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RADIATION DAMAGE TO ORGANIC ION-EXCHANGE MATERIALS

I. R. Higgins

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0.0 ABSTRACT

The stability of polystyrene and phenolic ion-exchange resins to radiation from a Co^{60} source and from absorbed Ce^{144}-Pr^{144} was investigated. Sulfonated polystyrene cation-exchange resins lost 10 to 20% of their capacity per watt-hour of radiation absorbed per gram of oven-dry resin, while the quaternary amine anion-exchange polystyrene resins lost about 40%. Phenolic cation-exchange resins lost only 1%.

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1.0 INTRODUCTION

Ion-exchange methods of processing radioactive solutions are attractive because of the simplicity of the equipment required, the high degree of separation that can be accomplished on very compact equipment, making shielding requirements low, and the ease of remote control. A knowledge of the effect of high-intensity radiation on ion-exchange materials is essential to further development of high-radiation-level ion-exchange processes.

The resin radiation-stability studies reported here were started in connection with the separation of kilocurie amounts of fission products by ion-exchange.(1) Experiments were made with a Co^{60} (gamma) source and with absorbed Ce^{144}-Pr^{144} (beta). The radiation damage problem is also of interest in the chemical processing of aqueous homogeneous reactor solutions, where it is desirable to process fuel continuously with a minimum cooling time.

This report is concerned only with the rate of decomposition of ion-exchange resins when exposed to radiation of a given intensity. The use of continuous ion-exchange to minimize contact time, and consequently radiation damage, is discussed in another report.(2)

2.0 SUMMARY

Dowex-50 resin, representing the sulfonated polystyrene type of cation exchanger, lost 10 to 20% of its capacity per watt-hour of energy absorbed per gram of oven-dry resin. The resin changed color from brown to dull red, but little, if any, colored material was released, and there appeared to be no breakdown of the resin particle.

Dowex-A-1 resin, representing the quaternary amine polystyrene type of anion exchanger, lost about 40% of its capacity per watt-hour of energy absorbed per gram of oven-dry resin. The color turned from pale yellow to dark brown, and the odor indicated that amines were released.

The phenolic cation-exchange resins Amberlite IR-105 and Dowex-30 and the Ionics, Inc., ion-exchange membrane CR-51 lost only 1% of their capacity per watt-hour of energy absorbed per gram of oven-dry resin. In the case of the CR-51 membrane, however, its Lumite support was warped by the radiation.

Although the polystyrene resins are known to have superior exchange properties and chemical durability, the phenolics are more resistant to radiation.

3.0 ACKNOWLEDGMENT

The Co^{60} gamma facilities were made available and calibrated by C. J. Hochanadel and J. A. Ghormley of the Chemistry Division. Curie quantities

of Ce^{144}-Pr^{144} were supplied by A. F. Rupp of the Isotopes Production Division. Ion-exchange samples were titrated by P. F. Thomason of the Analytical Chemistry Division. Nontechnical assistance was supplied by W. E. Shockley. Resin damage during the fission product runs was observed by R. E. Blanco.

4.0 RADIATION SOURCES AND CALIBRATION

The Co^{60} sources used in this study were 300 and 1500 curies in intensity. The energy absorbed in water was determined to be 0.01 calorie per minute per gram of water in a 4450-r/min field, and the energy absorbed by the ion-exchange material was assumed to be the same as for water.

Radiation damage from absorbed fission product ions on the exchanger material was determined with curie quantities of Ce^{144}-Pr^{144}. Beta energy absorption was assumed to be 100%. The beta energy of an equilibrium Ce^{144}-Pr^{144} mixture was calculated to be 0.00154 watt/curie. The Ce^{144}-Pr^{144} was absorbed in a few milliliters of resin in a 1/4-in. column, and the activity was handled by remote control and used repeatedly by means of a citrate cycling system.(3) Distribution of the activity over the sample in the column was not known.

