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REILLEX™ HEQ: A NEW, MACROPOREOUS POLYMERIZATION MEDIA FOR SEPARATING COPOLYMER USING NITRATE ANION EXCHANGE

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# REILLEX™ HPQ: A NEW, MACROPOROUS POLYVINYLPYRIDINE RESIN FOR SEPARATING PLUTONIUM USING NITRATE ANION EXCHANGE

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## ABSTRACT

Anion exchange in nitric acid is the major aqueous process used to recover and purify plutonium from impure scrap materials. Most strong-base anion exchange resins incorporate a styrene-divinylbenzene copolymer. A newly available, macroporous anion exchange resin based on a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene has been evaluated. Comparative data for Pu(IV) sorption kinetics and capacity are presented for this new resin and two other commonly used anion exchange resins. The new resin offers high capacity and rapid sorption kinetics for Pu(IV) from nitric acid, as well as greater stability to chemical and radiolytic degradation.

## INTRODUCTION

Anion exchange in nitric acid is the major aqueous process used to recover and purify plutonium from impure scrap materials at the Los Alamos Plutonium Facility. Data from an early study by Faris and Buchanan, Fig. 1(1), show why this system is nearly ideal for processing

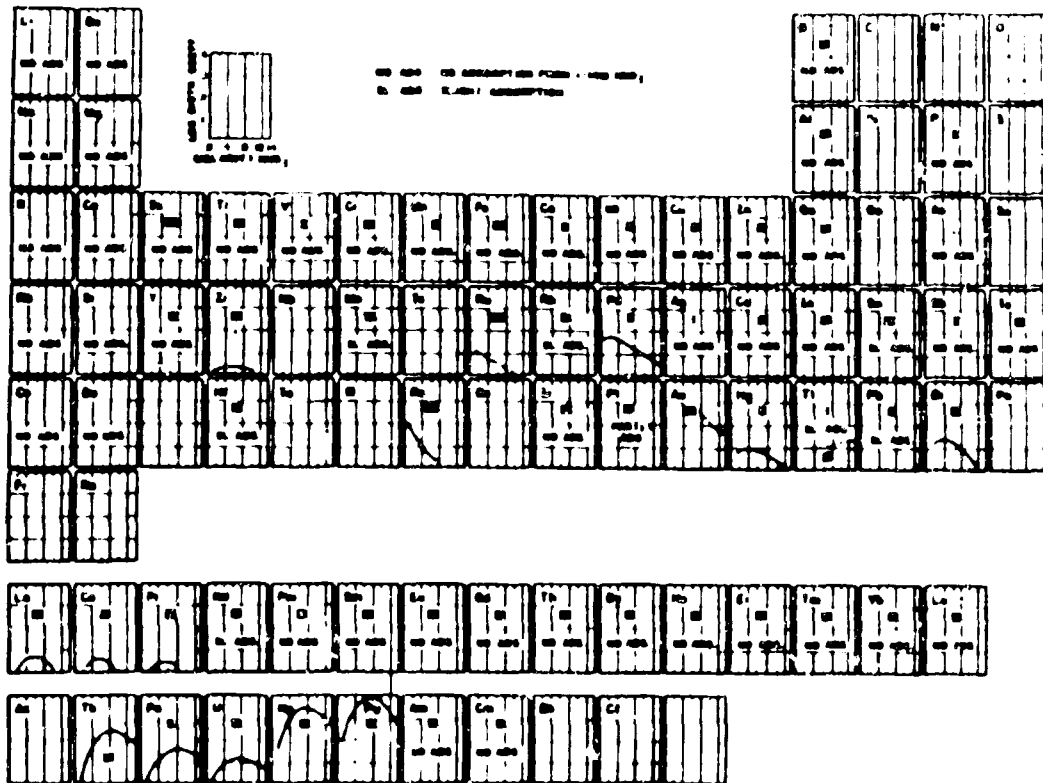


FIGURE 1. Distribution of elements from nitric acid onto strong-base anion exchange resin.(1)

plutonium; no metal ion is more strongly sorbed than Pu(IV), and few other ions show even moderate sorption from nitric acid.

