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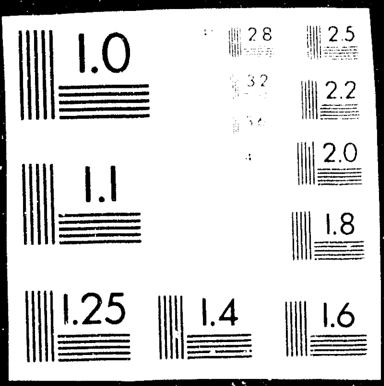

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TITLE: THE COMPARATIVE EFFECTS OF GAMMA RADIATION AND IN SITU ALPHA PARTICLES ON FIVE STRONG-BASE ANION EXCHANGE RESINS

AUTHOR(S): S. Fredric Marsh, Group NMT-2

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THE COMPARATIVE EFFECTS OF EXTERNAL GAMMA RADIATION AND IN SITU ALPHA PARTICLES ON FIVE STRONG-BASE ANION EXCHANGE RESINS

S. FREDRIC MARSH*
Nuclear Materials Process Technology Group,
Mail Stop E501, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, USA

ABSTRACT

The effects of external gamma radiation and *in situ* alpha particles were measured on a recently available, macroporous, strong-base polyvinylpyridine resin and on four strong-base polystyrene anion exchange resins. Each resin was irradiated in 7 M nitric acid to 1-10 megaGray of gamma radiation from external ^{60}Co, or to 5-14 megaGray of alpha particles from sorbed ^{238}Pu. Each irradiated resin was measured for changes in dry weight, wet volume, weak-base and strong-base chloride exchange capacities, and exchange capacities for Pu(IV) from nitric acid. Alpha-induced resin damage was significantly less than that caused by an equivalent dose of gamma radiation. The polyvinylpyridine resin offers the greatest resistance to damage from gamma radiation and from alpha particles.

INTRODUCTION

Anion exchange in nitric acid is the major aqueous process used to recover and purify plutonium from a variety of impure nuclear materials. Although this system is quite selective for Pu(IV), the sorption kinetics for Pu(IV) are particularly slow.(1)

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* The gamma-irradiation portion of this investigation was done at Harwell Laboratory, Oxfordshire, UK, during the year the author was attached to the Chemistry Division as a Visiting Scientist.

The Plutonium Facility at Los Alamos National Laboratory has an ongoing program whose objective is to develop anion exchange resins that provide improved sorption kinetics and increased safety for processing Pu(IV) in nitric acid. The best anion exchange resin previously available, in terms of performance, chemical resistance and radiation stability, was Permutit^{TM} SK, a vinylpyridine polymer.

Because Permutit^{TM} SK is no longer manufactured, we initiated a collaborative effort with Reilly Industries, Inc., Indianapolis, IN, to develop a related polyvinylpyridine resin. The resulting new resin, Reillex^{TM} HPQ, is a macroporous copolymer of 1-methyl-4-vinylpyridine and divinylbenzene. Its monomeric structure is compared with that of conventional polystyrene resin in Fig. 1.

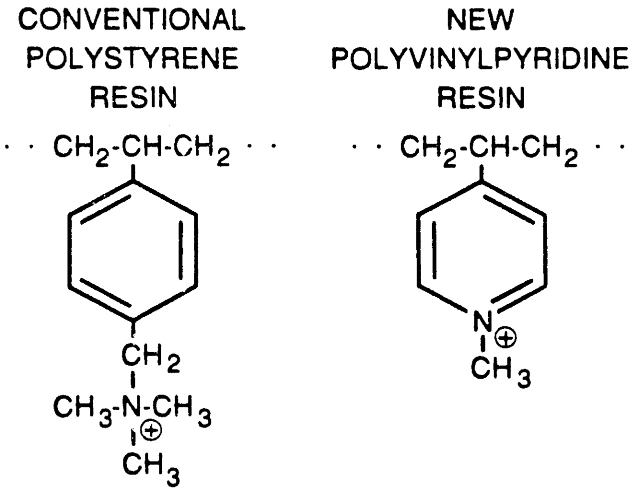

Fig. 1. Comparative structures of conventional polystyrene and new polyvinylpyridine resin.

