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The Effects of Ionizing Radiation on Reillex^{TM} HPQ, a New Macroporous Polyvinylpyridine Resin, and on Four Conventional Polystyrene Anion Exchange Resins

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TRADEMARKS

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THE EFFECTS OF IONIZING RADIATION ON REILLEX^{TM} HPQ, A NEW MACROPOROUS POLYVINYLPYRIDINE RESIN, AND ON FOUR CONVENTIONAL POLYSTYRENE ANION EXCHANGE RESINS*

by

S. Fredric Marsh

ABSTRACT

This study compares the effects of ionizing radiation on Reillex^{TM} HPQ, a recently available macroporous copolymer of 1-methyl-4-vinylpyridine/divinylbenzene, and on four conventional strong-base polystyrene anion exchange resins. The polystyrene resins investigated included one gel type, Dowex^{TM} 1x4, and three macroporous resins: Dow^{TM} MSA-1, Amberlite^{TM} IRA-900, and Lewatit^{TM} MP-500-FK. Each resin, in 7 M nitric acid, was subjected to seven different levels of ^{60}Co gamma radiation ranging from 100 to 1000 megarads. Irradiated resins were measured for changes in dry weight, wet volume, chloride and Pu(IV) exchange capacities, and thermal stability. In separate experiments, each resin was subjected to approximately 340 megarads of *in situ* alpha particles from sorbed plutonium. Resin damage from alpha particles was less than half that caused by gamma rays, which may be a consequence of different production rates of radiolytic nitrite and nitro radicals in the two systems. Reillex^{TM} HPQ resin provided the greatest radiation stability, whereas Lewatit^{TM} MP-500-FK was the least stable of the resins tested. Thermogravimetric analyses of dry, nitrate-form resin revealed that dry Reillex^{TM} HPQ resin offered the best thermal stability for absorbed gamma doses to 370 megarads, but the worst thermal stability after exposures of 550 megarads or more.

I. INTRODUCTION

A recent Los Alamos investigation of more than 30 anion exchange resins[1] established that high porosity and small bead size are the two properties that most improve the sorption kinetics and capacity for Pu(IV) from nitric acid. That study concluded that Lewatit^{TM} MP-500-FK, a macroporous, strong-base anion exchange resin manufactured (but since discontinued) by Bayer AG in the Federal Republic of Germany, offered the best performance for processing plutonium.

Because plutonium recovery operations subject anion exchange resin to nitric acid and ionizing radiation for extended periods, our next objective following that study was to identify how the anion exchange resin structure might be modified to provide increased safety in this aggressive environment, while maintaining recently achieved performance gains.

Most conventional strong-base anion exchange resins incorporate a copolymer of styrene and divinylbenzene. Because such styrene polymers can react violently with nitric acid under certain conditions, their safe use requires strict avoidance of conditions known to be hazardous. Potential safety hazards associated with using ion exchange resins in nitric acid have been addressed by Calmon and Gold.[2] A separate review by Miles[3] specifically deals with failures within the nuclear industry. The nuclear industry has given an understandably high priority to avoiding conditions that could result in exothermic reactions between ion exchange resins and nitric acid.

In addition to being susceptible to attack by nitric acid, organic resins are damaged by high levels of ionizing radiation. Moreover, radiolytic degradation can increase the risk of an exothermic reaction between resin and nitric acid. An important economic issue, apart from these essential safety considerations, is

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*The majority of the work described in this report was performed at Harwell Laboratory, United Kingdom Atomic Energy Authority, Oxfordshire OX11 0RA, England, during the year the author was attached to the Chemistry Division as a Visiting Scientist.

that exposure to high levels of ionizing radiation can significantly decrease the useful life of an ion exchange resin by degrading its physical properties and performance. Reliable operation of an ion exchange process for radionuclides therefore requires that the selected resin be reasonably tolerant toward ionizing radiation. Published compilations[4-6] of the effects of ionizing radiation on many different ion exchange resins facilitate resin comparisons and selection.

Although a polystyrene/divinylbenzene copolymer provides the skeletal structure for most synthetic ion exchange resins, other polymers also have been used. A particularly effective but discontinued anion exchange resin was Permutit™ SK, a 2-methyl-5-vinylpyridine/divinylbenzene copolymer. Permutit™ SK resin was reported to lose only 7.8% of its ion-exchange capacity after exposure to 267 megarads* of gamma radiation, whereas Dowex™ 1x4 resin lost 58.4% of its capacity after an identical exposure.[7] The authors of one compilation[4] state, "These resins with pyridine exchange groups are more stable to ionizing radiations than all other types of synthetic organic ion exchangers that have been examined for radiation-induced chemical changes."

Another advantage of vinylpyridine polymers is their resistance to attack by nitric acid. This difference in reactivity between polystyrene and polyvinylpyridine is attributed to the susceptibility of polystyrene to electrophilic aromatic substitution, whereas the electron deficiency of the aromatic system makes polyvinylpyridine highly resistant to such substitution. In fact, Morrison and Boyd[8] specify that potassium nitrate and sulfuric acid at 300°C are required for the nitration of pyridine.

Because polyvinylpyridine resins offered the potential for both superior chemical and radiation resistance, we contacted Reilly Industries, Inc., a manufacturer of vinylpyridine polymers. We encouraged Reilly to develop a new, macroporous form of polyvinylpyridine resin that would offer enhanced resistance to nitric acid and ionizing radiation, without sacrificing the recently achieved higher capacity and rapid sorption kinetics for Pu(IV).

Nearly two years of collaboration between Los Alamos and Reilly Industries, Inc., resulted in a macroporous, strong-base anion exchange resin composed of 1-methyl-4-vinylpyridine cross-linked with divinylbenzene. The monomeric structures of conventional strong-base polystyrene and polyvinylpyridine anion exchange resins are shown in Fig. 1. The new resin, designated Reillex™ HPQ, not only offers excellent sorption kinetics for Pu(IV) from nitric acid but also withstands boiling, concentrated nitric acid for several hours without significant damage![9] However, because Reillex™ HPQ resin has been available for only a relatively short time, our investigation provides the first comprehensive evaluation of its radiation stability.

The objective of this study was to quantify the radiolytic stability of Reillex™ HPQ and three macroporous polystyrene anion exchangers, previously used to process plutonium, whose radiolytic stabilities had received little or no investigation. Dowex™ 1x4, a gel-type polystyrene resin whose radiation stability has been extensively studied, also was included to provide a reference point by which our findings could readily be compared to those of other published studies. During our investigation we attempted to treat all five resins as identically as possible to provide directly comparable, relative data. To aid other experimenters who may want to duplicate portions of our study, we also tried to include important experimental details that often are omitted.

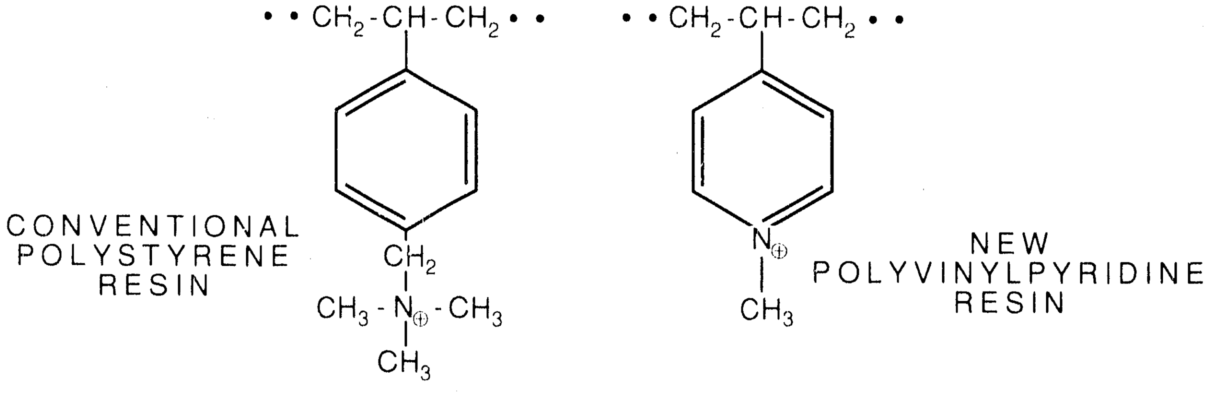

Fig. 1. Comparative monomeric structures of polystyrene and polyvinylpyridine resins.

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*For those who prefer SI units, 1 megarad = 10^4 Gray.

II. REAGENTS AND APPARATUS

The system used to measure the radiation stability of the five resins included the following:

Nitric Acid: Reagent-grade, ACS-specification nitric acid was used without additional purification.

Water: Water of at least 18 MΩ-cm from an Elgastat UHP system (Elga Ltd., High Wycombe, Bucks., England) was used to prepare all acid dilutions and aqueous solutions used for analytical measurements.

Anion Exchange Resins: Gel-type Dowex™ 1x4 (50–100 mesh) and macroporous Dow™ MSA-1 (20–40 mesh) resins were obtained from the Dow Chemical Company, Midland, Michigan. Macroporous Amberlite™ IRA-900 (20–40 mesh) resin was obtained from Rohm & Haas, Philadelphia, Pennsylvania. Macroporous Lewatit™ MP-500-FK (40–70 mesh) resin, manufactured by Bayer AG in the Federal Republic of Germany, was obtained from Mobay Chemical Company, Pittsburgh, Pennsylvania. (The manufacture of Lewatit™ MP-500-FK resin was discontinued in 1988.) Macroporous Reillex™ HPQ (30–60 mesh) polyvinylpyridine resin was obtained from Reilly Industries, Inc., Indianapolis, Indiana.

Irradiation Facility: All gamma irradiations were done in a ^{60}Co irradiation cell operated by the Actinide Chemistry and Analysis Group of the Chemistry Division at Harwell Laboratory, Didcot, Oxfordshire, England.

Irradiation Containers: All resin-irradiation containers were intentionally vented (as shown in Fig. 2) to prevent pressurization during the irradiations and were custom-fabricated from transparent fused silica (quartz), standard-taper sockets and borosilicate glass cones.

Dosimeters: Red 4034 Perspex dosimeters designed to measure 0.5 to 5 megarads were obtained from the Actinide Chemistry and Analysis Group at Harwell Laboratory. We used a Philips model PU 8800 UV/VIS spectrophotometer to measure the absorbance of each Perspex dosimeter at 640 nanometers within 2 hours of exposure, after which the thickness of each dosimeter was measured with a metric micrometer.

Thermogravimetric Analysis: All measurements were done on an STA-780 Series Thermal Analyzer, manufactured by Stanton-Redcroft, London.

Dynamic Mixing: All dynamic contacts of plutonium-containing solutions and resins used a model 400-110 Labquake Tube Rotator, manufactured by Lab Industries and obtained from VWR Scientific.