One of the few disadvantages of the nitrate anion exchange system is the particularly slow rate at which the anionic Pu(IV) nitrate complex equilibrates with the resin. As part of an earlier Los Alamos effort to improve the slow kinetics that limit this process, more than 30 commercial and experimental anion exchange resins were evaluated. That study(2) identified resin porosity and bead size as the two properties that most influence plutonium sorption kinetics. Based on these findings, gel-type Dowex™ 1x4 resin previously used at Los Alamos was replaced with macroporous Lewatit™ MP-500-FK resin, which resulted in a dramatic improvement in process efficiency.(3)

Nearly 30 years ago, Permutit™ SK, a gel-type resin no longer produced, was reported to offer better sorption and desorption kinetics(4) and capacity(5) for plutonium than other resins available at that time

Permutit™ SK consisted of poly-2-methyl-5-vinylpyridine, rather than the polystyrene used for Dowex™, Lewatit™, and most other strong-base anion exchange resins. In addition to the reported performance benefits of Permutit™ SK, polyvinylpyridine anion exchange resins have been reported to offer greatly increased stability to chemical attack(6) and radiolytic degradation.(7)

This expectation of increased safety and performance led us to actively seek a new commercial source of macroporous polyvinylpyridine anion exchange resin. Subsequent interaction between Los Alamos National Laboratory and Reilly Industries, Inc., a manufacturer of vinylpyridine polymers, has resulted in a new, macroporous anion exchange resin that consists of a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene.

A comparison of the chemical structures of this new polyvinylpyridine resin, designated as Reillex™ HPQ, and conventional polystyrene resin is shown in Fig. 2. In both structures a quaternized nitrogen is the anion exchange site. In polystyrene resin, the quaternary ammonium group attaches

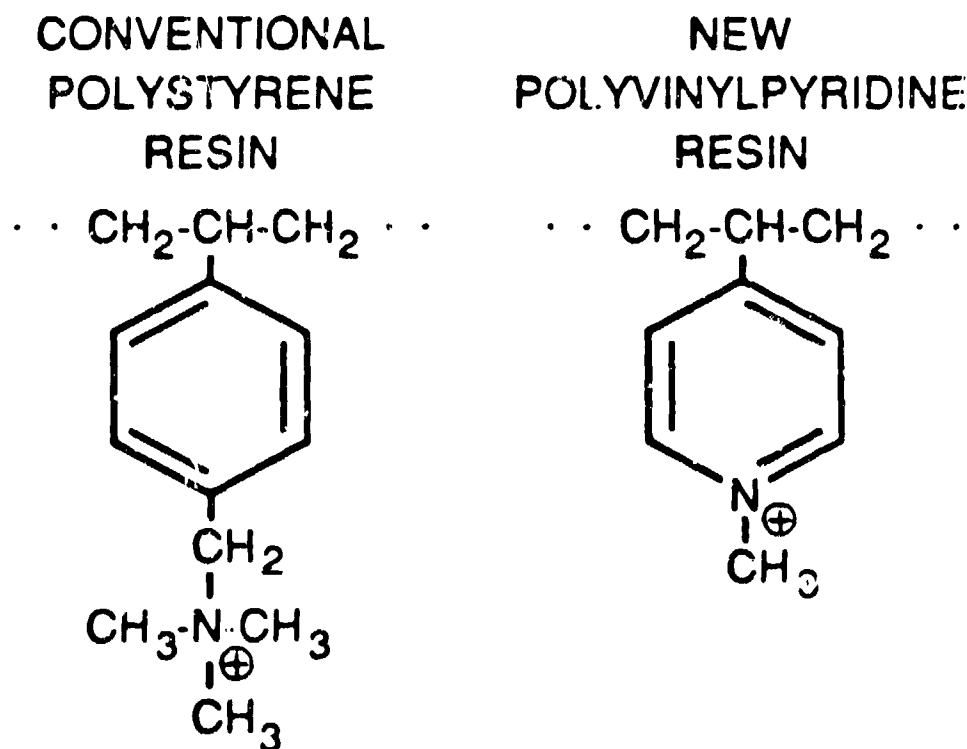


FIGURE 2. Comparative structures of conventional polystyrene resin and new polyvinylpyridine resin.

to the benzene ring, whereas polyvinylpyridine resin is quaternized by addition of a methyl group to the nitrogen in the pyridine ring.

Our initial small-scale evaluations of Reillex™ HPQ resin show that it provides Pu(IV) sorption kinetics comparable or superior to that obtained with Lewatit™ MP-500-FK resin, the best polystyrene resin we had previously identified.(2) This resin also offers persuasive safety advantages. Production-scale testing is currently under way using Reillex™ HPQ resin in one of our full-scale ion exchange systems.

### REAGENTS

Reagent-grade nitric acid was diluted as needed using deionized water that had a resistivity of at least 17 megohms.

