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ABSTRACT

The radiation stability of Amberlite IRA-938, an anion exchange resin, and Bio-Rad AG MP-50, a cation exchange resin, was investigated. The resins were gamma irradiated and analyzed for exchange capacity, gas generation, thermal stability, and plutonium capacity. The radiation stabilities were comparable to those of Dowex 11 and Dowex 50W-X8, the resins presently used in Rocky Flats recovery operations.

INTRODUCTION

Ion exchange resins are used at Rocky Flats for the recovery of plutonium and americium. A continuing effort is made to find new resins with larger actinide capacities and improved loading and elution kinetics. Two new resins with improved characteristics are Amberlite IRA-938, an anion exchange resin, and Bio-Rad AG MP-50, a cation exchange resin. These resins are of the macroporous type rather than the usual gel type. Macroporous resins have a rigid pore structure, swell very little, and exhibit superior kinetics in some applications. In addition to their improved behavior with plutonium and americium recovery, these resins must have satisfactory radiation stability so that they can be used continually on a production basis.

The radiation stability has been investigated and the results are included in this report. The investigation consisted of gamma irradiating the resin and then analyzing for exchange capacity, gas generation, thermal stability, and plutonium capacity. The effects of gamma radiation would be similar to those produced by the alpha radiation from plutonium and americium, as shown by previous reports on this subject.[1,2]

EXPERIMENTAL

Irradiations were carried out in a commercial cobalt source (Gammacell®) that delivered a dose rate of 5.1×10^5 rads per hour. Resin irradiations were made in test tubes capped in aluminum foil; however, gas generation samples were contained in glass break-seal vials.

The Amberlite IRA-938, a 20-50 mesh strong base resin, was irradiated in the nitrate ion form. Resin samples that were to be irradiated in the air-dried form were prepared by vacuum filtering the resin for 10 minutes. Air-dried resin averaged 4.90 grams per 10 milliliters of wet tapped resin. Wet tapped resin refers to a volume measurement in which a resin-water slurry is tapped gently in a graduate. Samples to be irradiated in $7N$ HNO_3 were prepared by adding 6 ml of $7N$ HNO_3 to air-dried resin made from 10 ml of wet tapped resin. If the resins in this slurry form began drying out during the irradiation, $7N$ HNO_3 was added, and the mixture was stirred.

Bio-Rad AG MP-50, a 50-100 mesh strong acid resin, was irradiated in the hydrogen ion form. Samples to be irradiated in the air-dried form were prepared by vacuum filtering for 20 min with occasional stirring. Air-dried resin averaged 3.80 grams per 10 milliliter of wet tapped resin. Samples irradiated in $0.1N$ HCl were prepared by adding 8 ml $0.1N$ HCl to air-dried resin made from 10 ml of wet tapped resin.

Both the total and quaternary (or strong base) exchange capacities were measured for the anion exchange resin. The procedures for all the exchange

measurements are included in the Appendix. The gas analysis was made by mass spectrometry, and the thermal stability was analyzed by a DuPont Model 900 Differential Thermal Analyzer.

Plutonium loading and elution information on Amberlite IRA-938 was obtained by passing a solution of 1 gram of plutonium per liter in 7.5*N* HNO_3 through a 25-ml resin column at 2.3 ml/min cm^2. After washing with 7*N* HNO_3, the column was eluted in the reverse direction with 0.35*N* HNO_3 at 2.3 ml/min cm^2. Samples were taken at 15-ml intervals and analyzed for plutonium.

Plutonium loading and eluting information on Bio-Rad AG MP-50 was obtained by passing a solution containing 10 grams of plutonium per liter in 0.5*N* HCl through a 25-ml column of irradiated resin at 10.6 ml/min cm^2. After washing with 0.35*N* HNO_3, the column was eluted in the reverse direction with 7*N* HNO_3 at 5.3 ml/min cm^2. The values obtained were compared to those obtained previously using a 100-ml column.[3] Flow rates through the 100-ml column were 10.6 and 5.3 ml/min cm^2 for the loading and elution cycles, respectively.