5.0 DETERMINATION OF DAMAGE

Most capacity losses for the sulfonated polystyrene resins and for the phenolic resins were determined by converting the irradiated exchanger to the acid form, titrating with alkali, and comparing the results with those obtained on a nonirradiated control. The irradiated sample was also analyzed for sulfate ion derived from the severed active sulfonate group,(4) and capacity losses calculated from the sulfate analyses agreed well with those calculated from the alkali titrations. In early experiments the damage was determined by observing the breakthrough characteristics of various fission products absorbed from uranyl sulfate solution. The quantity of resin used for each experiment was measured volumetrically, and the capacity was determined by analyzing for final holdup uranium.

The capacity loss of the quaternary amine anion exchangers was determined by titrating the chloride form of the exchanger with a silver solution and comparing the results with those obtained on a nonirradiated control.

Results were reported on an oven-dry-weight basis.

6.0 EFFECTS OF RADIATION ON SULFONATED POLYSTYRENE RESIN (DOWEX-50)

Radiation from a Co^{60} source or from absorbed Ce^{144}-Pr^{144} caused a capacity loss in the cation exchanger Dowex-50 of 10 to 20% per watt-hour of energy absorbed per gram of dry resin (Figs. 1 and 3). The capacity losses

calculated from titration results agreed well with those calculated from sulfate-release determinations. The variations in the results are believed to be attributable to experimental errors in measurements of field intensity and volume of resin and to analytical errors in the resin alkali titrations. It is assumed that the effect of radiation on other sulfonated polystyrene resins would be the same as that on Dowex-50.

The sulfonated polystyrene resins are manufactured by sulfonating a styrene divinyl benzene polymer.(4) Apparently the bond holding the active sulfonate group is weakest and absorbs the radiant energy. It is interesting to note that the most significant radiation effect is a capacity loss with apparently little effect on the physical breakdown of the particle. A similar effect has been noted in radiation experiments with other substances.(5)

In the early experiments radiation was noted to cause a significant increase in the affinity of the resin for tracer Nb^{95}, which is usually considered(6) one of the colloidal fission products. This abnormality may indicate a change in surface properties or formation of a complexing bond. No abnormal effect on resin affinity was observed for the purely cationic species strontium (Fig. 2).

One determination was made of the capacity loss of the uranyl form of Dowex-50 that had been irradiated in the ORNL graphite reactor. The energy absorbed was calculated from the known energy of fission of U^{235}. The resin lost 8% of its capacity per watt-hour of fission energy per gram of dry resin.

7.0 EFFECTS OF RADIATION ON QUATERNARY AMINE POLYSTYRENE RESIN (DOWEX-A-1)

Radiation from a Co^{60} source caused a capacity loss in the anion exchanger Dowex-A-1 of 40% per watt-hour of energy absorbed per gram of dry resin (Fig. 4). Capacity losses were determined by comparison of results of chloride capacity determinations with similar results from nonirradiated controls. No attempt was made to determine changes in exchange behavior as was done with irradiated Dowex-50.

The quaternary amine polystyrene resins are made from the same styrene divinyl benzene polymer as the sulfonated resins. Instead of a sulfonate group, which exchanges cations, being added, an amine is attached which provides an immobile negative charge and makes possible anion exchange. The mechanism of the radiation damage is apparently similar to that of the cation resin. The odor of the irradiated resin indicates that amines are released. The resin particles retain their shape but turn from pale yellow to dark brown.

8.0 EFFECTS OF RADIATION ON PHENOLIC RESINS

The sulfonated phenolic resins Amberlite IR-105 and Dowex-30 and the Ionics, Inc., ion-exchange membrane CR-51, which is also a phenolic, showed

under irradiation a capacity loss of about 1% (Fig. 5). Other radiation studies[5] had indicated that the phenolic resins are the most stable to radiation of all the common plastics.

The first organic cation exchangers commercially available were phenolics. Amberlite IR-105 and Dowex-30 are not now being produced because of the superior exchange properties and chemical durability of the polystyrene resins. However, the Ionics, Inc., CR-51 membrane is in production. The Lumite support for the membrane was considerably warped by the radiation, and a more resistant support would have to be provided if this membrane should be put into use in radiation work.