Dowex™ 1x4 gel-type, strong-base anion exchange resin, 50 to 100 mesh, was obtained from Dow Chemical Company, Midland, Michigan. (A 50 to 60 mesh fraction, separated by dry-screening, was used in this study.)

Lewatit™ MP-500-FK macroporous, strong-base anion exchange resin, 40 to 70 mesh, was obtained from Mobay Chemical Corp., Pittsburgh, Pennsylvania. (A 50 to 60 mesh fraction, separated by dry-screening, was used in this study.)

Reillex™ HPQ macroporous, polyvinylpyridine anion exchange resin, 30 to 60 mesh, was obtained from Reilly Industries, Inc., Indianapolis, Indiana. (A 50 to 60 mesh fraction, separated by dry-screening, was used in this study.) Specific properties of this new resin, as supplied by the manufacturer, are:

Chloride exchange capacity = 0.85 moles per liter (in water)

Total exchange capacity in acid = 1.34 moles per liter (in water)

Surface area = 75 square meters per gram

Functional groups quaternized = 63%

## EXPERIMENTAL

### Resin Form Conversion

As specified above, only 63% of the pyridine rings are quaternized by the addition of a methyl group. However, the unquaternized nitrogen atoms in the pyridine rings readily acquire a proton in acid solution. In either case, a positive anion-exchange site results.

A two-step process was therefore used to convert the as-received, chloride-form Reillex™ HPQ resin to the desired nitrate form. Most of the chloride ions were first displaced by passing two resin-bed volumes of 0.7 M aluminum nitrate solution through the resin-containing column. This was followed by four resin-bed volumes of 2 M nitric acid to complete the displacement of chloride and also to protonate any unquaternized pyridine rings.

It is essential that the resin bed be given adequate free space within the column for expansion during this conversion, and also that both solutions are passed through in an upflow direction to keep the resin suspended during the expected volume increase of ~ 11%.

### Assay Technique

Small-scale dynamic contacts between resin and plutonium solutions of specified compositions were effected for designated contact periods on a wrist-action shaker. Measured portions of aqueous solution were removed after each contact period for gamma spectrometric assay. The 129-keV gamma-ray peak of Pu-239 was measured in all aqueous portions, both before and after contact with the resin. The difference between these two measurements represented the quantity of plutonium sorbed on the resin. A more detailed description of the experimental assay technique is presented elsewhere.(2)

### Computation of Distribution Coefficients

Distribution coefficient (Kd) values were calculated to represent the concentration of plutonium per milliliter of wet resin (nitrate-form in water) divided by the concentration of plutonium per milliliter of solution. This differs from the common practice of calculating Kd values from the

weight of dry resin, rather than the volume of wet resin. We feel that resin volume is a more useful parameter because process columns contain a given volume of wet resin, rather than a measured dry weight. For readers who prefer to work with values calculated from dry resin weight, those  $K_d$  values are higher than ours by approximately a factor of 3.

## RESULTS AND DISCUSSION

### Sorption Kinetics

Distribution coefficients for Pu(IV) were measured as a function of dynamic contact time for various resin loadings. As expected, measured  $K_d$  values decrease as the quantity of plutonium per volume resin increases, as seen in Fig. 3. (A solution-to-resin volume ratio of 10 was used for these