RESULTS AND DISCUSSION

Amberlite IRA-938

Exchange Capacity

The results on exchange capacity and moisture content are shown in Table 1 and in Figures 1 and 2. The capacities are presented in units of milliequivalents (meq) per oven-dried gram, per air-dried gram,

TABLE 1. Capacity and Moisture Content of Amberlite IRA-938 Resin

Dose (Rads X 10^{-8})	Milliequivalents Per Oven-Dried Gram		Milliequivalents Per Air-Dried		Milliequivalents Per Milliliter		Percent H_2O
	Total	Quaternary	Total	Quaternary	Total	Quaternary	
			Air-Dried, Nitrate Form				
0	3.58	3.58	1.38	1.38	0.47	0.47	6.15
1.70	2.30 (2.19)*	2.16 (1.88)*	0.99	0.93	0.35	0.30	56.9 (57.7)*
3.11	1.45 (1.48)	1.22 (1.30)	0.78	0.66	0.25	0.22	46.2 (11.3)
4.47	0.68 (1.06)	0.55 (0.89)	0.57	0.46	0.19	0.16	16.3 (15.8)
5.69	0.90 (0.60)	0.61 (0.43)	0.42	0.29	0.14	0.10	52.6 (23.6)
			7*N* Nitric Acid				
0	3.58	3.58	1.38	1.38	0.47	0.47	61.5
1.70	2.45	2.09	0.96	0.82	0.32	0.28	60.7
3.11	1.77	1.32	0.69	0.52	0.21	0.16	61.2
4.47	1.22	0.89	0.45	0.33	0.15	0.09	63.0
5.69	0.71	0.33	0.30	0.13	0.08	0.04	58.8

Note: Average values of duplicate results.

*Numbers in parentheses are recalculated values using data obtained from Table 2. See page 5.