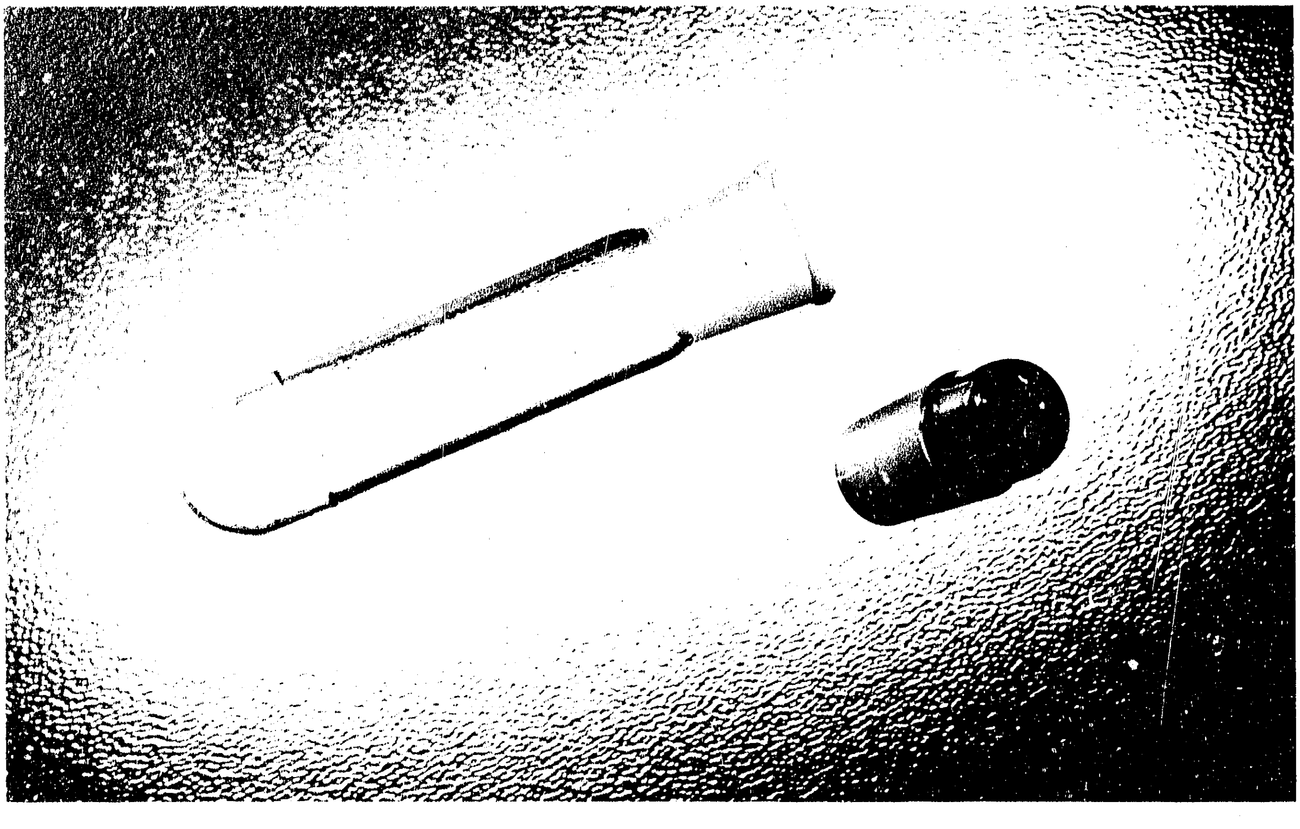

Fig. 2. Vented quartz container for gamma irradiations.

III. EXPERIMENTAL PARAMETERS

A. Resins

Approximately 200 milliliters of each wet resin initially was converted from the as-received chloride form to a nitrate form by passing ten bed volumes of 4 M nitric acid through the resin. Residual nitric acid was removed by washing the resin with a similar volume of demineralized water. The residual chloride content of each resin was determined by thermal neutron activation analysis in the Los Alamos Omega West Reactor. Residual chloride contents (expressed as a percentage of total exchange capacity) were 0.75% for Amberlite™ IRA-900, 0.18% for Dow™ MSA-1, 0.17% for Dowex™ 1x4, 0.13% for Reillex™ HPQ, and 0.06% for Lewatit™ MP-500-FK.

B. Irradiations

Resins were gamma-irradiated in one of the eight ^{60}Co cells operated by the Actinide Chemistry and Analysis Group of the Chemistry Division at Harwell Laboratory. Four individual ^{60}Co sources that totaled 5000 curies provided a combined dose rate that ranged from 0.32 to 0.53 megarads per hour for the individual irradiation positions used for this study.

All resins were irradiated in 7 M nitric acid to simulate the actual plutonium-processing medium. Gamma rays from external ^{60}Co sources were the ionizing radiation in most of our experiments. In a few additional experiments plutonium was sorbed on the resin to obtain comparable irradiations with *in situ* alpha particles (see Alpha-Particle Irradiations section). All resins were immersed in static nitric acid during these irradiations, whereas resin columns are continually flushed by flowing nitric acid during actual processing operations.

Although one might intuitively expect radiolytic species to have more opportunity to react with resin in a static system, Gangwer and coworkers state, "Prolonged exposure of ion exchange resins to radiation in flowing (dynamic) systems causes more drastic changes in their physical and chemical properties than ion exchange resins irradiated in static systems."[4] There is no consensus on this, however, because Ryan[10] has reported that flowing systems greatly decreased the autocatalytic damage to Dowex™ 1x4 caused by radiolytic nitrite.

C. Gamma Dosimetry

The gamma dose rates of approximately 0.5 megarad per hour used to irradiate resins in our study would deplete ferrous sulfate (Fricke) dosimeters in only 3 minutes. Measuring exposure times of only a few minutes duration, during which the dose rate unavoidably changes as the ^{60}Co sources are lowered into position and are then withdrawn, involves unacceptably large uncertainties. To eliminate the uncertainties involved in accurately timing such short exposures, we measured the dose rates with red 4034 Perspex dosimeters, whose higher dose range of 0.5 to 5 megarads allowed much longer exposure periods of 3 to 4 hours.

Perspex dosimeters were developed by the United Kingdom Atomic Energy Authority at the Wantage Laboratory near Harwell to support investigations directed toward using ^{60}Co for industrial radiation processing.[11] These radiation-sensitive polymethylmethacrylate dosimeters, in the form of optically transparent 3- x 30- x 11-millimeter pieces, are supplied in individual, hermetically sealed, laminate sachets. The radiation-induced darkening, which is proportional to the absorbed (water-equivalent) dose, can be measured accurately by spectrophotometry.

When used as directed with the appropriate calibration table, red Perspex 4034 dosimeters are stated to be accurate to ± 2%.[11] Perspex dosimeter calibrations are directly traceable to UK National Physical Laboratory standards and also have been calibrated using a certified radiation source at the US National Institute of Standards and Technology (formerly known as the US National Bureau of Standards.)[12]

The absorbance of each irradiated Perspex dosimeter vs air was measured at 640 nanometers. Each absorbance reading first was converted to optical density, based on an accurate measurement of the dosimeter thickness using a metric micrometer. Finally, each computed optical density value was converted to the corresponding total absorbed dose using the calibration table provided by the Actinide Chemistry and Analysis Group at Harwell Laboratory.

The dose rate of each of the 20 irradiation positions (Fig. 3) was measured before and after the series of irradiations. The integrated dose for each position was computed for every irradiation period (maximum of 101 days) using 5.27 years as the half-life of ^{60}Co

D. Temperature

The relatively low dose rates and open design of the aluminum holder (Fig. 3) used to position specimens during gamma irradiations resulted in no significant increase above the ambient temperature of 25 ± 3°C. Neither did the *in situ* alpha irradiations, also performed at ambient temperature, exhibit any noticeable temperature increase.

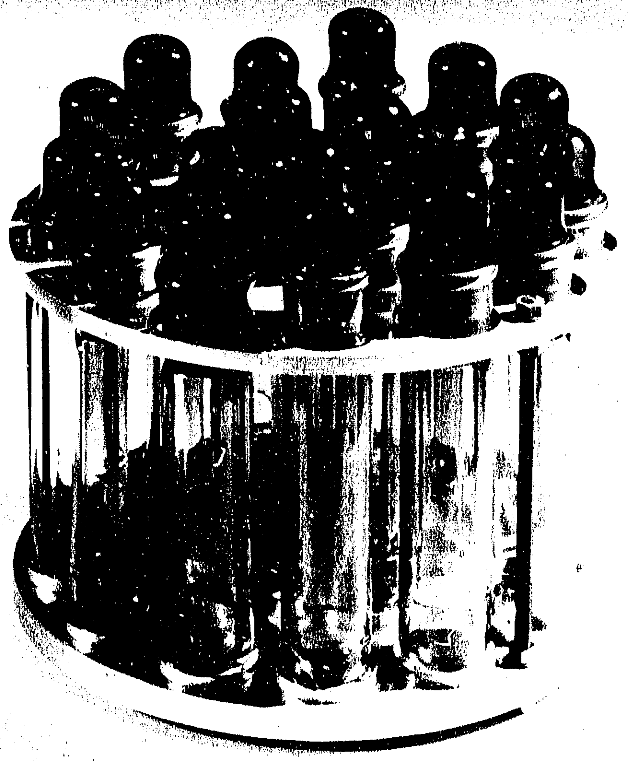

Fig. 3. Aluminum support used to position quartz containers during irradiation.

E. Resin-Drying Conditions

Experimentally measured resin properties are generally reported relative to initial "dry" resin weights. A wide variety of techniques to obtain dry resin have been reported. Some investigators air-dry the resin, some dry it under vacuum, some use elevated temperatures, some remove excess water by centrifugation, and some merely touch the wet resin to dry filter paper to absorb excess liquid.

Because the residual water content of the resin using these dissimilar techniques is highly variable and can be influenced by local altitude and humidity, such drying conditions are difficult to reproduce. Resins designated as "dry" in this report (unless otherwise specified) were equilibrated to constant weight in a sealed desiccator, over a saturated solution of magnesium nitrate that maintained an atmosphere of 52% relative humidity (52% RH).[13]

IV. RESULTS AND DISCUSSION

A. Gamma Irradiations

1. Nitric Acid Concentration. Initially, 5 grams of each dry (52% RH) resin was combined with 25 milliliters of 7 M nitric acid for all gamma irradiations. Unirradiated control resins were similarly immersed in 7 M nitric acid for three months to separately identify the effects of prolonged acid contact in the absence of radiation. Liquid levels of all irradiated resins were periodically inspected to determine whether significant liquid was being lost.

The aqueous solutions of the gamma-irradiated resin experiments showed an initial rapid decrease in nitric acid concentration, which thereafter decreased slowly and never dropped below 4.6 M, as seen in the second column of Table I. Nitric acid solutions in which unirradiated resins had been stored as controls also showed a decrease in nitric acid concentration. In both cases, this rapid initial decrease in acid concentration is attributed to dilution of the original 7 M acid by water contained in "dry" resin.