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Dwg. #16099

FIGURE 1

CAPACITY LOSS OF DOWEX 50 ION EXCHANGE RESIN FROM Co^{60} GAMMA IRRADIATION

Capacity determined from uranyl hold-up of a unit volume of resin.

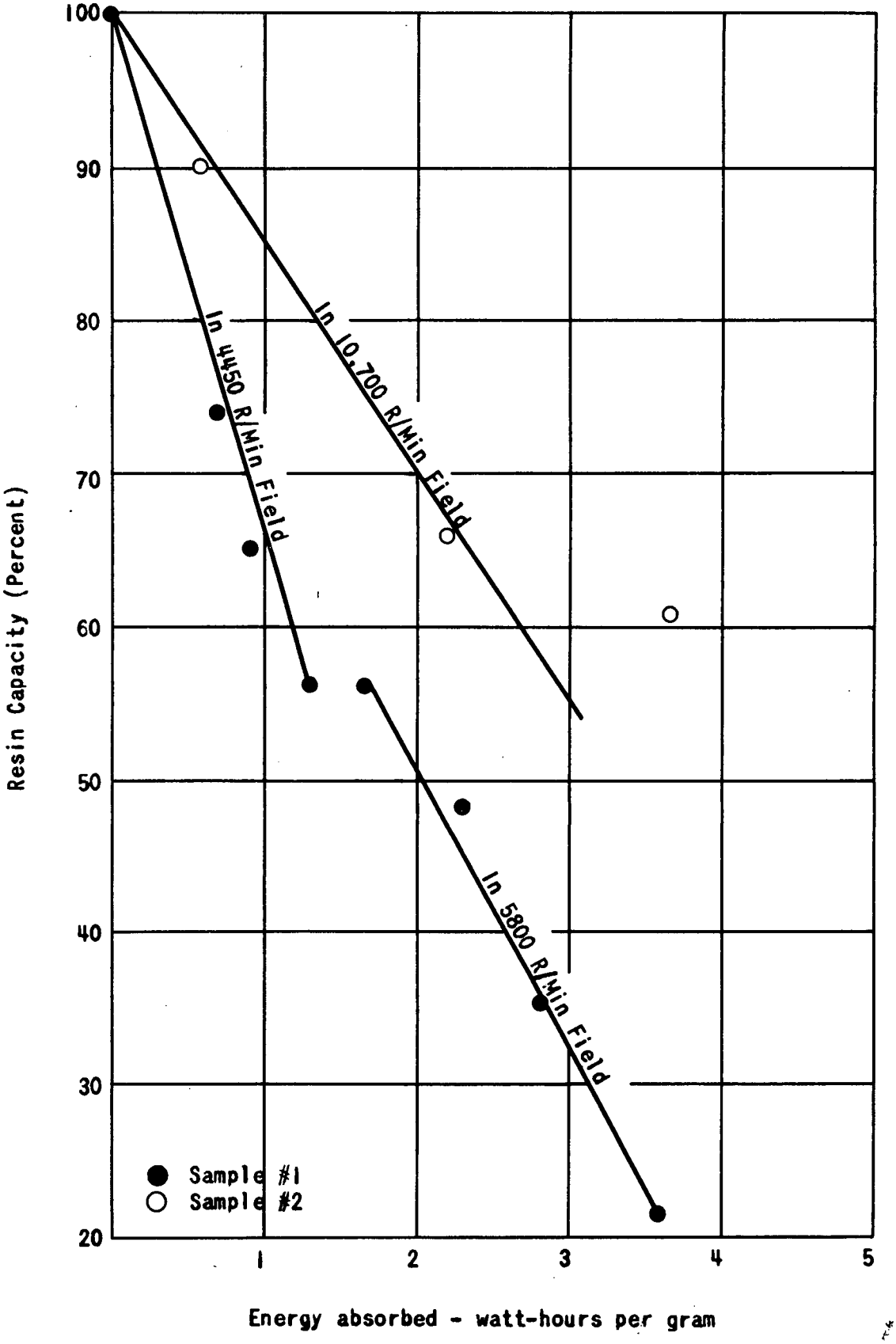

FIGURE 2

