of resins in contact with 8*N* HNO_3. Both of these instruments measure the exotherms and endotherms that occur when heating the resin at a constant rate. The difference between the two methods is that DSC also provides a quantitative value for the heat release or uptake. The thermal analysis was made with the resin in either opened or sealed capillary tubes. Closed capillary tests probably give a closer simulation of actual resin column conditions.

Gas generation data were obtained by irradiating the resins (in air) in break-seal glass vials and analyzing the gases by mass spectrometry.

RESULTS AND DISCUSSION

Ion Exchange Capacity and Moisture Content

Results from the exchange capacity and moisture content measurements are shown in Table 1 and Figures 1 and 2. The gradual decrease in capacity with radiation doses up to 10^9 rads indicates that the resins have good radiation stability. Cation exchange resins of the styrene-divinylbenzene-sulfonic acid type, such as these three resins, are known to be relatively radiation stable.[2,5]

TABLE 1. Exchange Capacity and Moisture Content

Dose (rads × 10^{-8})	Milliequivalents Per Oven Dried Gram	Milliequivalents Per Air Dried Gram	Milliequivalents Per Milliliter	Final Volume (mℓ)	Percent H_2O
		Dowex MSC-1 Resin			
0	4.90 ± 0.14	2.67 ± 0.22	1.84 ± 0.03	–	45.7 ± 4.7
1.00	5.01	2.54	1.76	5.4	49.2
4.43	4.47	2.07	1.52	5.2	53.6
6.35	4.24	2.19	1.48	5.5	48.4
9.95	3.88	1.71	1.22	6.3	55.8
13.8	3.59	1.42	1.10	6.8	60.4
		Amberlite 252 Resin			
0	5.18 ± 0.04	2.59 ± 0.13	1.85 ± 0.04	–	51.4 ± 1.0
1.00	4.93	2.70	1.75	5.4	45.2
4.43	4.51	1.90	1.56	5.6	58.0
6.35	4.40	1.79	1.48	6.1	59.4
9.95	4.25	1.24	1.23	8.6	71.0
13.8	4.08	0.52	1.03	15.7	87.3
		Duolite C-264 Resin			
0	5.24 ± 0.13	3.29 ± 0.05	2.32 ± 0.04	–	39.6 ± 4.3
1.00	5.34	3.11	2.32	5.4	41.7
4.43	5.15	2.63	2.26	5.6	48.9
6.35	5.41	2.53	2.20	6.0	53.2
9.95	4.69	2.34	1.77	6.5	44.8
13.8	4.62	1.53	1.64	8.2	67.0

NOTE: All values are averages of duplicate results except for the unirradiated resin for which the standard deviation was obtained from quadriplicate results.