Although the levels of liquid above the anion exchange resins were inspected periodically throughout the gamma irradiations, neither the volumes nor concentrations of nitric acid decreased enough to justify restoration to their initial values, even during the longest irradiation period of 101 days. The greatest decrease in acid concentration occurred with Lewatit™ resin, presumably because of its nearly complete decomposition during the higher exposures. No attempt was made to identify or assign the specific reactions that caused acid depletion.

TABLE I. GAMMA-IRRADIATED RESIN VOLUMES IN NITRIC ACID

Resin	Dose (Mrad)	Nitric Acid (M)	Volume per Postirrad. Gram (cm^3/g)	Volume per Preirrad. Gram (cm^3/g)
Dowex™ 1X4	none[a]	6.35	NA	2.30
	104	6.15	2.26	2.25
	204	6.05	2.33	2.27
	367	5.70	2.56	2.40
	548	5.60	2.64	2.18
	723	5.25	2.56	2.04
	806	5.10	2.46	2.00
	1058	4.85	2.10	1.60
Dow™ MSA-1	none[a]	6.35	NA	2.78
	108	6.25	2.62	2.60
	199	6.05	2.92	2.78
	374	5.70	3.42	3.02
	551	5.65	4.05	3.04
	700	5.10	4.43	2.99
	839	5.20	4.58	2.94
	1050	4.85	4.23	2.04
Amberlite™ IRA-900	none[a]	6.40	NA	2.60
	104	6.15	2.62	2.60
	220	6.05	2.71	2.62
	367	5.80	3.00	2.80
	549	5.50	3.37	2.80
	727	5.20	4.04	3.04
	835	5.15	3.99	2.80
	1064	4.80	4.10	2.20
Lewatit™ MP-500-FK	none[a]	6.45	NA	2.98
	103	6.14	2.84	2.35
	198	6.05	2.99	2.63
	374	5.80	4.89	3.47
	543	5.50	7.84	2.75
	722	4.95	___[b]	___[b]
	834	5.15	___[b]	___[b]
	1040	4.60	___[b]	___[b]
Reillex™ HPQ	none[a]	6.35	NA	2.94
	106	6.18	3.00	2.99
	202	6.15	3.31	3.28
	370	___[c]	3.51	3.50
	559	5.75	3.90	3.50
	702	5.40	4.32	3.64
	822	5.45	4.46	3.72
	992	4.85	5.47	3.74

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[a] These unirradiated resins were stored in 7 M nitric acid for three months to isolate the effects of prolonged acid contact.

[b] The extensive radiolytic decomposition of Lewatit™ MP-500-FK at these exposure levels left insufficient surviving resin for measurements.

[c] This volume was inadvertently not measured.

2. Resin Volume in Nitric Acid. The settled volume of each nitrate-form resin was measured in a graduated cylinder, first in the nitric acid irradiation medium, and again in water after the resin had been washed free of nitric acid. Table I shows these resin volumes in nitric acid for both pre- and postirradiated dry (52% RH) resin weights. Although many resins increase in volume during irradiation, a simultaneous radiolytic weight loss, discussed later, offsets a portion of the volume increase that would otherwise occur. These experimentally determined values for resin volume vs exposure might be used to predict resin volumes after specified gamma exposures, an important consideration for resin enclosed in production columns, whether the columns are of glass or stainless steel.

3. Resin Volume in Water. Table II shows the settled volume of each nitrate-form resin in water, after being washed free of nitric acid. As in Table I, resin volumes are presented relative to both pre- and post-irradiated 52% RH resin weights. Because many resins increase in volume as the medium is changed from acid to water, the information in Table II might be used to estimate volume increases that could be expected from various resin/exposure combinations. Unexpected resin swelling in a production column could, of course, have very serious consequences.

The two previous tables reveal that Lewatit™ MP-500-FK resin, after irradiation to high gamma doses, occupies larger volumes, especially in water. Irradiated Lewatit™ resin appeared to consist of two fractions: one fraction retained the initial bead-like appearance, whereas the other fraction (that contributed most to the wet volume) was gelatinous. Except for the absence of discrete particles, the appearance and swelling characteristics of this gelatinous fraction were similar to low-cross-linked, gel-type resin.

4. Radiolytic Weight Loss. All gamma-irradiated resins were dried, equilibrated in an atmosphere of 52% RH, and weighed. These weights were compared to preirradiation dry weights to quantify the extent of radiolytic resin decomposition. All resins showed significant weight losses after higher exposures. As shown in the second column of Table III, Reillex™ HPQ resin lost the least weight during all exposures below 1000 megarads, whereas Lewatit™ MP-500-FK consistently lost the most weight; less than 10% of the initial weight of Lewatit resin survived exposures greater than 600 megarads. This unusual susceptibility of Lewatit™ resin to radiation damage was unexpected because no studies of its radiation stability had previously been published.

In addition, portions of all unirradiated and gamma-irradiated resins, after equilibration at 52% RH, were heated overnight at 105°C to drive off physically sorbed water, then cooled in a desiccator, and reweighed. Shown in the third column of Table III, these moisture weight losses are presented as a percentage of the preheated weights.

5. Irradiated Resin Appearance. All resins became darker as a consequence of increased gamma radiation, although the degree of color change varied considerably among the resins studied. Because these color changes might serve to indicate the approximate gamma dose absorbed by a particular resin, a color photograph of 37 resin portions, representing the 5 resin types exposed to different gamma doses, has been included as Fig. 4. Note that three spaces remain empty in the Lewatit™ MP-500-FK resin row of Fig. 4 because this resin was almost completely decomposed by the higher gamma doses.

6. Chloride Exchange Capacity. A weighed quantity of each dry, nitrate-form resin was transferred to a small column and washed with 100 milliliters of 1 M hydrochloric acid per gram of dry resin to completely convert the resin to the chloride form. Excess hydrochloric acid was displaced from the converted resin with ethanol (rather than water, which could hydrolyze the salt forms of weak bases) until the effluent was neutral, as confirmed by methyl orange indicator.

Chloride was removed from the weak-base exchange sites first by elution with 200 milliliters of 0.15 M ammonium hydroxide per gram of dry resin, after which chloride was recovered from the strong-base exchange sites by elution with 200 milliliters of 0.28 M sodium sulfate solution per gram of dry resin.[14] Each portion of eluate was separately acidified and titrated with 0.1 N silver nitrate solution to the disappearance of the pink color of the ferric thiocyanate indicator, using the Volhard method as modified by Swift, et al.[15]

Table IV presents the anion exchange capacities of gamma-irradiated resins as milliequivalents of chloride per gram of dry (52% RH), postirradiated, nitrate-form resin. The data in this table reveal that strong-base anion exchange sites consistently are converted to weak-base sites by gamma radiation, which is in agreement with the findings of many other investigations.

TABLE II. GAMMA-IRRADIATED RESIN VOLUMES IN WATER

Resin	Dose (Mrad)	Volume per Postirrad. Gram (cm^3/g)	Volume per Preirrad. Gram (cm^3/g)
Dowex™ 1X4	none[a]	NA	2.44
	104	2.38	2.37
	204	2.46	2.39
	367	3.07	2.88
	548	4.25	3.93
	723	4.02	3.20
	806	3.22	2.62
	1058	2.36	1.80
Dow™ MSA-1	none[a]	NA	2.80
	108	2.70	2.68
	199	2.80	2.67
	374	3.62	3.20
	551	5.01	3.76
	700	6.04	4.07
	839	6.63	4.25
	1050	7.46	3.60
Amberlite™ IRA-900	none[a]	NA	2.60
	104	2.58	2.56
	220	2.60	2.52
	367	3.06	2.85
	549	3.87	3.21
	727	4.81	3.62
	835	5.84	4.10
	1064	12.30	6.59
Lewatit™ MP-500-FK	none[a]	NA	3.02
	103	2.90	2.84
	198	3.10	2.73
	374	5.03	3.57
	543	24.80	8.70
	722	—[b]	—[b]
	834	—[b]	—[b]
	1040	—[b]	—[b]
Reillex™ HPQ	none[a]	NA	2.84
	106	2.90	2.89
	202	3.13	3.10
	370	3.35	3.34
	559	3.68	3.30
	702	4.08	3.44
	822	4.53	3.78
	992	5.85	3.73

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[a] These unirradiated resins were stored in 7 M nitric acid for three months to isolate the effects of prolonged acid contact.

[b] The extensive radiolytic decomposition of Lewatit™ MP-500-FK at these exposure levels left insufficient surviving resin for measurements.

TABLE III. RESIN WEIGHT LOSS AFTER GAMMA IRRADIATION AND HEATING

Resin	Dose (Mrad)	Postirrad. Wt./ Preirrad. Wt.	Weight Loss @ 105°C (%)
Dowex™ 1X4	none[a]	NA	10.4
	104	0.996	10.9
	204	0.973	10.0
	367	0.937	10.8
	548	0.824	11.1
	723	0.796	10.5
	806	0.814	10.7
	1058	0.762	10.3
Dow™ MSA-1	none[a]	NA	10.7
	108	0.994	11.2
	199	0.952	10.4
	374	0.884	11.8
	551	0.750	12.0
	700	0.674	12.1
	839	0.641	11.5
	1050	0.483	11.6
Amberlite™ IRA-900	none[a]	NA	11.1
	104	0.992	12.2
	220	0.968	10.8
	367	0.933	12.3
	549	0.830	12.8
	727	0.753	13.2
	835	0.702	10.3
	1064	0.536	13.0
Lewatit™ MP-500-FK	none[a]	NA	11.1
	103	0.978	12.2
	198	0.881	11.2
	374	0.710	12.5
	543	0.351	11.8
	722	0.059	—[b]
	834	—[b]	—[b]
	1040	—[b]	—[b]
Reillex™ HPQ	none[a]	NA	11.2
	106	0.997	12.5
	202	0.990	10.6
	370	0.997	12.1
	559	0.898	12.4
	702	0.842	12.3
	822	0.834	11.5
	992	0.683	12.0

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[a] These unirradiated resins were stored in 7 M nitric acid for three months to isolate the effects of prolonged acid contact.

[b] The extensive radiolytic decomposition of Lewatit™ MP-500-FK at these exposure levels left insufficient surviving resin for measurements.