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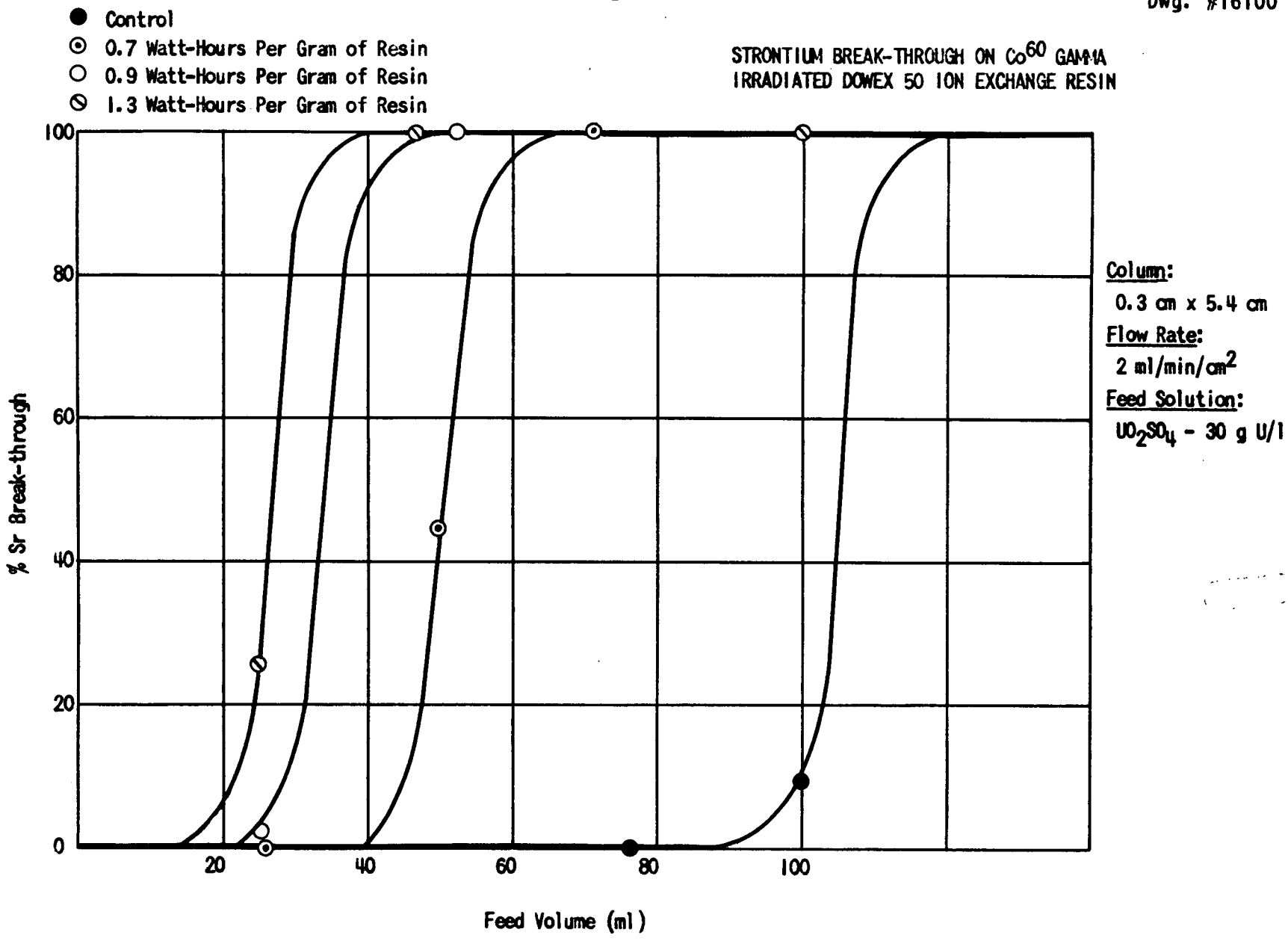

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FIGURE 3

CAPACITY LOSS OF DOWEX 50 ION EXCHANGE RESIN
FROM ABSORBED Ce-Pr^{144} BETA IRRADIATION

Ce-Pr^{144} Beta Energy 0.00154 Watts Per Curie
100% Beta Energy Absorption Assumed