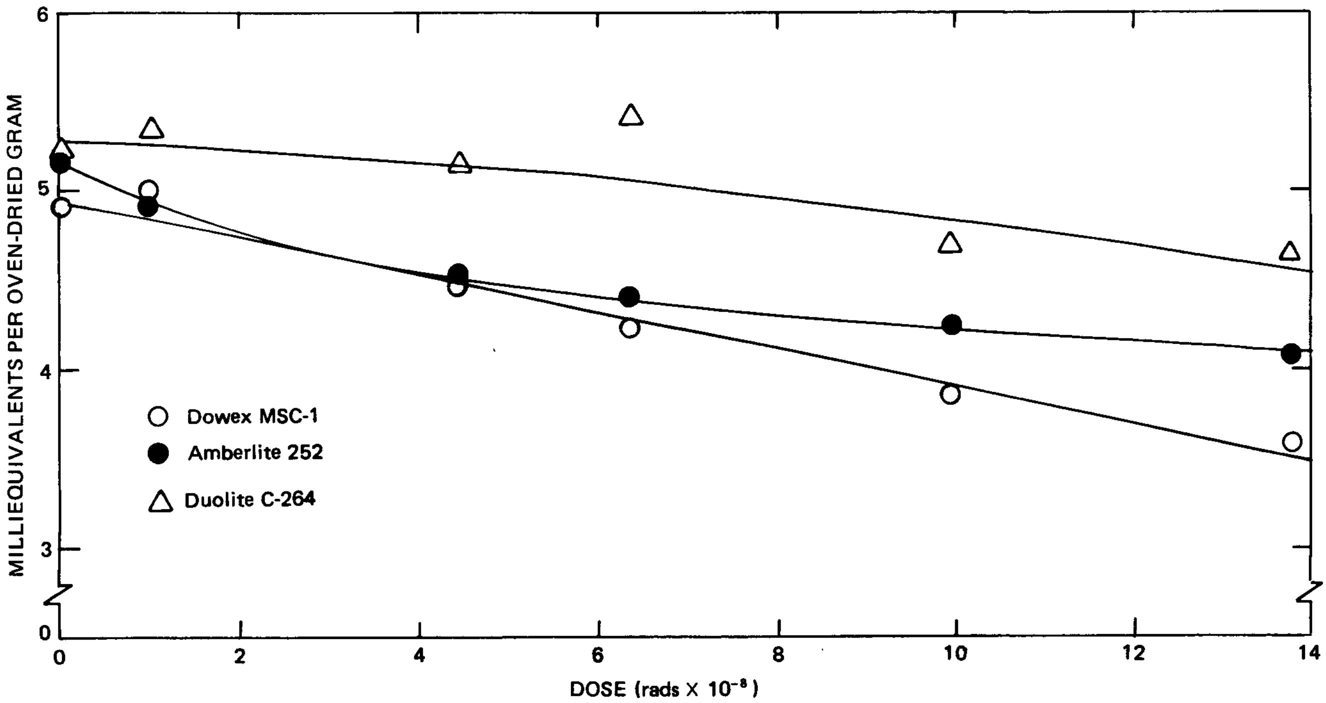
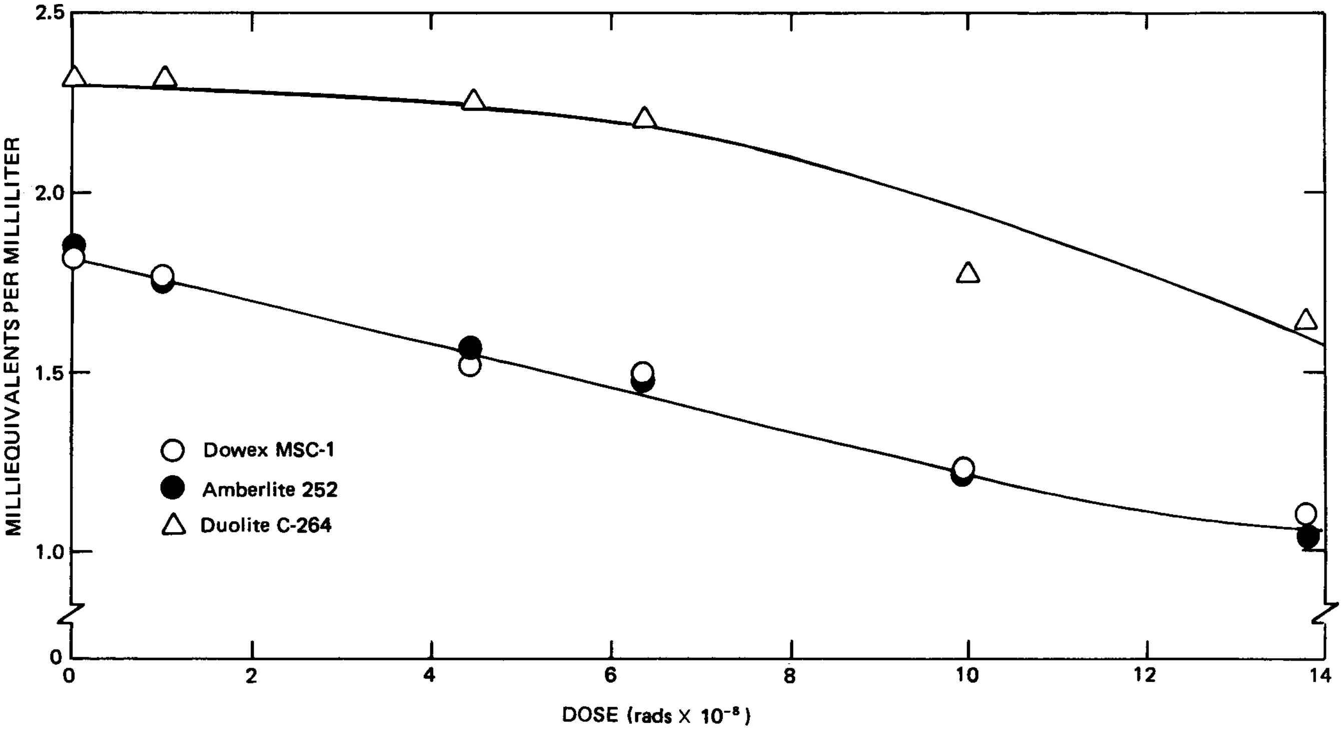


FIGURE 1. Dry Weight Ion Exchange Capacity

FIGURE 2. Wet Volume Ion Exchange Capacity



Exchange capacities in units of milliequivalents per milliliter were calculated on the basis of the 5 mℓ samples that were irradiated and analyzed. However, there was a volume expansion during irradiation as shown in column 5 of Table 1. If the milliequivalents per milliliter were calculated using the expanded volumes the values would be smaller and perhaps more appropriate for a practical evaluation.