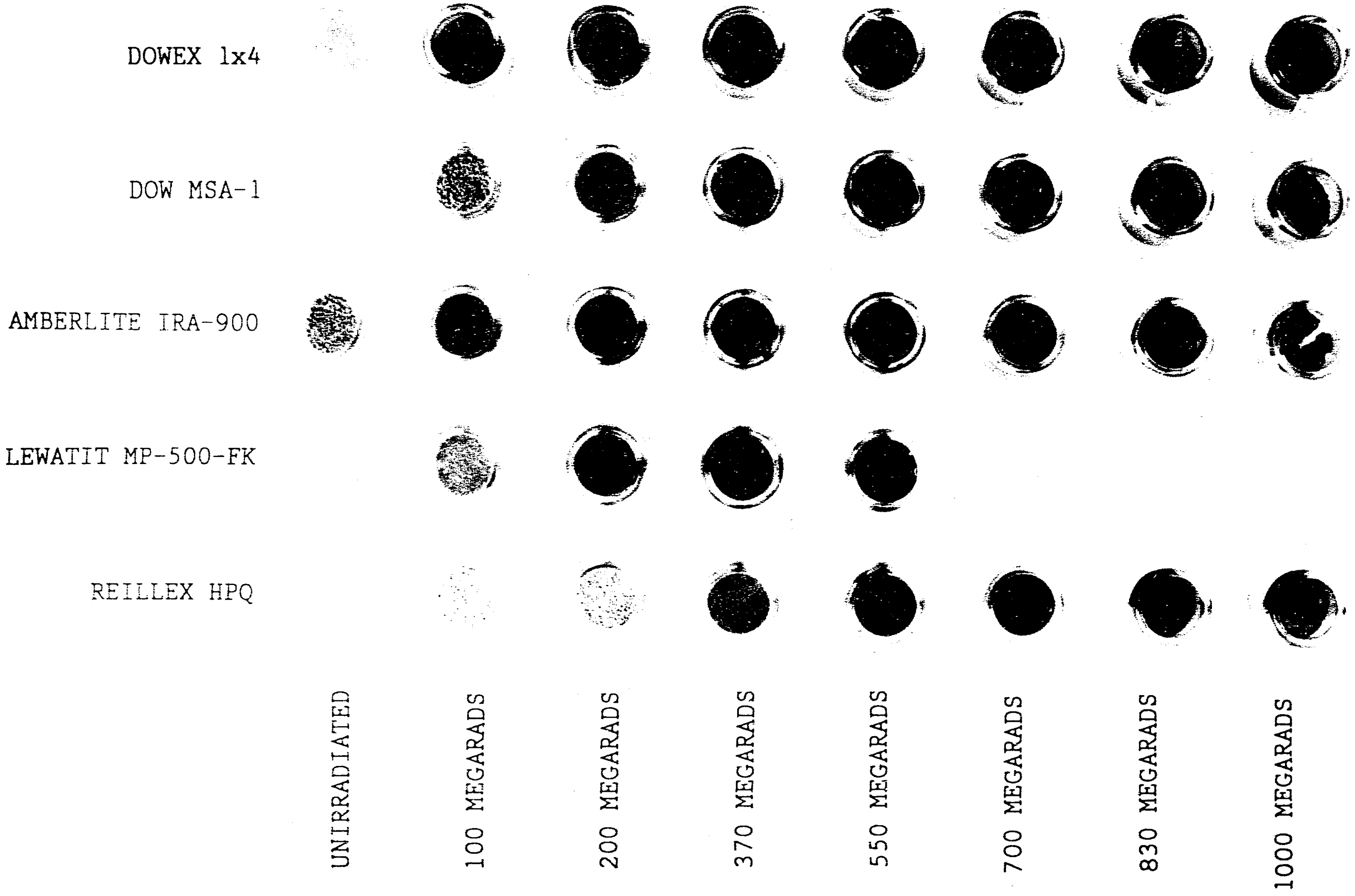

Fig. 4. Color of all surviving resins, in dry nitrate form, as a function of absorbed gamma dose.

TABLE IV. WEAK-BASE AND STRONG-BASE EXCHANGE CAPACITIES OF GAMMA-IRRADIATED RESINS

Resin	Dose (Mrad)	Weak-base Capacity (meq Cl/g)	Strong-base Capacity (meq Cl/g)	Total Capacity (meq Cl/g)
Dowex™ 1X4	none	0.43	2.69	3.12
	none[a]	0.60	2.49	3.09
	104	0.83	2.09	2.92
	204	1.12	1.65	2.77
	367	1.48	0.85	2.33
	548	1.88	0.31	2.19
	723	1.97	0.02	1.99
	806	1.86	0.00	1.86
	1058	1.77	0.00	1.77
Dow™ MSA-1	none	0.29	3.06	3.35
	none[a]	0.48	2.82	3.30
	108	0.69	2.47	3.16
	199	1.02	1.97	2.99
	374	1.47	1.31	2.78
	551	1.89	0.57	2.46
	700	2.09	0.24	2.33
	839	2.15	0.02	2.17
	1050	1.91	0.00	1.91
Amberlite™ IRA-900	none	0.19	2.98	3.17
	none[a]	0.55	2.79	3.34
	104	0.82	2.36	3.29
	220	1.14	1.89	3.03
	367	1.60	1.15	2.75
	549	1.94	0.61	2.55
	727	2.21	0.22	2.43
	835	2.28	0.02	2.30
	1064	2.02	0.00	2.02
Lewatit™ MP-500-FK	none	0.37	3.39	3.76
	none[a]	0.45	3.32	3.77
	103	0.80	2.73	3.53
	198	1.09	2.18	3.27
	374	1.51	1.41	2.92
	543	1.83	0.63	2.46
	722	—[b]	—[b]	—[b]
	834	—[b]	—[b]	—[b]
	1040	—[b]	—[b]	—[b]
Reillex™ HPQ	none	1.49	2.29	3.78
	none[a]	1.91	1.85	3.76
	106	2.12	1.60	3.72
	202	2.56	1.16	3.72
	370	2.67	0.89	3.56
	559	2.99	0.44	3.43
	702	3.08	0.23	3.32
	822	3.18	0.18	3.36
	992	3.21	0.00	3.21

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[a] These unirradiated resins were stored in 7 M nitric acid for three months to isolate the effects of prolonged acid contact.

[b] The extensive radiolytic decomposition of Lewatit™ MP-500-FK at these exposure levels left insufficient surviving resin for measurements.

All capacities presented in Table IV are relative to postirradiated resin weight. Because a significant portion of every resin was destroyed by higher doses of gamma radiation, however, presentation of the exchange capacities relative to postirradiation resin weight can be misleading. Irradiated resin exchange capacities relative to their preirradiated resin weights, presented in Table V, are more relevant because these values represent the portions of the initial exchange capacity that remain after specified gamma exposures.

TABLE V. TOTAL EXCHANGE CAPACITIES OF GAMMA-IRRADIATED RESINS RELATIVE TO PREIRRADIATED WEIGHTS

Resin	Dose (Mrad)	Postirrad. Wt./ Preirrad. Wt.	Total Capacity (meq Cl/g)
Dowex^{TM} 1X4	none[a]	1.000	3.09
	104	0.996	2.91
	204	0.973	2.70
	367	0.937	2.18
	548	0.824	1.80
	723	0.796	1.58
	806	0.814	1.51
	1058	0.762	1.35
Dow^{TM} MSA-1	none[a]	1.000	3.30
	108	0.994	3.14
	199	0.952	2.85
	374	0.884	2.46
	551	0.750	1.85
	700	0.674	1.57
	839	0.641	1.39
	1050	0.483	0.92
Amberlite^{TM} IRA-900	none[a]	1.000	3.34
	104	0.992	3.26
	220	0.968	2.93
	367	0.933	2.57
	549	0.830	2.12
	727	0.753	1.83
	835	0.702	1.61
	1064	0.536	1.08
Lewatit^{TM} MP-500-FK	none[a]	1.000	3.77
	103	0.978	3.45
	198	0.881	2.88
	374	.710	2.07
	543	0.351	0.86
	722	0.059	—[b]
	834	—[b]	—[b]
	1040	—[b]	—[b]
Reillex^{TM} HPQ	none[a]	1.000	3.76
	106	0.997	3.71
	202	0.990	3.68
	370	0.997	3.55
	559	0.898	3.08
	702	0.842	2.98
	822	0.834	2.80
	992	0.683	2.19

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[a] These unirradiated resins were stored in 7 M nitric acid for three months to isolate the effects of prolonged acid contact.

[b] The extensive radiolytic decomposition of Lewatit^{TM} MP-500-FK at these exposure levels left insufficient surviving resin for measurements.

TABLE VI. SUMMARY OF TOTAL EXCHANGE CAPACITIES OF GAMMA-IRRADIATED RESINS RELATIVE TO PREIRRADIATED WEIGHTS

Nominal Exposure (Mrad)	Dowex™ 1X4 (meq Cl/g)	Dow™ MSA-1 (meq Cl/g)	Amberlite™ IRA-900 (meq Cl/g)	Lewatit™ MP-500-FK (meq Cl/g)	Reillex™ HPQ (meq Cl/g)
none	3.09	3.30	3.34	3.77	3.76
100	2.91	3.14	3.26	3.45	3.71
200	2.70	2.85	2.93	2.88	3.68
360	2.18	2.46	2.57	2.07	3.55
550	1.80	1.85	2.12	0.86	3.08
700	1.58	1.57	1.83	___[a]	2.98
820	1.51	1.39	1.61	___[a]	2.80
1000	1.35	0.92	1.08	___[a]	2.19

[a] The extensive radiolytic decomposition of Lewatit™ MP-500-FK at these exposure levels left insufficient surviving resin to measure the exchange capacity.

Of greatest interest in the data summarized in Table VI is the comparison between Lewatit™ MP-500-FK and Reillex™ HPQ because these two resins have been shown to offer reasonably comparable performance for processing plutonium.[9] Lewatit™ MP-500-FK previously was selected as the resin that offered the best performance for processing plutonium;[1] since the cited study, however, Reillex™ HPQ became available. The enhanced stability of Reillex™ HPQ to radiation, when compared to Lewatit™ MP-500-FK and all other resins, is readily apparent.

7. Pu(IV) Exchange Capacity. Although anion exchange resin capacities are typically based on chloride capacity measurements, chloride capacities may not accurately represent exchange capacities for the much larger anionic nitrato complex of Pu(IV).

We therefore measured the Pu(IV) saturation capacities from 7 M nitric acid of each unirradiated and gamma-irradiated resin. The ratio of liquid volume to resin weight was maintained at 50 during our contacts of the dry resins with Pu(IV) in 7 M nitric acid solution. The quantity of plutonium in solution was about twice the maximum that could be loaded (740 milligrams plutonium per gram dry resin) to ensure the saturation of each portion of resin. Dynamic mixing periods of 15 minutes, 1 hour, and 6 hours were achieved on a Labquake Tube Rotator that inverted each resin-solution mixture 16 times per minute.

An aliquot of solution was withdrawn after each contact period for assay by gamma spectrometry as previously described.[9] The quantity of plutonium sorbed on the resin was computed from the difference between the measured plutonium in solution before and after each contact period. Appropriate corrections for the changing liquid-to-resin ratio and the decreased quantity of plutonium in the system were applied after each aliquot was removed.