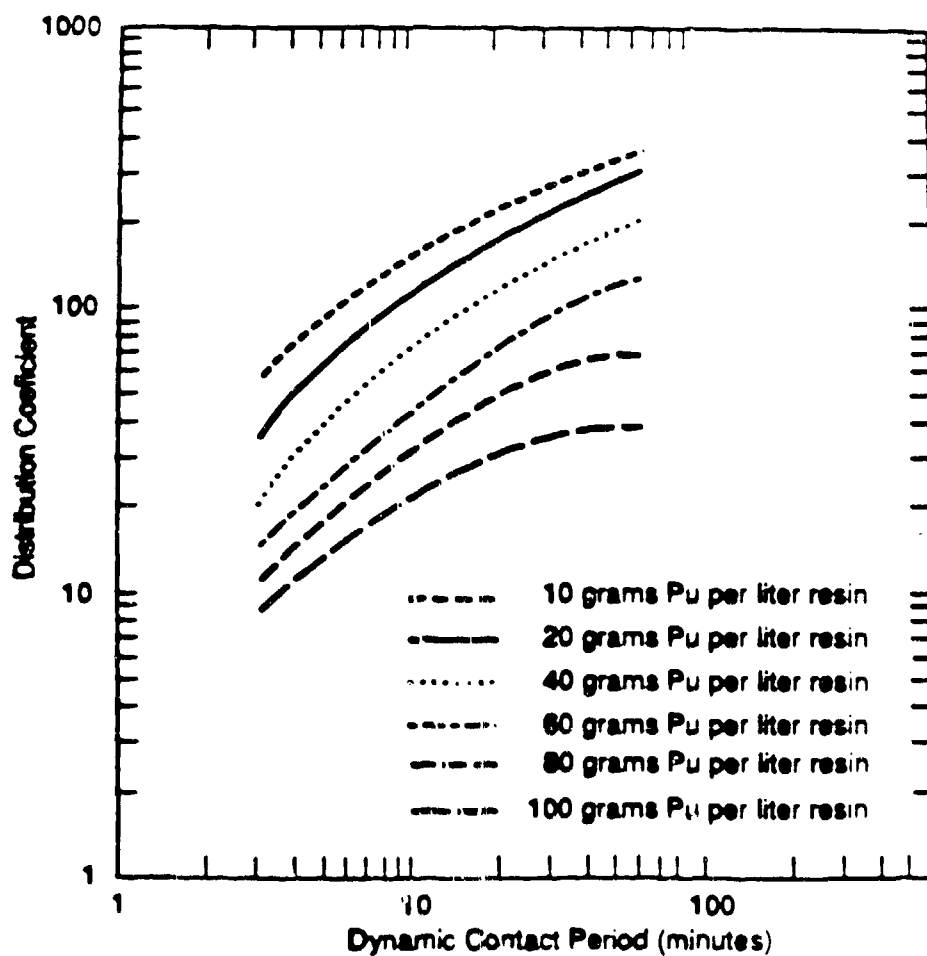


FIGURE 3. Sorption of Pu(IV) on Reillex™ HPQ anion exchange resin from 7 M nitric acid as a function of plutonium loading.



experiments. The concentration of plutonium in each experiment was therefore 1/10 of the specified plutonium quantity. For example, a plutonium solution concentration of 10 grams per liter was used for the experiment that resulted in 100 grams of plutonium loading per liter resin.)

The observed faster kinetics for lower resin loading levels is attributed to the rapid sorption of small quantities of Pu(IV) by highly accessible ion exchange sites on or near the surface of the resin beads. As the quantity of plutonium increases, the competition for exchange sites also increases. This competitive process requires Pu(IV) ions to migrate progressively deeper within the resin bead to find available exchange sites, a significantly slower process than when ions exchange only at sites on or near the surface.

Comparisons of Kd curves for different resins are therefore valid only when quantities of plutonium per resin volume are identical. Accordingly, we have measured and reported the sorption kinetics of Pu(IV) from 7 M nitric acid on Reillex™ HPQ, Lewatit™ MP-500-FK, and Dowex™ 1x4 resins only under such equivalent plutonium-loading conditions. The effect of resin bead size differences was eliminated by using dry-screened, 50 to 60 mesh resin in all cases.

#### Resistance to Nitric Acid

Most conventional strong-base anion exchange resins incorporate a polymer of styrene and divinylbenzene. Because these 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 systems have been addressed by Calmon.(8) Avoiding conditions that could result in violent reactions between organic polymers and nitric acid obviously is given an especially high priority within the nuclear industry.

Vinylpyridine polymers are known to be unusually resistant to attack by nitric acid. Marston(6) attributes the difference in reactivity of polystyrene and polyvinylpyridine to the fact that polystyrene is especially susceptible to electrophilic aromatic substitution, whereas the electron deficiency of the aromatic system makes polyvinylpyridine quite resistant to such substitution.

Polyvinylpyridine resins are therefore expected to be significantly safer than polystyrene resins; however, caution is always encouraged when one combines organic polymers and nitric acid. In the specific case of Reillex™ HPQ resin, only about 70% of the polymer is vinylpyridine; the remaining 30% is divinylbenzene, whose chemical stability is considerably lower.

Conspicuous on Calmon's list of the potentially most dangerous conditions involving resin and nitric acid are high concentrations of nitric acid and high temperatures.(8) To evaluate the new resin under worst-case conditions, we intentionally violated both of these safety precautions by subjecting a portion of nitrate-form Reillex™ HPQ resin to boiling, concentrated nitric acid, under reflux, for 3 hours. Although a small amount of NO<sub>2</sub> was observed during this period, there was no indication of any vigorous reaction. The weight of the post-treatment, air-dried resin agreed closely with the initial weight of air-dried resin, which was additional evidence that no significant resin decomposition had occurred.