We first evaluated the performance and chemical resistance of Reillex^{TM} HPQ.(2) Next, we measured the effects of external gamma radiation on this resin and four polystyrene resins: Dowex^{TM} 1x4, a gel-type resin; and three macroporous resins: Dow^{TM} MSA-1, Amberlite^{TM} IRA-900, and Lewatit^{TM} MP-500-FK.(3) Finally, we measured the effects of *in situ* alpha particles on the five cited resin and on one other resin, Lewatit^{TM} UMP-950.

EXPERIMENTAL

Effects of Nitric Acid

Vinylpyridine resins are expected be more resistant than polystyrene resins to attack by nitric acid because polystyrene is susceptible to electrophilic aromatic substitution, whereas the electronegativity of nitrogen in the pyridine ring makes polyvinylpyridine highly resistant to such substitution.

To evaluate the chemical resistance of Reillex^{TM} HPQ resin under worst-case conditions, we subjected a portion of this resin to boiling concentrated nitric acid, under reflux, for 3 hours. A slight amount of NO_2 was the only indication of any reaction. Although the wet resin volume increased by about 10%, the weight of the treated, air-dried resin was nearly identical to the initial, untreated resin weight.

Because the resin damage appeared to have been minor, we next compared the capacities for Pu(IV) from 7 M nitric acid, as a function of contact time, for treated and untreated resin. These measurements demonstrated that, not only was there no loss in capacity for the acid-boiled Reillex^{TM} HPQ resin, its capacity was approximately 20% higher!(3)

Reillex^{TM} HPQ resin consists of 1-methyl-4-vinylpyridine cross-linked with approximately 30% divinylbenzene (DVB). The most vulnerable portion of the polymer therefore would be the DVB crosslinking groups. Oxidative cleavage of DVB during nitric acid refluxing would relax the resin network structure by lowering the crosslinking density and allow the resin beads to expand. Such resin swelling, in accord with the observed increase in wet resin volume, would make the deeply buried exchange sites more accessible and thus explain the increased resin capacity and faster sorption kinetics.

Effects of Radiation

Because Reillex^{TM} HPQ resin also was expected to be more resistant to radiolytic degradation, we tested the radiation stability of Reillex^{TM} HPQ and various other anion exchange resins previously used to process plutonium.

Each resin was irradiated in 7 M nitric acid (the plutonium-processing medium) to total absorbed doses of 1-10 megaGray of external gamma radiation from ^{60}Co, or to 5-14 megaGray of *in situ* alpha particles from sorbed ^{238}Pu. All irradiated resins were measured for changes in dry weight, wet volume, chloride exchange capacity, and Pu(IV) capacity.

Irradiated resin weight loss data for gamma and alpha irradiations are presented in Tables I and II. (Lewatit^{TM} MP-500-FK is absent at the highest gamma doses in Table I because this resin was almost completely destroyed at these levels.) Note that all resins survived alpha-particle irradiation (Table II) better than gamma radiation, and that 97% of the initial weight of Reillex^{TM} HPQ resin survived even the highest alpha dose of 14.3 MGray.

TABLE I. Resin Weight Loss from Gamma Irradiations (postirradiated wt./preirradiated wt.)

Nominal Exposure	Dowex^{TM} 1x4	Dow^{TM} MSA-1	Amberlite^{TM} IRA-900	Lewatit^{TM} MP-500-FK	Reillex^{TM} HPQ
None	1.000	1.000	1.000	1.000	1.000
1.0 MGray	0.996	0.994	0.992	0.978	0.997
2.0 MGray	0.973	0.952	0.968	0.881	0.990
3.6 MGray	0.937	0.884	0.933	0.710	0.997
5.5 MGray	0.824	0.750	0.830	0.351	0.898
7.0 MGray	0.796	0.674	0.753	0.059	0.842
8.2 MGray	0.814	0.641	0.702	---	0.834
10.0 MGray	0.762	0.483	0.536	---	0.683

TABLE II. Resin Weight Loss from Alpha-Particle Irradiations (postirradiated wt./preirradiated wt.)