A comparison of Pu(IV) sorption on the five unirradiated resins, Fig. 5, demonstrates that Lewatit™ MP-500-FK resin (no longer manufactured) has the highest sorption capacity throughout the dynamic contact range of 15 minutes to 6 hours. Reillex™ HPQ has the next highest capacity for Pu(IV) during the 15-minute contact period, which simulates the residence time of feed solution as it passes through a plutonium recovery process. The excellent sorption kinetics of these two resins is the reason that their 1-hour capacities are nearly equal to their 6-hour capacities. The much poorer sorption kinetics of Amberlite™ IRA-900 and Dow™ MSA-1 resins results in 15-minute capacities of only about half those of the two highest resins; however, their 6-hour capacities exceed that of Reillex™ HPQ and might, after longer contact periods, even exceed that of Lewatit™ MP-500-FK resin. Dowex™ 1X4, the only gel-type resin studied, offers by far the lowest capacity and slowest sorption kinetics.

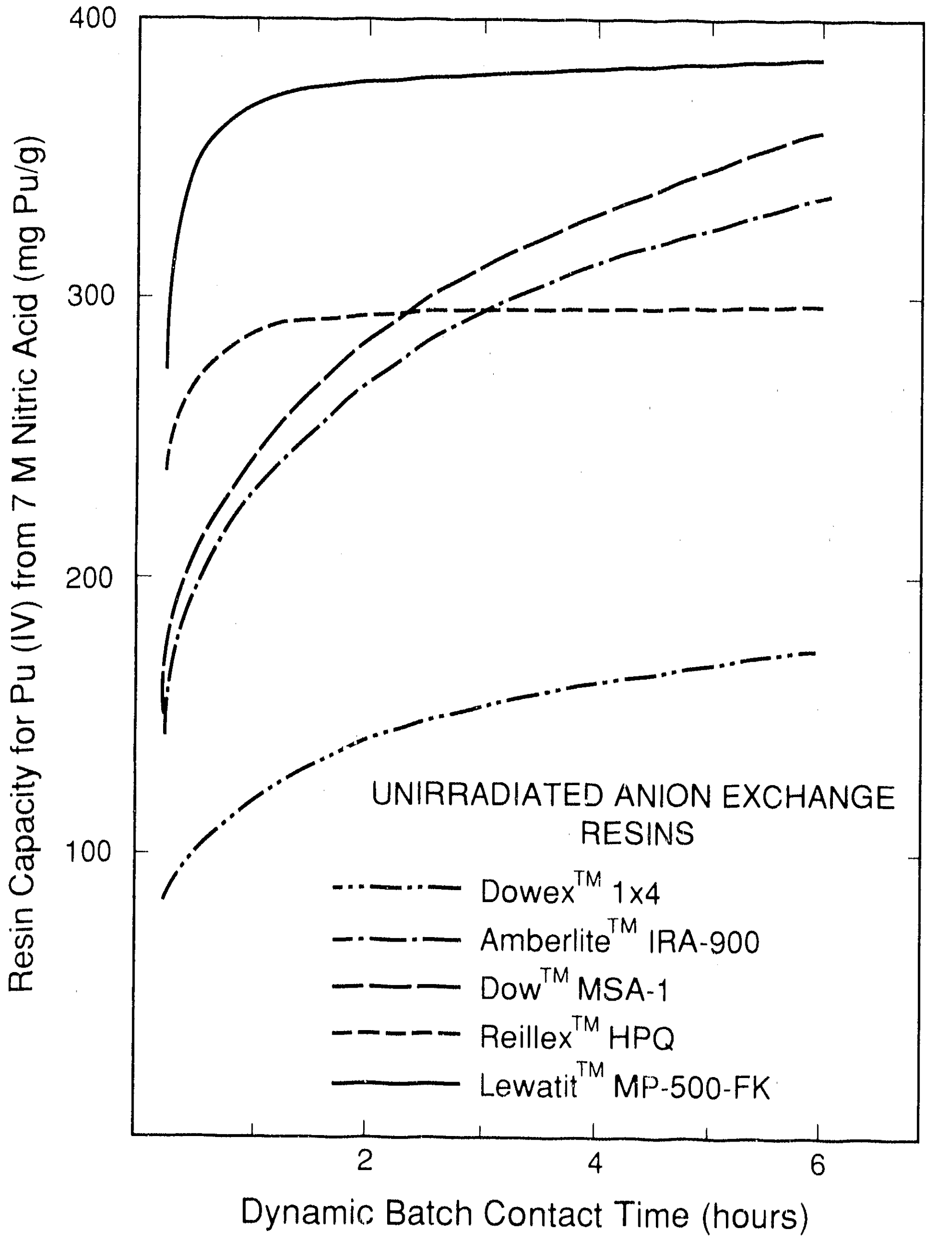

Fig. 5. Sorption of Pu(IV) onto five unirradiated anion exchange resins from 7 M nitric acid.

The sorption of Pu(IV) on these five resins after gamma irradiation, during a dynamic batch contact time of 15 minutes, is presented in Table VII. Note that these capacities are per gram of postirradiated dry resin. The 15-minute capacity of Reillex^{TM} HPQ resin is virtually unchanged after 550 megarads, whereas an equivalent dose has essentially destroyed the Lewatit^{TM} MP-500-FK resin and has drastically decreased the capacity of the other three resins. Readers are reminded that any attempt to directly compare sorption kinetics among various resins must also consider the differences in resin bead sizes (provided in the earlier Reagents and Apparatus section).

Comparing the Pu(IV) capacities of postirradiated dry resin weights, as in Table VII, ignores the substantial radiolytic weight losses experienced by some resins. Table VIII, however, incorporates the resin weight loss factors from Table III to provide the Pu(IV) capacities of preirradiated resins. These data permit us to estimate the capacity of a given quantity of anion exchange resin after it has absorbed a specified gamma dose.

TABLE VII. SORPTION OF Pu(IV) ON GAMMA-IRRADIATED RESINS FROM 7 M NITRIC ACID DURING 15-MINUTE DYNAMIC BATCH CONTACTS RELATIVE TO POSTIRRADIATED RESIN WEIGHTS

Nominal Exposure (Mrad)	Dowex^{TM} 1X4 (mg Pu/g)	Dow^{TM} MSA-1 (mg Pu/g)	Amberlite^{TM} IRA-900 (mg Pu/g)	Lewatit^{TM} MP-500-FK (mg Pu/g)	Reillex^{TM} HPQ (mg Pu/g)
none	85	150	143	273	237
100	80	147	143	240	220
200	77	150	130	220	230
360	73	123	100	193	223
550	45	77	90	___[a]	227
700	57	70	97	___[a]	150
820	47	43	77	___[a]	147
1000	50	37	23	___[a]	127

[a] The extensive radiolytic decomposition of Lewatit^{TM} MP-500-FK at these exposure levels left insufficient surviving resin to measure the exchange capacity.

TABLE VIII. SORPTION OF Pu(IV) ON GAMMA-IRRADIATED RESINS FROM 7 M NITRIC ACID DURING 15-MINUTE DYNAMIC BATCH CONTACTS RELATIVE TO PREIRRADIATED RESIN WEIGHTS

Nominal Exposure (Mrad)	Dowex^{TM} 1X4 (mg Pu/g)	Dow^{TM} MSA-1 (mg Pu/g)	Amberlite^{TM} IRA-900 (mg Pu/g)	Lewatit^{TM} MP-500-FK (mg Pu/g)	Reillex^{TM} HPQ (mg Pu/g)
none	85	150	143	273	237
100	80	146	142	234	219
200	75	143	120	194	228
360	68	109	93	137	222
550	37	58	75	___[a]	204
700	45	47	73	___[a]	126
820	38	28	54	___[a]	123
1000	38	18	12	___[a]	87

[a] The extensive radiolytic decomposition of Lewatit^{TM} MP-500-FK at these exposure levels left insufficient surviving resin to measure the exchange capacity.

The capacities of the five resins for Pu(IV) after an intermediate dynamic batch contact time of 1 hour are presented in Table IX. Again radiolytic decomposition is taken into account, and the capacities are presented per gram preirradiated dry resin. Note that for this contact period the capacity of Reillex^{TM} HPQ resin is virtually unchanged even after 550 megarads, whereas the capacities of the other four other resins are decreased to less than half.

Although the anionic nitrato complex of Pu(IV) is notoriously slow to equilibrate on anion exchange resin,[1] the longest dynamic batch contact times of 6 hours, shown in Table X, provide our best estimate of the Pu(IV) equilibrium saturation capacities for these resins. Although the absolute values differ, the general pattern for Pu(IV) capacities, again presented per gram of dry preirradiated resin, is quite similar to that observed after the 1-hour dynamic batch contacts.

TABLE IX. SORPTION OF Pu(IV) ON GAMMA-IRRADIATED RESINS FROM 7 M NITRIC ACID DURING 1-HOUR DYNAMIC BATCH CONTACTS RELATIVE TO PREIRRADIATED RESIN WEIGHTS

Nominal Exposure (Mrad)	Dowex$^{\text{TM}}$ 1X4 (mg Pu/g)	Dow$^{\text{TM}}$ MSA-1 (mg Pu/g)	Amberlite$^{\text{TM}}$ IRA-900 (mg Pu/g)	Lewatit$^{\text{TM}}$ MP-500-FK (mg Pu/g)	Reillex$^{\text{TM}}$ HPQ (mg Pu/g)
none	120	243	230	370	287
100	103	239	215	326	282
200	104	228	203	282	284
360	94	156	149	201	286
550	55	100	114	—[a]	272
700	50	83	103	—[a]	233
820	46	64	72	—[a]	189
1000	36	21	20	—[a]	137

[a] The extensive radiolytic decomposition of Lewatit$^{\text{TM}}$ MP-500-FK at these exposure levels left insufficient surviving resin to measure the exchange capacity.

TABLE X. SORPTION OF Pu(IV) ON GAMMA-IRRADIATED RESINS FROM 7 M NITRIC ACID DURING 6-HOUR DYNAMIC BATCH CONTACTS RELATIVE TO PREIRRADIATED RESIN WEIGHTS

Nominal Exposure (Mrad)	Dowex$^{\text{TM}}$ 1X4 (mg Pu/g)	Dow$^{\text{TM}}$ MSA-1 (mg Pu/g)	Amberlite$^{\text{TM}}$ IRA-900 (mg Pu/g)	Lewatit$^{\text{TM}}$ MP-500-FK (mg Pu/g)	Reillex$^{\text{TM}}$ HPQ (mg Pu/g)
none	174	360	337	387	297
100	149	345	320	352	292
200	156	330	300	308	297
360	134	248	245	218	299
550	91	175	185	—[a]	285
700	66	140	151	—[a]	253
820	65	111	114	—[a]	248
1000	48	34	31	—[a]	196

[a] The extensive radiolytic decomposition of Lewatit$^{\text{TM}}$ MP-500-FK at these exposure levels left insufficient surviving resin to measure the exchange capacity.