○ Capacity Loss Determined by Titration of H-Form Resin

● Capacity Loss Determined by Free SO_4 Released

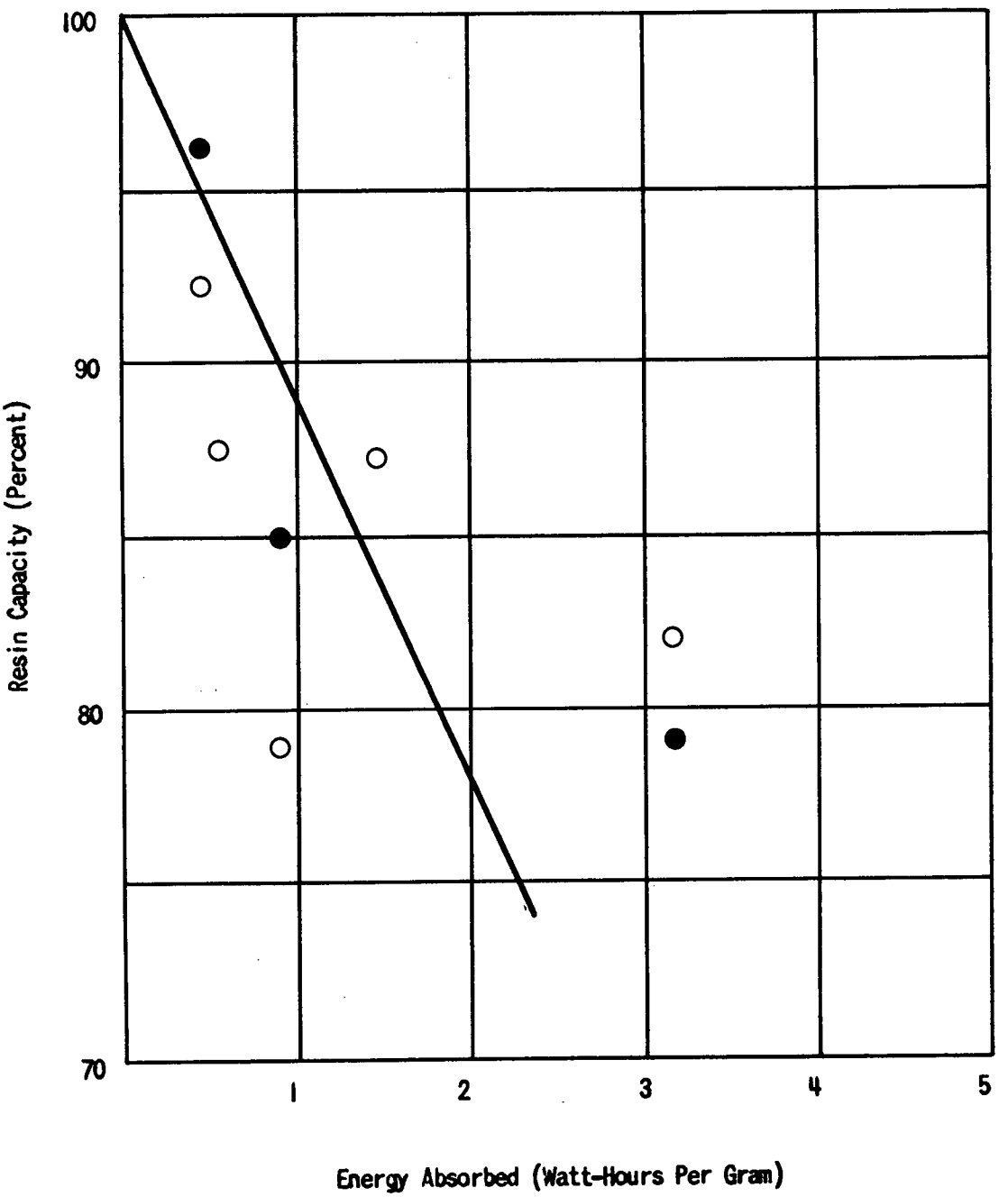

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