Moisture content of the resins increases with radiation dose although some of the results are erratic. This increase can be directly related to the volume increase. Radiation in these polymers is causing degradation by reducing the amount of crosslinking thereby allowing more water to be incorporated into the resin beads. The beads are therefore expanded into a more gelled state. Further irradiation of these resins (particularly Amberlite 252, the inferior resin in this respect) would increase the gelling to the extent that solution flow through a resin column would be prevented.

Plutonium Loading and Elution

The results from the measurements on plutonium loading and elution are shown in Table 2. Radiation decreased the plutonium capacity as expected. However, the percentage decrease at a dose of 5.85 X 10^8 rads was much larger than the percentage decrease in total exchange capacity (Table 1). The plutonium capacity was not the total capacity but the capacity when the plutonium concentration in the effluent is 10% of that in the feed solution. This difference is probably due to the change in flow characteristics caused by the increase in gelling. The plutonium capacities of the irradiated resins were calculated on the basis of the 50 mℓ samples and not on the expanded volumes (about 10% increase for each resin). Duolite C-264 had more radiation stability than the other two resins with regard to decrease in plutonium capacity.

Radiation appeared to increase the elution efficiency in all the resins. Even when elution efficiency is expressed in units of eluent volume per gram of plutonium eluted, radiation improves elution from Amberlite 252 and Duolite C-264. Dowex MSC-1 is not significantly affected. These results can be directly related to the increase in moisture content and volume caused by radiation. The reduced crosslinking responsible for these changes in moisture content and volume also increases the porosity so that the plutonium solution can flow through the resin bead more readily. Elution is thereby facilitated. Amberlite 252 experienced the greatest change in elution efficiency as well as the greatest change in volume and moisture content.

Thermal Stability

Resin samples were irradiated to doses of 4.18 X 10^8 and 8.50 X 10^8 rads and analyzed by Differential Scanning Calorimetry (DSC). The medium of 0.5*N* HCl was selected to simulate the ion exchange feed solution in Rocky Flats

TABLE 2. Plutonium Loading and Elution

	Plutonium Capacity at 10% Breakthrough (g Pu/ℓ resin)		Eluent Volume to Elute 90% of Plutonium (mℓ)	
	Unirradiated	Irradiated	Unirradiated	Irradiated
Dowex MSC-1	118	78	300	212
Amberlite 252	134	91	550	185
Duolite C-264	155	125	412	242

NOTE: 50 mℓ resin irradiated to a dose of 5.85 X 10^8 rads.
Values were the result of single measurements.

operations. There were no exotherms observed upon heating to 450 °C, so that all of the resins are considered to be thermally stable in dilute HCl. The observed endotherms (Table 3) would not create thermal instabilities. The endotherms that occur in open capillaries below 100 °C are probably caused by vaporization of the liquid. The higher temperature endotherms in the closed capillaries are because of transformations in the polymers.

Thermal stabilities were also determined in 8*N* HNO_3 by Differential Thermal Analysis (DTA). No radiation was administered in these tests.

Very small exotherms occurred in all the closed capillary tests. The onset temperatures (Table 4) were lower than those previously reported.[6] This could be caused by the presence of more HNO_3 in contact with the resin. Even the "air dried" samples were merely dried for a few minutes on an evacuated filter. It is well established that styrene-divinylbenzene resins will react with HNO_3 at elevated temperatures and that precautions should be taken to prevent thermal explosions in production operations.[7] It is difficult to assess the significance of the differences in onset temperatures. The magnitudes of the exotherms are as important, but they could

TABLE 3. Effect of Radiation on Thermal Stability (DSC)

Onset Temperatures (°C) for Endotherms

	0 rads	4.18×10^8 rads	8.50×10^8 rads
Dowex MSC-1			
Open Capillary	87	88	87
Closed Capillary	207	196	198
Amberlite 252			
Open Capillary	92	85	90
Closed Capillary	210	211	205
Duolite C-264			
Open Capillary	85	85	87
Closed Capillary	205	207	207

NOTE: In the open capillary tests endotherms also occurred at about room temperature. The temperatures listed above are for the second endotherms.