Finally, changes in the measured Pu(IV) capacity do not necessarily parallel the changes in total measured chloride capacity, nor should they. Therefore, the measured 6-hour saturation capacities presented in Table X were recomputed in terms of Pu(IV) capacity per total chloride capacity values obtained from Table VI. From these data, presented in Table XI, we can see that the relative capacities of the resins increase slightly with absorbed gamma dose and then decrease, with the exception of the Reillex$^{\text{TM}}$ HPQ capacities, which generally increase throughout the entire range.

TABLE XI. CAPACITIES OF GAMMA-IRRADIATED RESINS FOR Pu(IV) FROM 7 M NITRIC ACID DURING 6-HOUR DYNAMIC BATCH CONTACTS RELATIVE TO TOTAL CHLORIDE CAPACITIES

Nominal Exposure (Mrad)	Dowex^{TM} 1X4 (mg Pu/meq Cl)	Dow^{TM} MSA-1 (mg Pu/meq Cl)	Amberlite^{TM} IRA-900 (mg Pu/meq Cl)	Lewatit^{TM} MP-500-FK (mg Pu/meq Cl)	Reillex^{TM} HPQ (mg Pu/meq Cl)
none	56	109	101	103	79
100	51	110	98	102	79
200	58	116	102	107	81
360	61	101	95	105	84
550	51	95	87	—[a]	93
700	42	89	83	—[a]	85
820	43	80	71	—[a]	89
1000	36	37	29	—[a]	89

[a] The extensive radiolytic decomposition of Lewatit^{TM} MP-500-FK at these exposure levels left insufficient surviving resin to measure the exchange capacity.

8. Thermal Stability. Thermogravimetric analysis (TGA) was used to measure the thermal stability of each unirradiated and most gamma-irradiated resins. During these analyses all resins were dry and in the nitrate form, the sample chamber was sparged by 1.8 liters of moist air per hour, and the temperature was increased from 25 to 500°C at a uniform rate of 10°C per minute. Approximately 20 milligrams of each resin was heated in its unmodified postirradiated form, rather than being ground into powder as is often done before TGA. The decision to analyze intact resin beads may have caused excessive internal bead pressurization that, at times, resulted in the ejection of resin beads from the sample crucible during analysis. Intact beads, however, were intentionally analyzed to realistically simulate the behavior of dry resin that might become heated during solid waste disposal operations.

Although during these TGA measurements small quantities of dry, nitrate-form resins were heated to temperatures as high as 500°C, large quantities of resin should never be dried and heated. In his review of ion exchange system accidents, Miles[3] listed as his first precaution the need to avoid drying sizeable quantities of nitrate-form resin. Miles stated, "From the evidence available, the drying of ion exchange resins must be viewed as potentially very dangerous and unpredictable—an operation to be avoided without prior experimental work to ensure reliability of the results expected."

Therefore, TGA data should be viewed as a diagnostic tool that may contribute to a better understanding of radiation damage mechanisms and effects, not as a prediction of how resin will behave during normal operations. Any large-scale operation that allows nitrate-form resins to be dried and heated represents a flagrant safety violation that deserves the top ranking assigned to it by Miles.

Note that the TGA weight losses of irradiated resins do not and cannot reflect the significant radiolytic weight losses experienced by many resins during the irradiations. Thermogravimetric analyses, of necessity, were performed on the irradiated resin portions that survived the specified gamma doses.

Nearly all resins analyzed exhibited a gradual weight loss until about 180°C. The endothermic reaction of DTA traces confirmed that this weight decrease reflected only a loss of water. These weight losses were slightly more than 10% and agree well with the weight lost during overnight drying of the same resins at 105°C, as presented previously in Table III.

Figure 6 shows the thermal decomposition profiles of all five unirradiated resins. Reillex^{TM} HPQ resin loses approximately 25% of its weight below 250°C but thereafter loses less weight than any of the other four resins. Between 400 and 500°C, Lewatit^{TM} MP-500-FK and Amberlite^{TM} IRA-900 resins undergo significantly greater decomposition than the other three resins.

Presented in Figs 7 through 9 are the thermal decomposition profiles of all five resins gamma-irradiated to 200, 370 and 550 megarads, respectively.

In Fig. 7, the pattern is similar to that of the unirradiated resins, except that at temperatures above 400 C the decomposition of Dow^{TM} MSA-1 resin is greater and that of Lewatit^{TM} MP-500-FK resin is less.

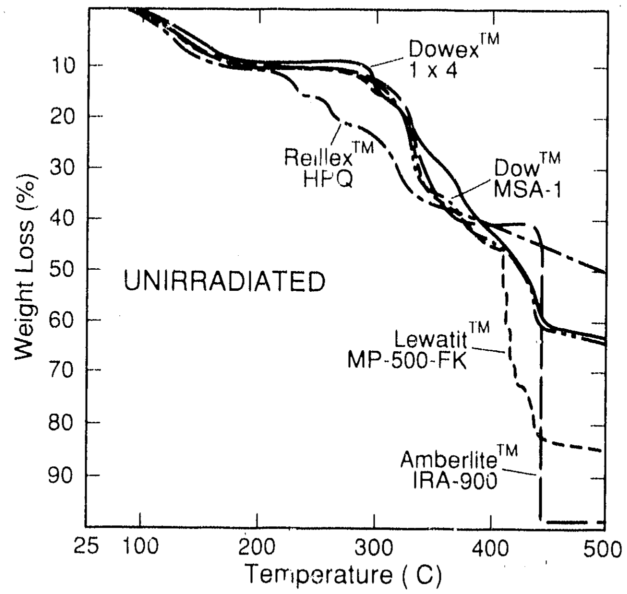

Fig. 6. Thermal decomposition profiles of five unirradiated anion exchange resins

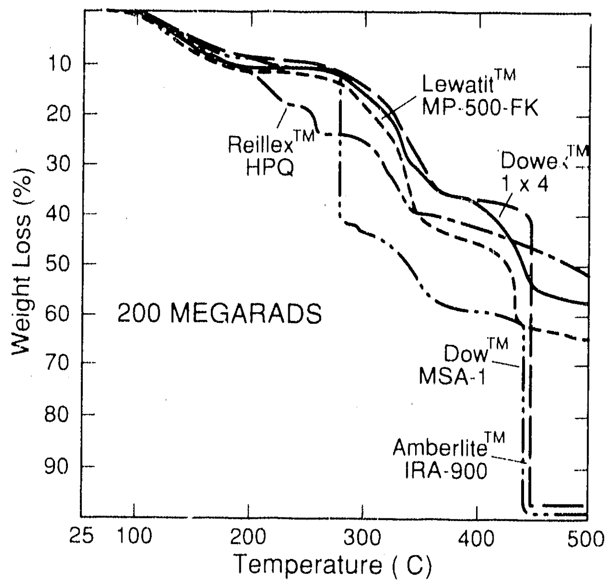

Fig. 7. Thermal decomposition profiles of five anion exchange resins after an absorbed gamma dose of 200 megarads.

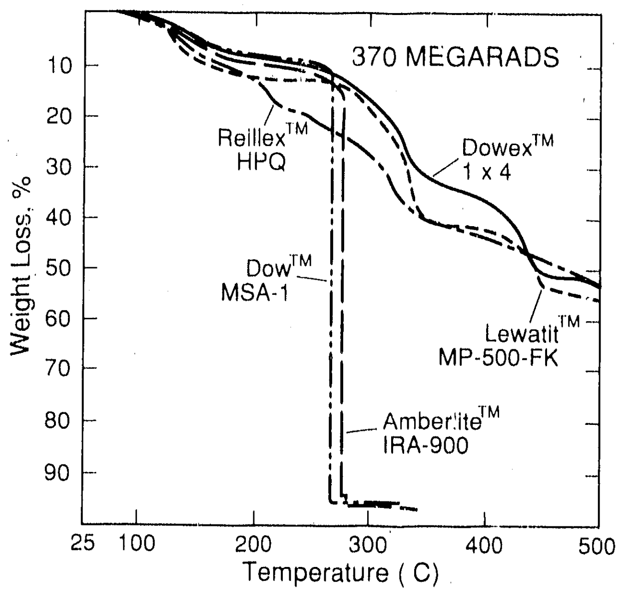

Fig. 8. Thermal decomposition profiles of five anion exchange resins after an absorbed gamma dose of 370 megarads.

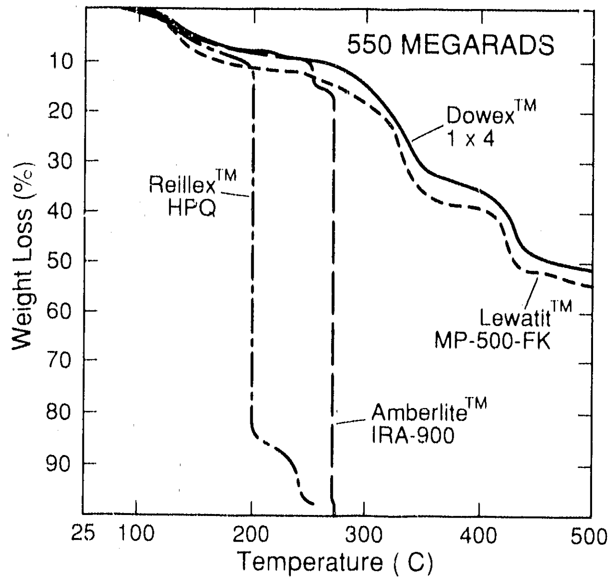

Fig. 9. Thermal decomposition profiles of four anion exchange resins after an absorbed gamma dose of 550 megarads.

Thermal decomposition profiles after exposures of 370 megarads, shown in Fig. 8, are similar to Fig. 7 for three resins; however, now Dow^{TM} MSA-1 and Amberlite^{TM} IRA-900 resins lose nearly all of their weight below 300°C, rather than near 450°C as they did after the lower exposure of 200 megarads.

After an absorbed gamma dose of 550 megarads (Fig. 9), Dowex^{TM} 1x4, Lewatit^{TM} MP-500-FK, and Amberlite^{TM} IRA-900 resins behave much as shown in Fig. 8. However, now Reillex^{TM} HPQ resin loses most of its weight just below 200°C.

Although the weight loss of Reillex^{TM} HPQ resin after an exposure of 550 megarads was rapid and large, simultaneous DTA traces showed only small exothermic reactions, as if the weight loss resulted from beads being ejected, rather than being decomposed within the sample crucible. Our suspicion was supported, after the heating cycle was completed, by the observation of intact resin beads outside the sample crucible. Nevertheless, the cited thermal instability was judged sufficient to warrant review. Because this behavior is known to occur after an absorbed dose higher than 370 megarads, but less than 550, we can state only that the threshold for such thermal instability is above 370 megarads.