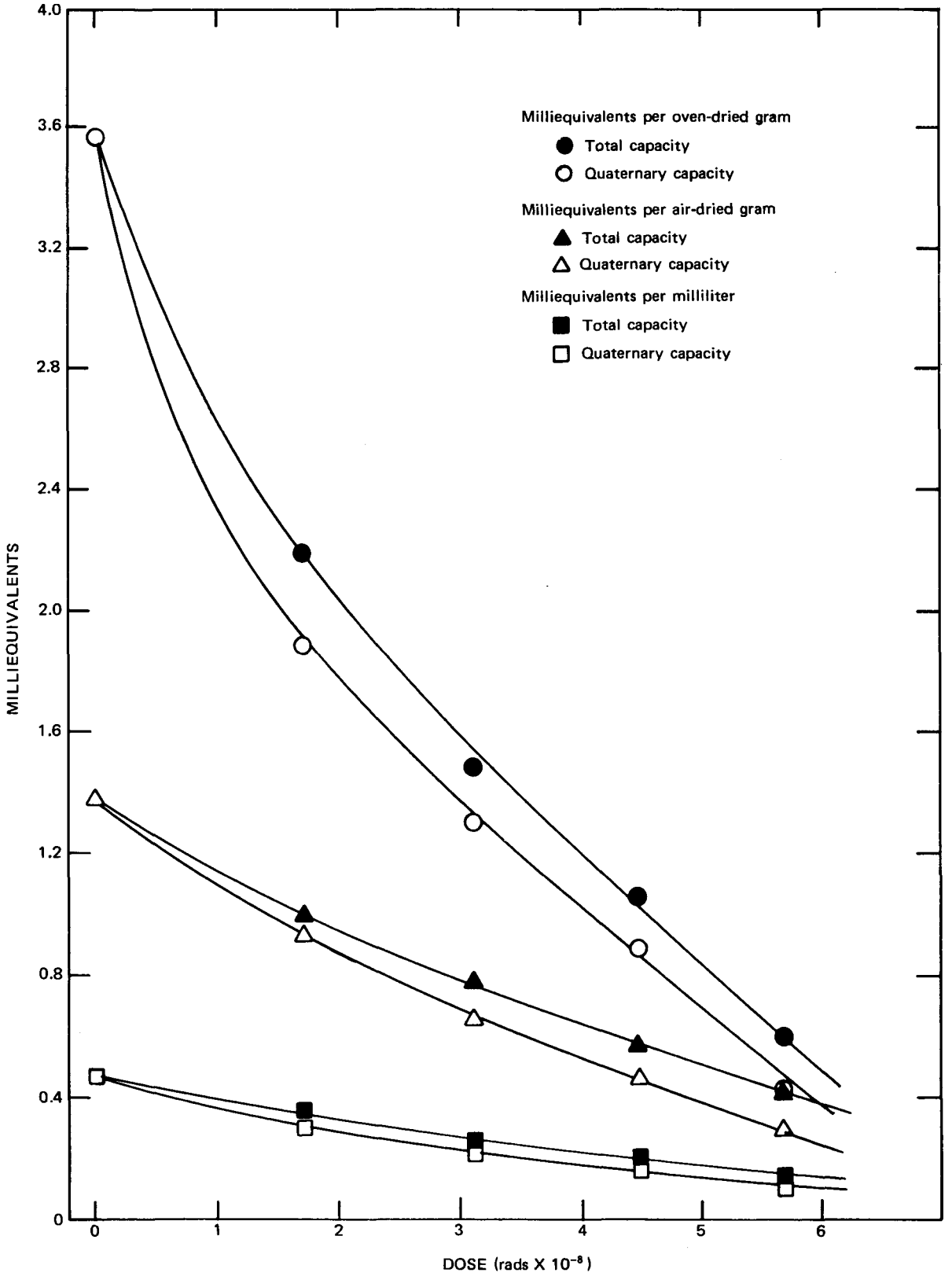


FIGURE 1. Resin Irradiated in Air-Dried Form

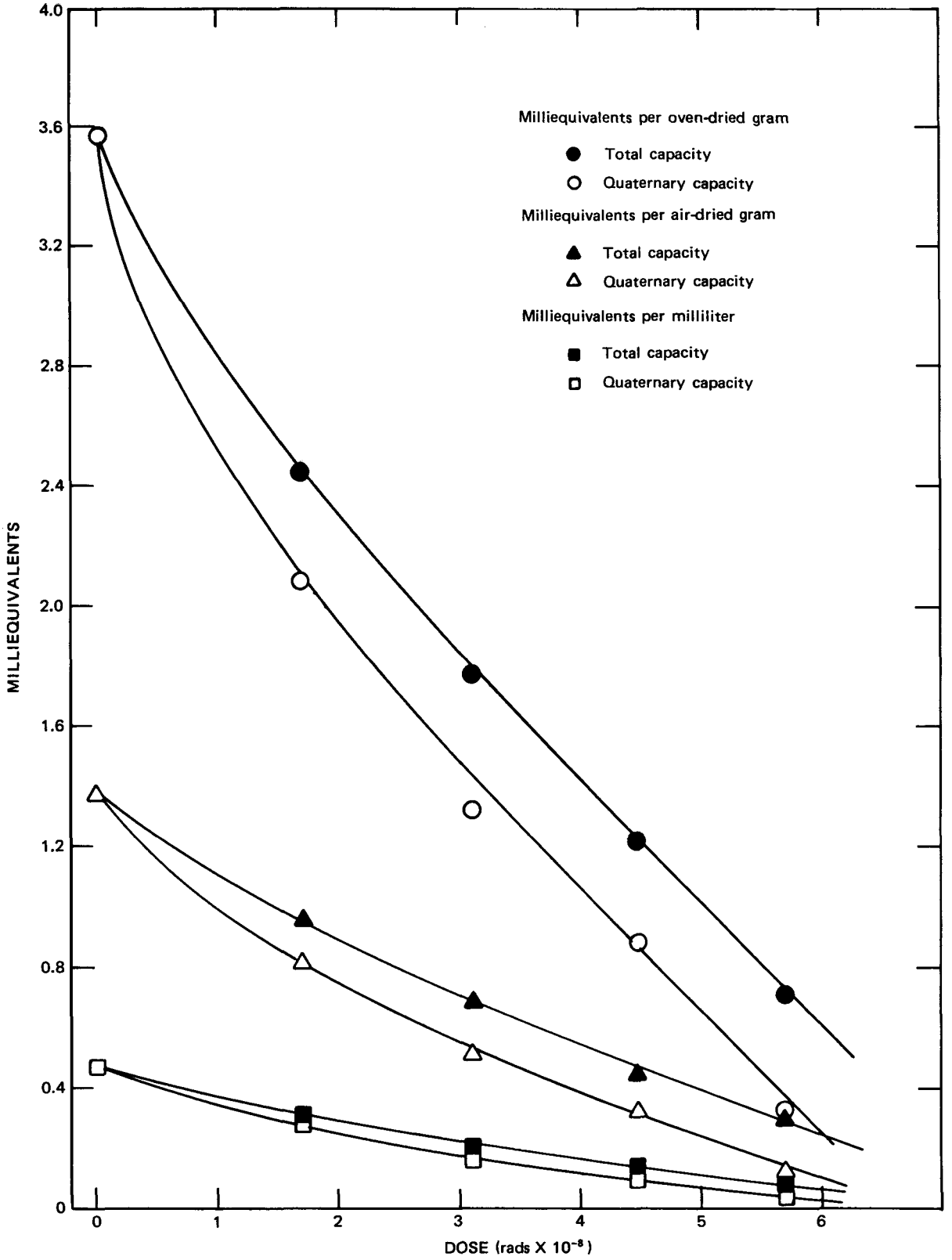


FIGURE 2. Resin Irradiated in 7*N* HNO_3

and per milliliter. Capacities reported on the basis of volume were calculated using the volumes obtained after irradiation. These volumes for the air-dried, irradiated samples were considerably less then the original volumes because irradiation-induced crosslinking of the polymer reduces the swelling of the resin. Additional samples were irradiated to measure this "shrinkage" in addition to the moisture content. The results are shown in Table 2. The average moisture content values from these measurements are shown in parentheses in Table 1 for comparison. The moisture content of the resin irradiated in 7*N* HNO_3 remains unchanged. There is little or no "shrinkage" because most of the radiation damage occurs indirectly through the aqueous media, and there is little direct crosslinking of the polymer.[1]

The oven-dried weight capacities are the most meaningful, although they may not be as accurate for resin samples irradiated in the air-dried form. The reason is that the oven-dried weight capacities are calculated using erratic moisture content values. To obtain more reliable results, the oven-dried weight capacities were recalculated using the ratios of oven-dried weight to final resin volume obtained from the supplementary set of irradiated samples mentioned previously. These values are shown in parentheses in Table 1 and are the ones plotted in Figure 1.

Results show (Figure 1 and 2) that most of the exchange capacity is eliminated in the radiation dose range of 1×10^8 to 5×10^8 rads. The quaternary or strong base capacity decreases a little more readily then the total capacity. The loss in exchange capacity of resin irradiated in 7*N* HNO_3 was about the same as that for resin irradiated in the air-dried form.

TABLE 2. Resin Irradiated in Air-Dried Form

Rads × 10^{-8}	Initial Volume (ml)	Final Volume (ml)	Percent H_2O
	5.0	4.5	54.0
1.78	5.0	4.5	61.5
	5.0	4.0	9.4
3.12	5.0	4.0	13.2
	5.0	3.75	13.5
4.47	5.0	3.75	18.2
	5.0	2.75	19.4