TABLE 4. Thermal Stability in HNO_3 (DTA)

Onset Temperatures (°C)

	Exotherms in Closed Capillary	Endotherms in Open Capillary
Dowex MSC-1, wet	110	100
Amberlite 252, wet	145	103
Duolite C-264, wet	130	107
Dowex 50WX8, air dried	110	116
Dowex 50WX8, wet	125	100
Dowex 50WX2, air dried	130	120
Dowex 50WX2, wet	170	102

not be analyzed because they were so small. Exotherms may have been present in the open capillary tests and obscured by the endotherms.

Gas Generation

Gases generated by irradiating the resins to a dose of 1.08 X 10^8 rads are shown in Table 5. The yields, given in units of molecules produced per 100 electron volts (eV) of absorbed energy, are about the same for all three resins. The production of hydrogen (the only gas with a significant yield) is reasonable for these polymers in acid solution.

TABLE 5. Gas Generation

	Molecules Produced/100 eV		
	Dowex MSC-1	Amberlite 252	Duolite C-264
H_2	0.46	0.53	0.38
CO_2	< 0.01	0.09	0.07

CONCLUSIONS

The differences between the radiation stabilities of the resins were not sufficient to recommend or disapprove of any one of them. The decrease in exchange capacity with radiation was about the same for all the resins. However, there were differences in the volume change and related moisture content. The inferior resin in this respect was Amberlite 252, followed by Duolite C-264 and Dowex MSC-1. Relatively large doses (10^9 rads) were required to make excessive changes in the volumes. Differences were also observed in plutonium loading and elution. Radiation had less affect on the plutonium loading capacity of Duolite C-264 than on the other two resins. Radiation actually improved plutonium elution efficiencies, particularly with Amberlite 252. This effect was directly related to the radiation-induced volume change. There were no significant differences between the resins with respect to thermal stability and gas generation.

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APPENDIX

PROCEDURE FOR EXCHANGE MEASUREMENTS*

Sulfonic Cation Exchangers (Strong Acid)

1. Place about 10 mℓ of wet, swollen sample in a 0.5-in.-i.d. column.
2. Pass 200 mℓ of 5% HCl through the resin at a relatively constant flow rate for one hour.
3. Rinse the resin with deionized or distilled water at the same flow rate until the effluent is neutral of pH paper (200 mℓ is normally satisfactory).
4. Remove the sample from the column and tap and settle two 4-5 mℓ aliquots of resin.
5. Attach the vacuum flask with sintered glass filter to a vacuum and wash one aliquot into the filter. Apply the vacuum for 10 min. (no more).
6. Carefully remove the entire sample and place in a previously tared weighing bottle. Reweigh and leave overnight in an oven set at 105-115 °C. Be sure to vent the weighing bottle.
7. Repeat steps 5 and 6 for the other aliquot.
8. Remove the samples from the oven, cool in a desiccator, and reweigh.
9. Wash the dry sample into a 400-mℓ beaker and dilute to 200 mℓ with deionized or distilled water. Allow the sample to rehydrate for 0.5 hour.
10. Add approximately 5 g of reagent grade NaCl to the beaker and titrate the liberated acid with 1*N* NaOH to a pH of 7, following the pH with a pH meter while stirring vigorously. Record the milliliters of NaOH required. Phenolphthalein end point can be used.
11. Calculate the wet volume total capacity as follows:

    Capacity, H^+,

    $$\text{wet} = \frac{\text{m}\ell\ \text{NaOH X normality NaOH}}{\text{m}\ell\ \text{wet sample}} = \text{meq/m}\ell$$

12. Calculate the dry weight total capacity as follows:

    Capacity, H^+,

    $$\text{dry} = \frac{\text{m}\ell\ \text{NaOH X normality NaOH}}{\text{g dry sample}} = \text{meq/dry g}$$

13. Calculate the wet (air dried) weight total capacity as follows:

    Capacity, H^+,

    $$\text{wet} = \frac{\text{m}\ell\ \text{NaOH X normality NaOH}}{\text{g wet sample}} = \text{meq/wet g}$$

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*Dowex: ION Exchange, the Dow Chemical Company, Midland, MI, 1964, p 35.

14. Calculate the moisture content as follows:

    % moisture,

$$H^{+} = \frac{(\text{g wet sample} - \text{g dry sample}) \times 100}{\text{g wet sample}}$$

15. If the properties obtained in steps 11 to 14 are desired to sodium-form resin rather than hydrogen-form resin, the sample should be titrated prior to the dewatering and drying in steps 5 to 8. After titration, the resin should be rinsed and the tapped and settled volume (the resin is now in the sodium form) measured. Steps 9 and 10 are then omitted.