Nominal Exposure	Dowex^{TM} 1x4	Dow^{TM} MSA-1	Amberlite^{TM} IRA-900	Lewatit^{TM} MP-500-FK	Reillex^{TM} HPQ	Lewatit^{TM} UMP-950
None	1.000	1.000	1.000	1.000	1.000	1.000
4.9 MGray	0.958	0.964	0.953	0.902	0.992	0.929
8.2 MGray	0.931	0.920	0.937	0.838	0.995	0.875
11.1 MGray	0.898	0.890	0.905	0.770	0.992	0.832
14.3 MGray	0.880	0.835	0.871	0.680	0.970	0.771

Capacities of these same resins for Pu(IV) from 7 M nitric acid during a 15-minute dynamic contact are presented in Tables III and IV. These Pu(IV) capacity data IV confirm that the resin damage caused by alpha particles is significantly less than that caused by a comparable dose of gamma radiation.

TABLE III. Sorption of Pu(IV) on Gamma-Irradiated Resins from 7 M Nitric Acid During 15-Minute Dynamic Batch Contacts (mg Pu per gram preirradiated resin)

Nominal Exposure	Dowex^{TM} 1x4	Dow^{TM} MSA-1	Amberlite^{TM} IRA-900	Lewatit^{TM} MP-500-FK	Reillex^{TM} HPQ
None	85	150	143	273	237
1.0 MGray	80	146	142	234	219
2.0 MGray	75	143	120	194	228
3.6 MGray	68	109	93	137	222
5.5 MGray	37	58	75	--	204
7.0 MGray	45	47	73	--	126
8.2 MGray	38	28	54	--	123
10.0 MGray	38	18	12	--	87

TABLE IV. Sorption of Pu(IV) on Alpha-Irradiated Resins from 7 M Nitric Acid During 15-Minute Dynamic Batch Contacts (mg Pu per gram preirradiated resin)

Nominal Exposure	Dowex™ 1x4	Dow™ MSA-1	Amberlite™ IRA-900	Lewatit™ MP-500-FK	Reillex™ HPQ	Lewatit™ UMP-950
None	85	150	143	273	237	210
4.9 MGray	52	120	103	220	210	168
8.2 MGray	50	123	89	216	208	148
11.1 MGray	43	95	93	174	193	130
14.3 MGray	35	54	64	153	212	107

Both our gamma- and alpha-irradiation containers included a measured excess of nitric acid above the resin. Alpha particles, whose range in solution is only about 30 microns, would interact with only a very small volume of nitric acid, whereas gamma rays from external ^{60}Co would irradiate the entire volume of nitric acid present.

It therefore appears that much of the resin damage is caused by secondary reactions between the resin and radiolysis products of nitric acid. That fact that more resin damage occurs during gamma irradiations is consistent with the larger quantities of nitric acid radiolyzed by gamma rays.

A previous Soviet study(5) showed that otherwise identical irradiation of polyvinylpyridine resin immersed in water or 7 M nitric acid resulted in dramatic differences in resin damage. Their data, shown in Table V, support our contention that the radiolysis products of nitric acid play a major role in the resin damage mechanisms.

TABLE V. Results of Related Soviet Study(5)

Irradiation Medium	Resin Weight Loss	Resin Capacity Loss
Vacuum	0	7.1%
Water	0	13.7%
7 M HNO_3	35.8%	58.0%

(Nitrate-form polyvinylpyridine resin irradiated to 11.2 MGray with accelerated electrons in all cases.)

CONCLUSIONS

1. Strong-base exchange sites are radiolytically converted to weak-base sites by either gamma rays or alpha particles.(3,4)

2. Alpha particles cause less resin damage than does an equivalent dose of gamma radiation. This is attributed to secondary reactions involving highly reactive radiolysis products of nitric acid.

3. Reillex^{TM} HPQ resin consistently retained more of its initial weight and more of its initial exchange capacity than any of the other resins evaluated. Reillex^{TM} HPQ resin also offers greater resistance to attack by nitric acid.(2)

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