5.69	5.0	2.75	27.8

Gas Generation

Resin in the air-dried form was irradiated in air to a dose of 3.86×10^8 rads and under vacuum to a dose of 2.16×10^8 rads. Small amounts of CO_2, H_2, and NO were produced. The yields, expressed in units of molecules produced per 100 electron volts of absorbed energy, are shown in Table 3.

Plutonium Loading and Elution

Plutonium loading was determined at 1% breakthrough, 10% breakthrough, and when the resin was completely loaded. One percent (or 10%) refers to the point at which plutonium concentration in the effluent is 1% (or 10%) of that in the feed solution. The elution cycle was used to determine the total loading as well as the volume of eluant (0.35*N* HNO_3) required to elute 90% of the plutonium. Table 4 offers a comparison of the results obtained from irradiated (to a dose of 1.95×10^8 rads) and unirradiated resin.

Results indicate that the practical plutonium loading is unaffected at this radiation dose whereas the elution efficiency is decreased considerably. A dose of 1.95×10^8 rads can be equated to the alpha dose that the resin would absorb from plutonium. At a

TABLE 3. Gas Generation
(molecules per 100 electron volts)

	In Air	In Vacuum
CO_2	0.31	0.18
H_2	0.15	0.21
NO	0.04	0.03
TOTAL	0.50	0.42

plutonium loading of 25 milligram per milliliter of resin, about 400 days would be required for the resin to achieve this dose.

Thermal Stability

To determine whether radiation produced thermal instabilities in Amberlite IRA-938, resin in the air-dried nitrate form was irradiated with 4.47×10^8 and 5.69×10^8 rads and analyzed by differential thermal analysis. The samples were run in open and closed capillaries, and although both the exotherm and endotherm data are included in Table 5, only the exotherms (the temperature and peak size) are a direct measure of thermal instability. Temperatures shown before the parentheses in Table 5 are the maximum and minimum temperatures of the exotherms and endotherms, respectively. The temperature ranges of the thermal excursions are in parentheses.

The results do not indicate any radiation-induced change in thermal stability.