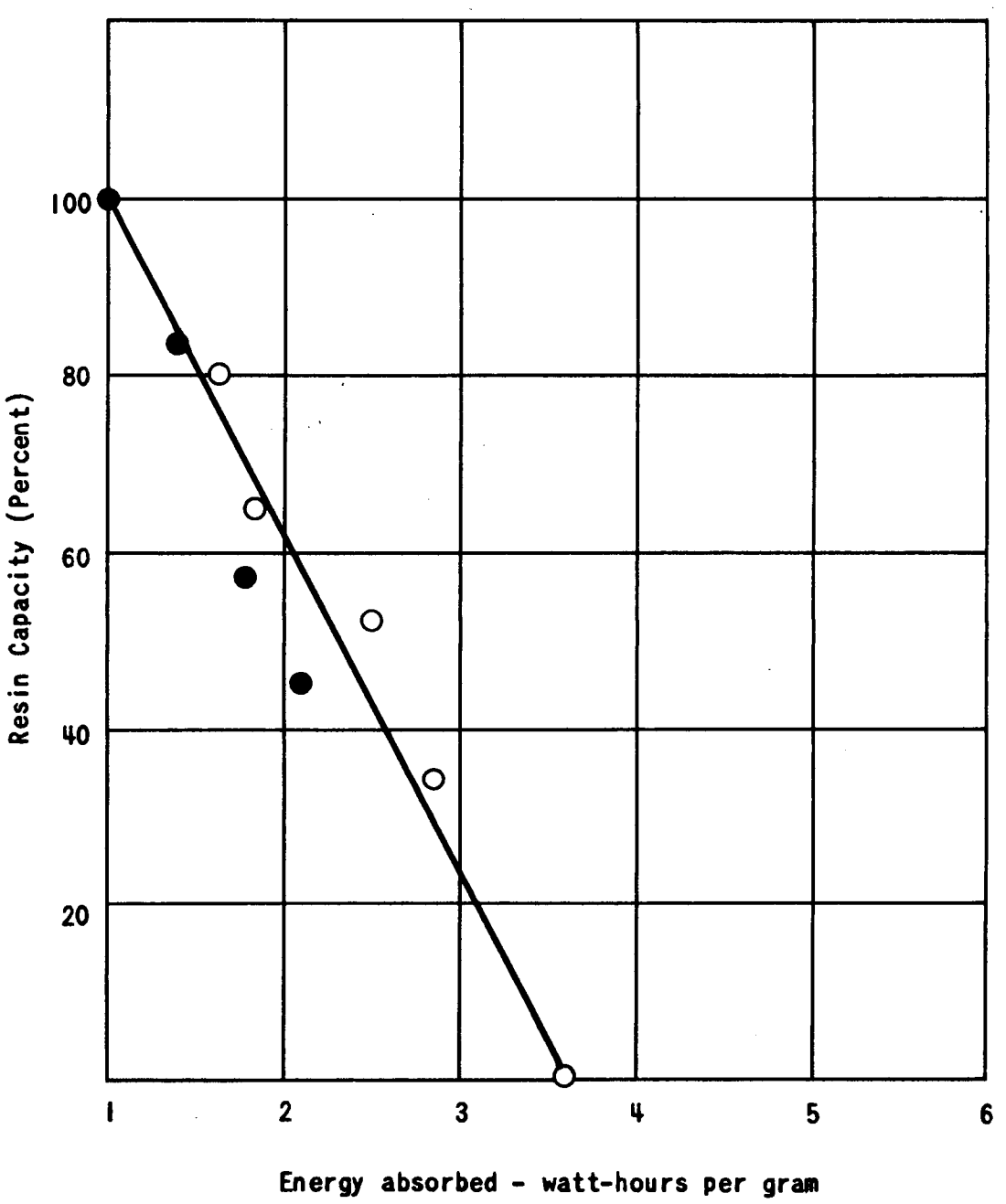
FIGURE 4

CAPACITY LOSS OF DOWEX A-1 ANION EXCHANGE RESIN
FROM Co^{60} GAMMA IRRADIATION

Capacity determined by titration of R-Cl.