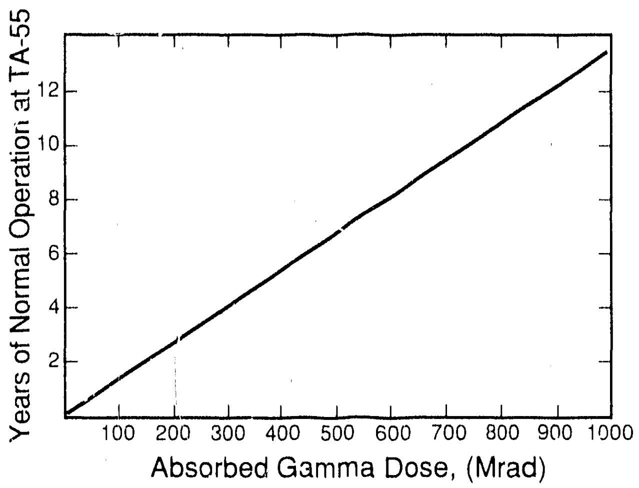

Fig. 10. Correspondence between absorbed gamma dose and years of normal operations at TA-55.

As shown in Fig. 10, an absorbed dose of 370 megarads corresponds to about 5 years of normal plutonium-processing operations at the Los Alamos Plutonium Facility (TA-55), which would indicate that the threshold for the observed thermal instability of Reillex$^{\text{TM}}$ HPQ resin could occur only after 5 years of routine operation at TA-55. (The Los Alamos Plutonium Facility, which operates a single shift five days per week and stores ion exchange columns in 1 M nitric acid between shifts, should not be used to estimate resin lifetime elsewhere.) Because resin damage from alpha particles is lower by at least a factor of two (see the following Alpha-Particle Irradiations section), however, the threshold for the cited thermal instability of Reillex$^{\text{TM}}$ HPQ resin actually corresponds to more than ten years of normal operations in the Los Alamos Plutonium Facility.

The combination of two factors—the improbability of resin becoming dried and heated during production operations and the required induction period of greater than 10 years at Los Alamos—virtually eliminates any possibility that thermal instability could occur in a production environment. Nevertheless, we recommend that Reillex$^{\text{TM}}$ HPQ resin be replaced after not more than 5 years of service, or 700 megarads of alpha-particle irradiation, or 400 megarads of absorbed gamma dose.

We also feel that the practice of disposing of spent, nitrate-form, organic resins as solid radioactive waste should be discontinued. Instead, appropriate safe procedures should be developed to dissolve or destroy such resin before its disposal to minimize the possibility of radiolytic gas production during storage.

B. Alpha-Particle Irradiations

1. Background. Gamma rays from external ^{60}Co sources provided the ionizing radiation for all resin/irradiation-level experiments thus far described, whereas resins used during actual plutonium processing operations are irradiated by *in situ* alpha particles.

The extensive compilation by Pillay[5] lists 288 studies wherein anion exchange resins were irradiated by a variety of external sources that included gamma rays, x-rays, accelerated electrons, or spent reactor fuel. It is notable that not one of these 288 studies, however, employed *in situ* alpha particles.

The preference of investigators for gamma irradiations is quite understandable because the absence of residual radioactivity in resins greatly facilitates subsequent measurement of resin properties. Nevertheless, any assumption that resin damage caused by external gamma irradiation realistically simulates that of *in situ* bombardment by alpha particles is unwarranted in the absence of experimental confirmation.

Kazanjian and Horrell[16] compared the effects of gamma rays and alpha particles on cation exchange resin and concluded that ion exchange sites were similarly affected by both, but that alpha particles did greater damage to the polymer matrix.

Paramonova and coworkers[17] evaluated the effect of alpha bombardment of sorbed plutonium on AV-23M anion exchange resin, a copolymer of 2-methyl-5-vinylpyridine cross-linked with 7% *tri*vinylbenzene. Although AV-23M resin differs from Reillex$^{\text{TM}}$ HPQ in the positions of both the methyl and vinyl groups on the pyridine ring and also in the cross-linking compound, the findings with AV-23M resin are nevertheless of interest. For example, AV-23M resin was reported to retain 91% of its initial capacity after 257 megarads of alpha radiation (the highest exposure of the cited study), whereas Reillex $^{\text{TM}}$ HPQ retained 94% of its initial capacity after 370 megarads of gamma radiation.

Although Paramonova and coworkers did not report resin weight loss, they calculated that 342 megarads of alpha irradiation (virtually identical to our alpha dose) caused a decrease in resin cross-linking from 7.0% to 3.3%. If our alpha-irradiated resins had experienced a comparable decrease in cross-linking, the wet resin volumes should have increased significantly, something not shown by our data in Table XII. Regardless of the cited superficial similarity in the decreased capacity values, major differences in the structures of AV-23M resin and Reillex$^{\text{TM}}$ HPQ resin invalidate any direct comparison.

The only direct comparison of the effects of gamma and alpha radiation on anion resin in nitric acid is that of Ahrens,[18] who compared his own alpha-irradiation results with earlier gamma-irradiation data of a different investigator.

Ahrens found that the loss of the strong-base capacity of Dowex™ 1x4 resin, which had been subjected to an absorbed dose of 100 megarads from alpha particles, was only 36% of the loss reported after a comparable gamma exposure. Likewise, the loss of total capacity for alpha-irradiated resin was only 46% of that reported for a comparable gamma dose.

Assuming an equal distribution of ^{238}Pu throughout the resin beads, Ahrens computed that the beads would absorb 84% of the total alpha energy. After accounting for the 65% volume increase of dry resin in 8 M nitric acid, Ahrens recalculated the alpha energy absorbed by the resin on a bulk volume basis. These calculations resulted in strong-base and total exchange capacity losses that were only 58% and 76%, respectively, of their gamma-irradiated counterparts. Thus, even after applying volume-correction factors, Ahrens's capacity losses for Dowex™ 1x4 resin from alpha irradiations remain much lower than those from equivalent gamma irradiations.

The only comparison of alpha- and gamma-irradiation experiments done by a single investigator was reported in a dissertation by Ahmed.[19] Although Ahmed studied sulfate-form resin, rather than nitrate-form resin, he found the capacity loss caused by gamma radiation to be between 2 and 2.5 times greater than that caused by a comparable exposure to alpha particles.

2. Experimental Details. In our limited alpha-irradiation investigation, each of the five resins was irradiated with alpha particles to approximately 340 megarads. A loading of 20 milligrams of plutonium (8.6% ^{238}Pu) per dry gram of resin was selected to produce a dose rate of approximately 400 kilorads per hour that closely matched the average dose-rate of our gamma irradiations.

Dose-rates and total absorbed doses for *in situ* alpha-particle irradiations from sorbed plutonium were based on accurately measured plutonium concentration and isotopic distribution. Values used for the total energy per disintegration (Q values) of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu were 567.57, 1.9288, 7.0824, 3.412, and 0.1159 milliwatts per gram, respectively.[20]

After the absence of significant amounts of Pu(VI) was spectrophotometrically verified, the appropriate quantity of plutonium was added as a 7 M nitric acid solution to each batch of resin, and the resin/solution slurries were thoroughly shaken to achieve uniform distribution of plutonium. The plutonium-loaded resins were then transferred to individual, small ion-exchange columns. Americium was eluted from each column with 3 milliliters of 7 M nitric acid per gram of resin after which a measured excess of 7 M nitric acid was added to prevent the resin from drying during the 5-week irradiation period.

3. Results. When the resins had absorbed a total dose of 340 megarads from these *in situ* alpha-particle irradiations, the volumes of the plutonium-loaded resins were measured in their nitric acid irradiation media. (Note that these conditions differed from those of the gamma-irradiated resins, which were free of sorbed metal ions during irradiation and all subsequent measurements.) Sorbed plutonium then was eluted with dilute nitric acid, each resin was washed thoroughly with water, and the resin volumes were measured in water. Finally, the eluted, water-washed resins were air-dried in the glove box, with the objective of continuing the air-drying until the resins reached constant weight.

After ten weeks of air-drying, the alpha-irradiated resins had not yet reached constant weight, although they were losing weight at an increasingly slower rate. Unfortunately, the weighings had to be discontinued after ten weeks. However, of greater importance than absolute dry-weight values is the unusually long time required for the alpha-irradiated resins to dry. By contrast, unirradiated and gamma-irradiated resins easily attained constant weight within one week.

Although weight losses from alpha-particle irradiations shown in the second column of Table XII are small, the largest weight loss is exhibited by Lewatit™ MP-500-FK resin, as was true for gamma irradiations. Also similar to gamma-irradiation results, Reillex™ HPQ resin showed the smallest weight loss (it actually showed a significant weight gain). The observed weight gain of Reillex™ HPQ resin may have resulted from scission of divinylbenzene, the cross-linking molecule, which would allow the resin to expand and equilibrate at a higher water content.

All alpha-irradiated resins except Dowex™ 1x4 occupied volumes in nitric acid and water that were virtually unchanged from those of the unirradiated resins, as presented in Tables I and II. This lack of resin swelling provides another indication that the alpha-induced resin damage was minimal.

The procedure used earlier to determine the exchange capacities of gamma-irradiated resins employed ethanol, a flammable organic solvent, to remove residual hydrochloric acid from the anion exchange resin columns. However, because the low flash point of ethanol precludes its use in a glove box, ethylene glycol was substituted as a completely miscible organic that offered an acceptably high flash point. All resin capacities presented in Table XIII were determined using this modification.

TABLE XII. RESIN WEIGHT LOSS AND VOLUME OF ALPHA-IRRADIATED RESINS IN NITRIC ACID AND WATER

Resin	Dose (Mrad)	Postirrad. Wt./ Preirrad. Wt.	Volume in Nitric Acid (cm^3/g)	Volume in Water (cm^3/g)
Dowex^{TM} 1X4	339	1.0035	1.90	2.20
Dow^{TM} MSA-1	338	0.9893	2.72	2.72
Amberlite^{TM} IRA-900	338	0.9947	2.70	2.64
Lewatit^{TM} MP-500-FK	340	0.9727	2.90	3.00
Reillex^{TM} HPQ	339	1.0449	2.90	2.86

TABLE XIII. WEAK-BASE AND STRONG-BASE EXCHANGE CAPACITIES OF ALPHA-IRRADIATED RESINS RELATIVE TO PREIRRADIATED RESIN WEIGHTS

Resin	Dose (Mrad)	Weak-base Capacity (meq Cl/g)	Strong-base Capacity (meq Cl/g)	Total Capacity (meq Cl/g)
Dowex^{TM} 1X4	339	1.20	1.73	2.93
Dow^{TM} MSA-1	338	0.97	2.18	3.15
Amberlite^{TM} IRA-900	338	1.16	2.09	3.25
Lewatit^{TM} MP-500-FK	340	0.86	2.60	3.46
Reillex^{TM} HPQ	339	2.12	1.51	3.63

Note that all five resins lost substantially less of the initial capacities than did their gamma-irradiated counterparts. A calibration line was prepared by fitting the measured strong-base capacities from our gamma irradiations vs absorbed dose to a least-squares line. Based on this linear relationship, the measured strong-base capacities of the alpha-irradiated resins were comparable to those of gamma-irradiated resins that had received two- to threefold lower absorbed doses. These differences agree well with the findings of Ahrens[18] and Ahmed.[19]

Several investigators[10,16,21,22] have proposed that most of the radiation damage to resin is caused by secondary reactions that involve nitrite or its reactive precursors. That explanation is supported by Kiseleva et al.,[23] who studied VP-1AP anion exchange resin, a 2-methyl-5-vinylpyridine/divinylbenzene copolymer (similar to Permutit^{TM} SK resin). VP-1AP resin irradiated in water lost no weight during an 1120-megarad exposure to accelerated electrons, whereas the same resin irradiated in 7 M nitric acid lost 36% of its initial weight. Moreover, Kiseleva reported the loss of exchange capacity to be more than four times greater for resin irradiated in nitric acid than for a similar irradiation in water. Nitric acid therefore plays a major role in the damage mechanism of VP-1AP resin and may have a similar role with other resins.