TABLE 4. Plutonium Loading and Elution

	Unirradiated Resin	Irradiated Resin
Plutonium Loading at 1% Breakthrough (mg Pu/ml resin)	20.4	20.4
Plutonium Loading at 10% Breakthrough (mg Pu/ml resin)	24.8	24.5
Total Loading (mg Pu/ml resin)	36.5	30.8
Eluant (ml) to elute 90% of Pu from 1 ml resin	3.7	6.6

TABLE 5. Differential Thermal Analyses of Amberlite IRA-938

Unirradiated Resin

Open Capillary	Closed Capillary
Large exotherm 282 °C (264-290 °C) Very large endotherm 102 °C (93-149 °C)	Extremely small exotherm 322 °C (285-331 °C)

Resin Irradiated With 4.47×10^8 Rads

Open Capillary	Closed Capillary
Medium exotherm 279 °C (248-297 °C) Very large endotherm 104 °C (94-156 °C)	Very small exotherm 340 °C (310-354 °C)

Resin Irradiated With 5.69×10^8 Rads

Open Capillary	Closed Capillary
Medium exotherm 276 °C (238-298 °C) Very large endotherm 103 °C (94-156 °C)	Very small exotherm 368 °C (328-388 °C)

Bio-Rad AG MP-50

Exchange Capacity

The total exchange capacities of Bio-Rad AG MP-50 irradiated in the air-dried form and in 0.1*N* HCl are shown in Table 6 and Figures 3 and 4. Irradiation in either form produced essentially the same results. The exchange capacity was not altered much over the dose range shown in Table 6. In fact, after an initial decrease, the exchange capacity appeared to increase at the higher doses. This unusual behavior can be attributed to the formation of carboxylic and phenolic functional groups.[4] Although these weak acid groups become part of the exchange capacity, the kinetics of the exchange may not be as rapid as with the sulfonic acid groups originally present. The plutonium loading results, described later, may be an example of this retarded exchange rate.

Gas Generation

Resin in the air-dried form was irradiated in air to a dose of 4.14×10^8 rads and under vacuum to a dose of 2.30×10^8 rads. The gas yields in units of molecules produced per 100 electron volts of absorbed energy are shown in Table 7.