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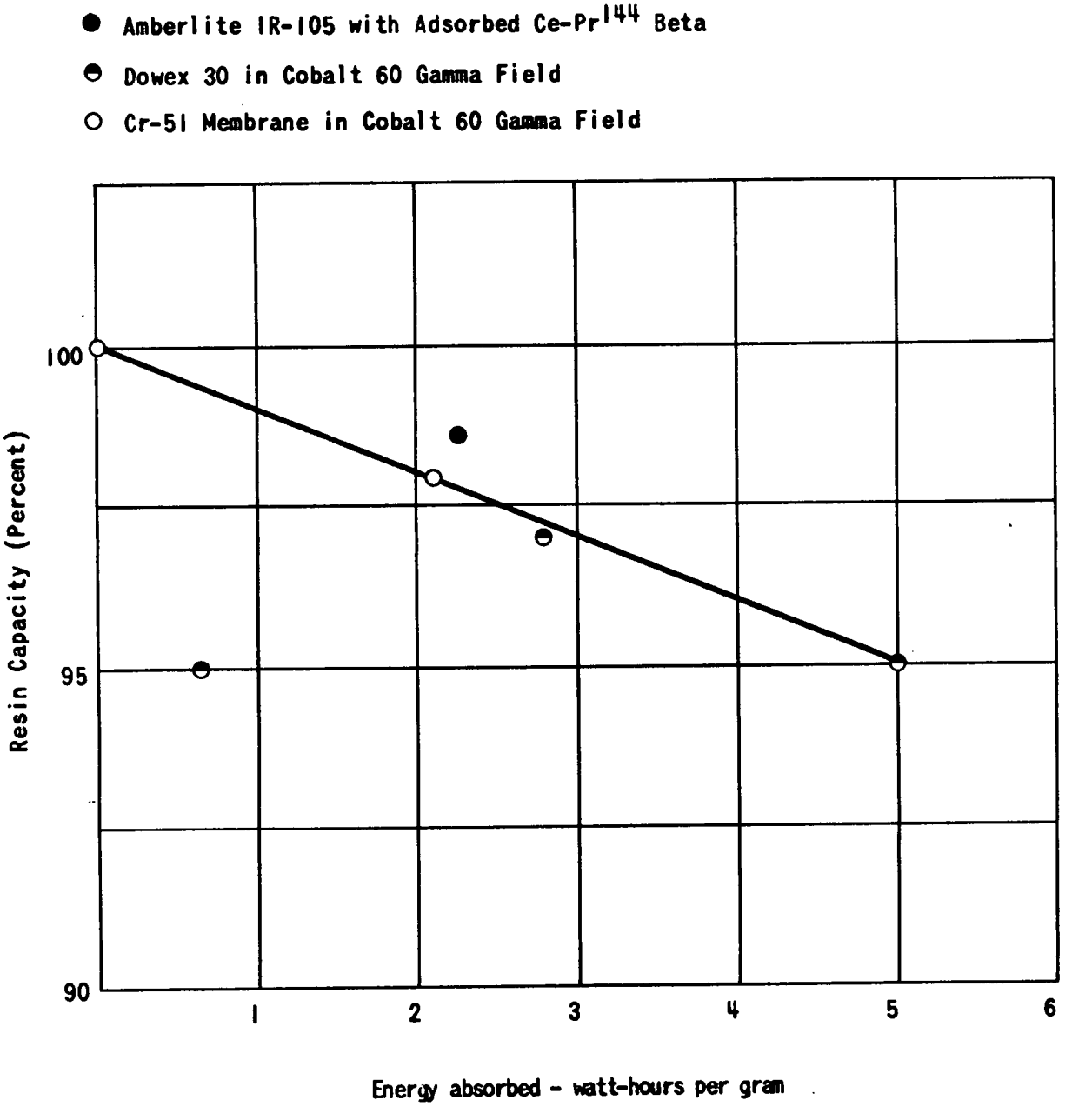
CAPACITY LOSS OF PHENOLIC CATION EXCHANGERS
WITH Co 60 GAMMA AND Ce-Pr^{144} BETA IRRADIATION