Furthermore, Kiseleva's reported value of 58% loss of the initial exchange capacity after 1120 megarads of absorbed dose in nitric acid compares reasonably well with our measured value of 42% capacity loss after a 992-megarad gamma irradiation of Reillex^{TM} HPQ, a related but slightly different vinylpyridine polymer.

If nitrite is the major cause of resin damage, we must account for not only the quantity of irradiated resin but also for the quantity of irradiated nitric acid. Therein lies a significant difference between our gamma- and alpha-irradiation experiments.

Both our gamma- and alpha-irradiation containers included a measured excess of nitric acid above the resin bed, as shown in Fig. 11, to ensure that the resin would not become dry during the irradiations. During the gamma irradiations, the resin and all acid present were exposed to the nearly uniform gamma dose. During *in situ* alpha irradiations, however, the very short range of alpha particles in solution limited the irradiation zone to less than 0.04 millimeters from the sorbed plutonium, which would include only the resin and immediately adjacent acid. The much smaller volume of nitric acid irradiated by *in situ* plutonium should have decreased the production of radiolytic nitrite and its reactive precursors.

Assuming that all of the interstitial nitric acid but none of the acid above the resin bed was irradiated during the alpha irradiations, we computed the relative volumes of nitric acid irradiated in these two systems to estimate the relative nitrite production. When these computed ratios were applied as correction factors to the gamma-irradiation results, the corrected values were within 1% for Dow^{TM} MSA-1, 14% high for Amberlite^{TM} IRA-900, 50% high for Dowex^{TM} 1x4, and 32% low for Lewatit^{TM} MP-500-FK and Reillex^{TM} HPQ.

Although the average for the five corrected values fortuitously provides good agreement between the alpha- and gamma-irradiation data, the large individual differences indicate that other significant factors may also exist. Therefore, these limited data from a single alpha-irradiation experiment for each type of resin are being augmented with additional higher-exposure, *in situ* alpha irradiations at Los Alamos. Until the results of that study are available, a factor of two should be applied to the gamma-irradiation data to estimate the alpha-irradiation dose that would be required to produce similar resin damage. Thus, the years of normal operations at TA-55 vs absorbed gamma dose shown in Fig. 10 should be doubled to estimate equivalent alpha-induced resin damage from sorbed plutonium.

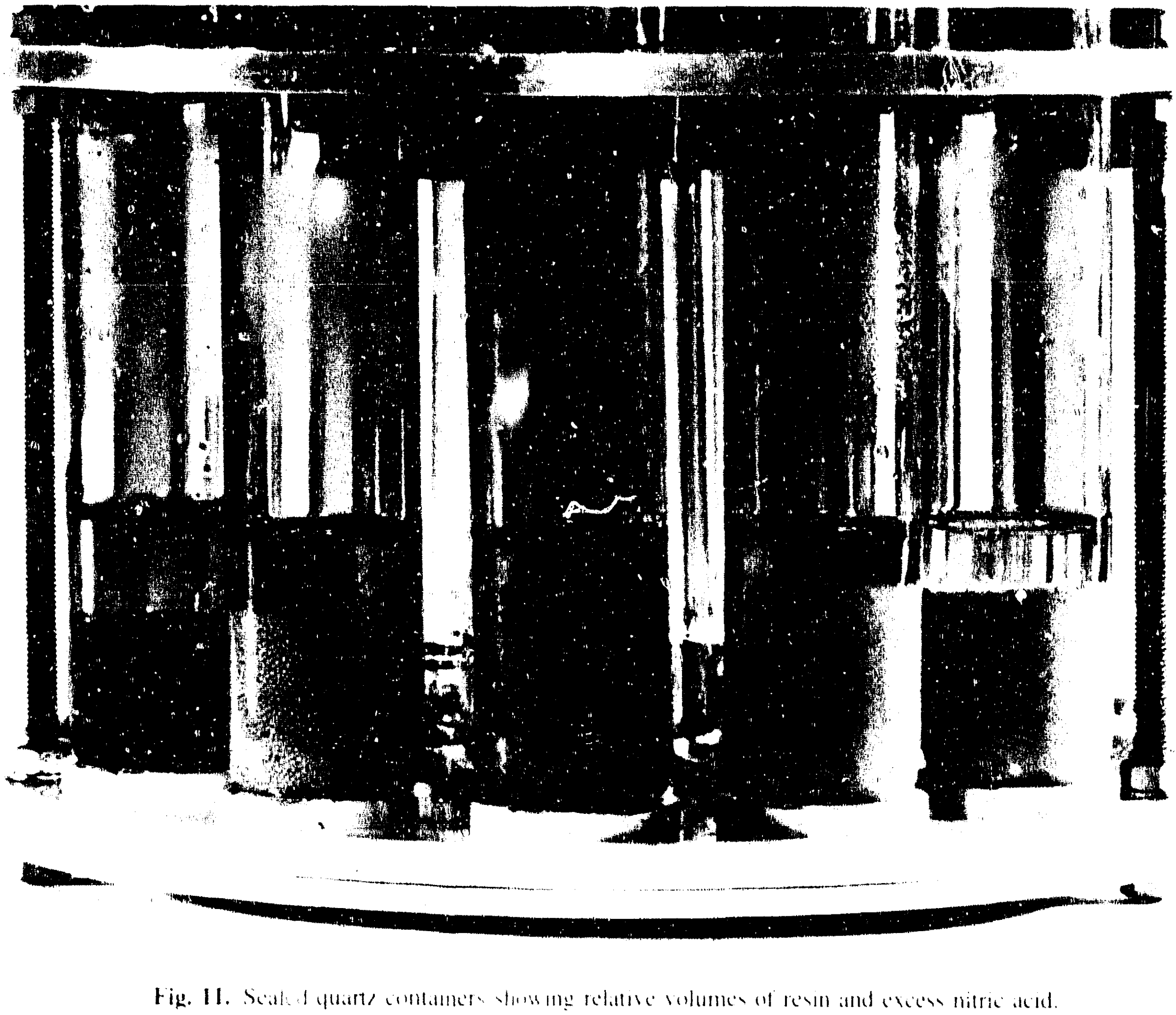

Fig. 11. Sealed quartz containers showing relative volumes of resin and excess nitric acid.

V. USEFUL FUTURE EXPERIMENTS

We are subjecting selected anion exchange resins to higher absorbed doses of *in situ* alpha particles from sorbed plutonium at Los Alamos to generate additional experimental data for alpha-induced resin damage.

The relative quantity of irradiated nitric acid may significantly contribute to resin damage because of secondary reactions. This possibility could be tested by gamma-irradiating a series of resins at differing nitric acid/resin ratios.

In separate experiments, a nonsorbed alpha emitter, such as ^{241}Am, could be employed to uniformly distribute the source of alpha particles throughout the nitric acid solution. The resulting resin damage could be compared to that from sorbed plutonium to provide a comparison of direct vs secondary radiolytic effects.

Additional experiments might clarify the effect of another significant difference in our gamma-ray and alpha-particle irradiations: anion exchange resins irradiated by gamma rays were free of metal ions, whereas alpha-irradiated resins were loaded with 20 milligrams of plutonium per gram resin. Sorbed Fe(III) or Cu(II),[24] and Cr(III) or UO_2(II)[25] have been shown to exert a protective influence on irradiated cation exchange resin. Plutonium, with its numerous stable oxidation states, might similarly interact with highly reactive radiolytic species to protect anion exchange resin. Conversely, the presence of plutonium ions might have the opposite effect and accelerate the destruction of anion exchange resin.

The effect of plutonium loaded on the resin could be determined by gamma-irradiating anion exchange resins on which ^{242}Pu is sorbed. The low specific activity of 3.76×10^5-year ^{242}Pu would contribute negligible exposure. If a sufficient quantity of isotopically enriched ^{242}Pu is not available, ^{237}Np, whose half life is greater than 2 million years, could be substituted to provide a reasonable approximation of plutonium chemical behavior during this experiment. The results could then be compared with those of gamma irradiations of metal-free anion exchange resins.

VI. CONCLUSIONS

1. Reillex™ HPQ polyvinylpyridine anion exchange resin retained more of its initial weight after gamma exposures (in 7 M nitric acid) of 100 to 820 megarads than any of the four polystyrene anion exchange resins studied.

2. Reillex™ HPQ retained more of its initial exchange capacity after gamma exposures (in 7 M nitric acid) of 100 to 1000 megarads than any of the four polystyrene anion exchange resins studied.

3. All five anion exchange resins experienced a conversion of strong-base exchange sites to weak-base exchange sites during gamma irradiations in 7 M nitric acid.

4. Reillex™ HPQ resin that had been gamma-irradiated to exposures as high as 370 megarads exhibited the best thermal stability of the five resins. However, Reillex™ HPQ resin subjected to 550 megarads or more displayed the poorest thermal stability, abruptly losing weight at approximately 185°C. Although the safe level of 370 megarads corresponds to more than ten years of *in situ* alpha exposure during normal operations at Los Alamos, we recommend that this resin be replaced at least every five years.

Thermogravimetric analysis, which involves heating dry, nitrate-form resin to temperatures as high as 500°C, in no way resembles process operating conditions; nevertheless, we recommend that absorbed gamma doses of Reillex™ HPQ resin be limited to 400 megarads of gamma radiation for maximum safety. We further recommend that appropriate safe processes be developed to dissolve or decompose spent, nitrate-form resins before their disposal to eliminate the possibility of gas-producing interactions between the nitrate and organic polymers during storage.

5. Irradiation damage caused by alpha particles is two- to threefold lower than that caused by comparable exposures to gamma radiation. We attribute this difference to the larger volume of nitric acid irradiated by gamma rays. This larger volume produces proportionately more nitrite and nitro radicals that may cause much of the resin damage through secondary reactions.

6. The capacities for Pu(IV) of anion exchange resins that were gamma-irradiated in 7 M nitric acid generally increase, relative to measured total chloride capacities, before they decrease. This increased capacity may be due to scissioning of cross-linking bonds, conversion of strong-base exchange sites to weak-base sites, or both. It may be related to the increased performance often observed for a new resin as it is conditioned by several months of operation with actinides in a nitric acid medium.

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