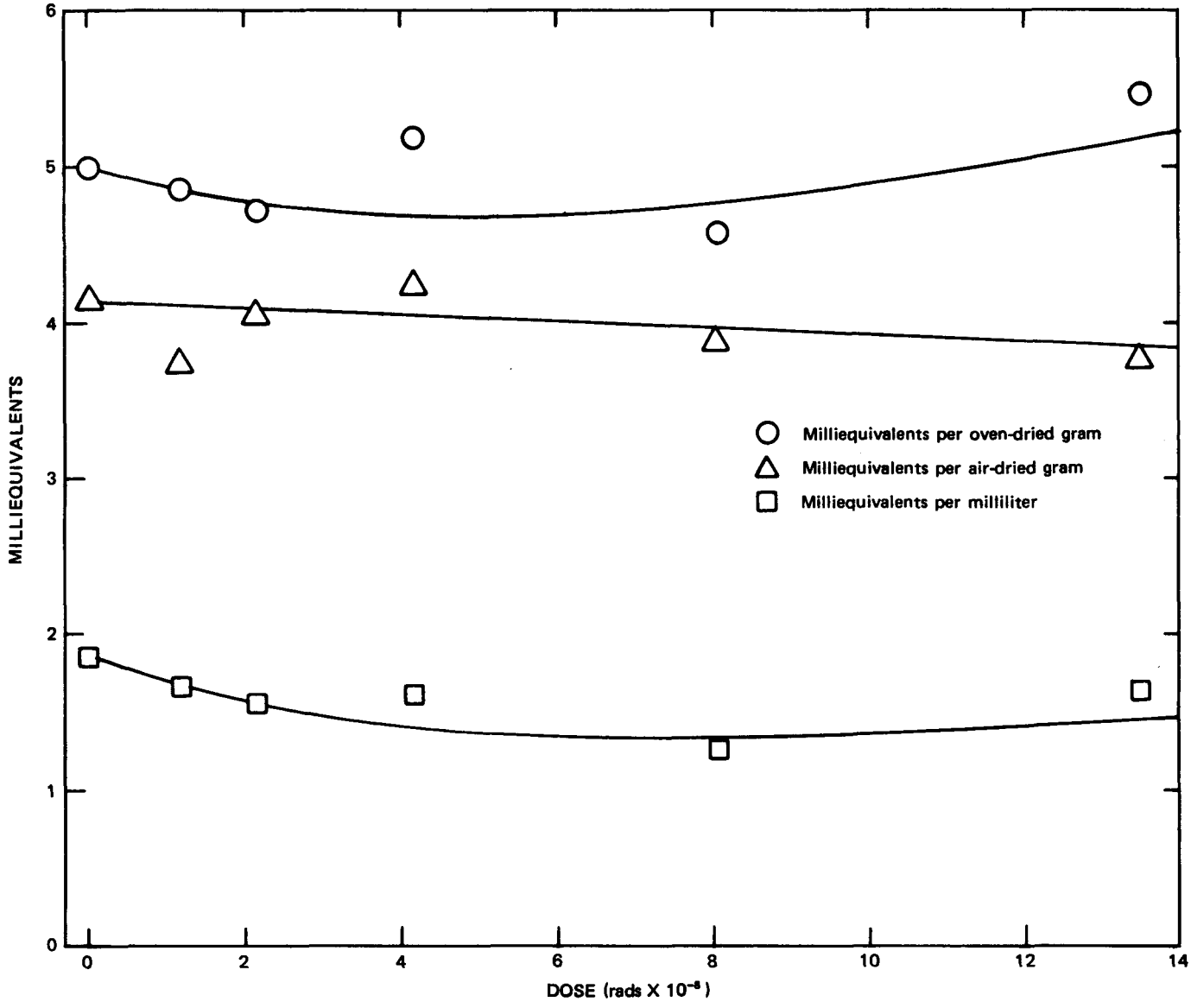
Plutonium Loading and Elution

The plutonium loading and elution characteristics were determined for resin irradiated to a dose of 5.96×10^8 rads. The results were compared to those obtained previously for unirradiated resin. Plutonium loading was calculated for 1% and 10% breakthrough, and the elution cycle was used to determine total plutonium loading as well as the volume of eluant (7*N* HNO_3) required to elute 90% of the plutonium. The results are summarized in Table 8.

TABLE 6. Capacity and Moisture Content of Bio-Rad AG MP-50

Dose (Rads × 10^{-8})	Milliequivalents Per Oven-Dried Gram	Milliequivalents Per Air-Dried Gram	Milliequivalents Per Milliliter	Percent H_2O
		Air-Dried, Hydrogen Form		
0	4.99 ± 0.23	4.12 ± 0.17	1.85 ± 0.09	17.2 ± 0.85
1.18	4.85	3.72	1.66	23.4
2.15	4.71	4.03	1.52	14.4
4.14	5.18	4.21	1.59	18.8
8.03	4.55	3.86	1.23	15.1
13.5	5.47	3.76	1.61	31.1
		0.1*N* Hydrochloric Acid		
0	4.99 ± 0.23	4.12 ± 0.17	1.85 ± 0.09	17.2 ± 0.85
1.18	4.70	3.72	1.62	20.8
2.15	4.48	3.62	1.38	19.4
4.14	5.03	3.62	1.34	27.9
8.03	4.24	3.26	1.10	23.2
13.5	5.14	3.39	1.48	34.0

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


MILLIEQUIVALENTS
DOSE (rads X 10⁻⁸)
Milliequivalents per oven-dried gram
Milliequivalents per air-dried gram
Milliequivalents per milliliter
0
1
2
3
4
5
6
0
2
4
6
8
10
12
14

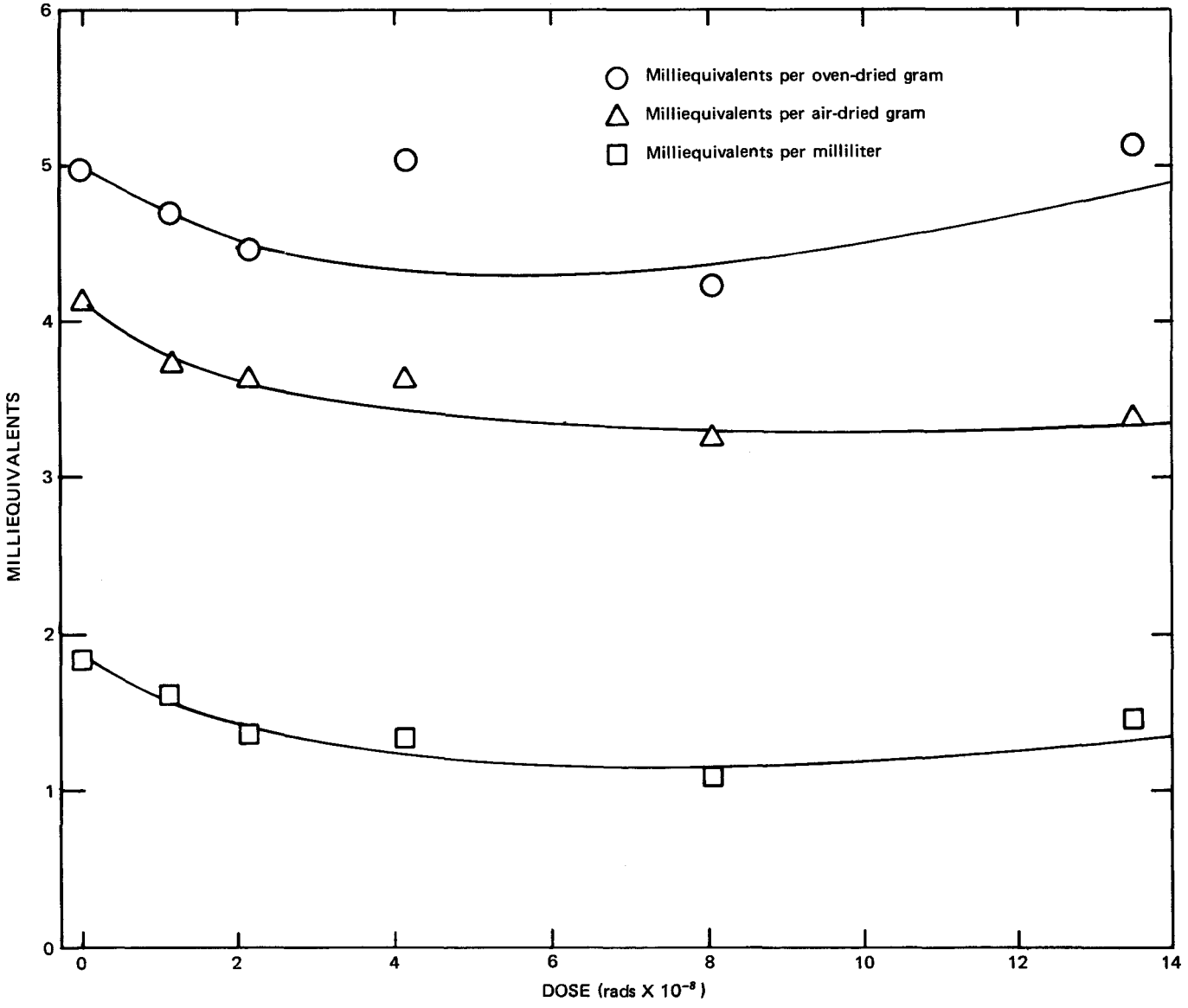


FIGURE 4. Resin Irradiated in 0.1*N* HCl

TABLE 7. Gas Generation
(molecules per 100 electron volts)

	In Air	In Vacuum
H_2	0.053	0.051
CO	0.016	0.033
CO_2	0.040	0.024
SO_2	0.002	0.023
TOTAL	0.11	0.13

TABLE 8. Plutonium Loading and Elution

	Unirradiated Resin	Irradiated Resin
Plutonium Loading at 1% Breakthrough (mg Pu/ml resin)	94.7	72.6
Plutonium Loading at 10% Breakthrough (mg Pu/ml resin)	101	78.4
Total Loading (mg Pu/ml resin)	84.0	85.0
Eluant (ml) to elute 90% of Pu from 1 ml resin	1.6	2.2

The breakthrough loading values for unirradiated resin should be somewhat lower than the total loading of 84.0 milligrams of plutonium per milliliter of resin. A slightly erroneous feed analysis could account for this discrepancy. These results indicate that plutonium loading is not affected up to a radiation dose of 5.96×10^8 rads; however, the elution kinetics have been altered; 2.2 ml (vs 1.6 ml) are now required to elute 90% of the plutonium from 1 ml of resin.

Thermal Stability

Bio-Rad AG MP-50 was irradiated in the air-dried hydrogen form with doses of 3.77×10^8 and 7.54×10^8 rads. The results of differential thermal analysis, using both open and closed capillaries, are shown in Table 9. Temperatures preceding the parentheses are the maximum and minimum of the exotherms and endotherms, respectively. The temperature ranges are shown inside the parentheses.

Thermal instability, as indicated by the exotherms, appears to occur at the relatively high temperature of 270 °C. However, the potential hazard is considered to be small because of the very small size of the exotherm.

Comparison to Presently Used Ion Exchange Resins

The overall radiation stability of Amberlite IRA-938 appears to be comparable to that of Dowex 11, the anion exchange resin presently used in Rocky Flats recovery operations. One property that is different is the moisture content. Irradiation decreases the water content of Amberlite IRA-938 but does not affect that of Dowex 11, indicating that radiation-induced cross-linking is greater for the Amberlite resin.

TABLE 9. Differential Thermal Analyses of Bio-Rad AG MP-50

Open Capillary	Closed Capillary
Unirradiated Resin	
Very large endotherm 97 °C (94-170 °C) Small broad endotherm 307 °C (250-345 °C)	No thermal changes to 400 °C
Resin Irradiated With 3.77×10^8 Rads	
Very small exotherm 270 °C (257-300 °C) Very large endotherm 112 °C (108-200 °C)	Very small endotherm 330 °C (309-350 °C)
Resin Irradiated With 7.54×10^8 Rads	
Very small exotherm 272 °C (254-300 °C) Very large endotherm 120 °C (112-200 °C)	No thermal changes to 325 °C

The Bio-Rad AG MP-50 resin is at least as radiation stable as Dowex 50W, which is also currently used in recovery operations.[1] Cation exchange resins are more radiation stable than anion exchange resins. Relatively high radiation doses were administered to the Bio-Rad resin, and it appears that the exchange capacity increases after an initial decrease. This behavior was explained earlier in this report.

CONCLUSIONS

The radiation stability of Amberlite IRA-938 and Bio-Rad AG MP-50 was found to be satisfactory. Radiation doses of greater than 10^8 rads would be required to affect the exchange capacity and thermal stability. Such large doses would allow these resins to be used for Rocky Flats plutonium and americium recovery operations for years before replacement.

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APPENDIX
PROCEDURES FOR EXCHANGE MEASUREMENTS

Sulfonic Cation Exchangers (Strong Acid)[5]

Procedure

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 to 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 CP 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:

$$\text{Capacity, } H^+, \text{ wet} = \frac{\text{ml NaOH} \times \text{normality NaOH}}{\text{ml wet sample}} = \text{meq/ml}$$

12. Calculate the dry weight total capacity as follows:

$$\text{Capacity, } H^+, \text{ dry} = \frac{\text{ml NaOH} \times \text{normality NaOH}}{\text{g dry sample}} = \text{meq/dry g}$$

13. Calculate the wet weight total capacity as follows:

$$\text{Capacity, } H^+, \text{ wet} = \frac{\text{ml NaOH} \times \text{normality NaOH}}{\text{g wet sample}} = \text{meq/wet g}$$

14. Calculate the moisture content as follows:

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

15. If the properties obtained in steps 11 to 14 are desired on 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.

Quaternary Ammonium Anion Exchangers (Strongly Basic)

Procedure

1. Place about 10 ml of wet swollen sample in a 0.5-in.-i.d. column.

2. Pass 170 ml of 4% NaOH through the resin at a relatively constant flow rate for 0.5 hour.

3. Rinse the resin with deionized or distilled water at the same flow rate for one hour.

4. Pass 100 ml of 1*N* NaCl through the resin at a relatively constant flow rate for 0.5 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 milliliters in each aliquot, then filter and get weights.

7. Transfer the samples to 400-ml beakers with minimum flush water.

8. Add 2 ml of CP H_2SO_4 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 the Volhard method.

11. Calculate the wet volume quarternary capacity of the resin as follows:

Capacity,

$$Cl^- = \frac{\text{ml } AgNO_3 \times \text{normality } AgNO_3}{\text{ml sample}} = \text{meq/ml}$$

12. Replace the remaining resin in the column and pass 100 ml of 1*N* HCl through the resin at a relatively constant flow rate for 0.5 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 to 10.

15. Calculate the wet volume total capacity of the resin as follows:

Capacity,

$$Cl^- = \frac{\text{ml } AgNO_3 \times \text{normality } AgNo_3}{\text{ml sample}} = \text{meq/ml}$$

16. Get percent of H_2O on separate samples.

17. Attach the vacuum flask with sintered glass filter to a vacuum and wash one sample into the filter for 10 minutes.

18. Place each sample in a previously tared weighing bottle, reweigh and place in an oven overnight at 105-115 °C. Be sure to vent the weighing bottles.

19. Cool each sample in a desiccator and reweigh.

20. Calculate the moisture content as follows:

% moisture,

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