Although refluxing the resin in concentrated nitric acid caused the initially white Reillex™ HPQ resin to acquire a slight yellow color, there was no significant change in the surface appearance, even at 10,000X. Moreover, thermal decomposition profiles of acid-refluxed and untreated Reillex™ HPQ resin (both air-dried in nitrate form), as determined by thermogravimetric analysis in an argon atmosphere, were found to be nearly identical (Fig. 4).

These similar thermal decomposition profiles for treated and untreated Reillex™ HPQ resin further confirm the absence of significant resin alteration by the treatment. A thermal decomposition profile of Lewatit™ MP-500-FK resin also was measured and is included in Fig. 4. The initial decomposition of Reillex™ resin at a lower temperature than Lewatit™ resin was unexpected, although there is no reason to expect thermal decomposition of resin in a dry argon atmosphere to simulate its reactivity in aqueous nitric acid.

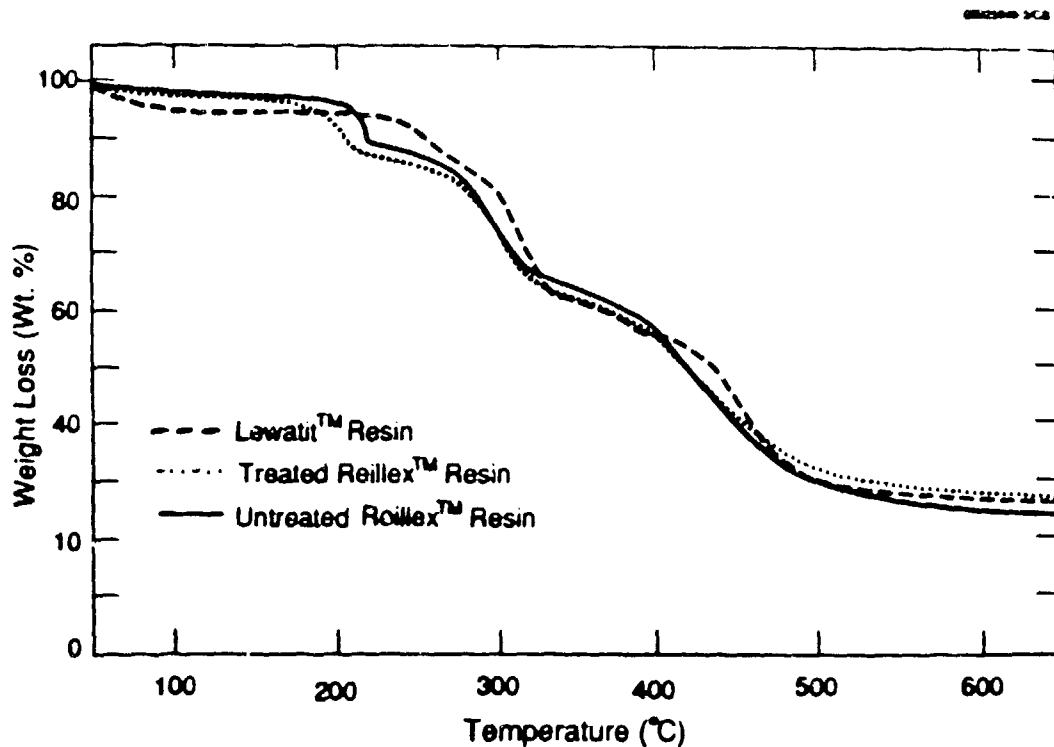


FIGURE 4. Thermal decomposition profiles of (1) nitric acid-refluxed Reillex™, (2) untreated nitrate-form Reillex™ HPQ resins, and (3) nitrate-form Lewatit™ MP-500-FK resin.

#### Resin Capacity.

To further determine whether resin refluxed in nitric acid had survived without significant damage, the capacity of treated resin for Pu(IV) from 7 M nitric acid was measured. Capacities were experimentally determined from batch contacts, in which the Pu(IV) quantity of 182 grams per liter of resin exceeded the total resin capacity. The rate at which the resin loaded also was determined in these experiments by assaying the solution for nonsorbed plutonium after dynamic contact periods of 0.5, 1, 3, 5, and 8 hours.

Figure 5 shows the measured capacities of Dowex™ 1x4, Lewatit™ MP-500-FK, and Reillex™ HPQ resin before and after the refluxing nitric acid treatment. Not only was there no loss in capacity of the treated resin for Pu(IV) from nitric acid, relative to untreated resin, there was a substantial increase!

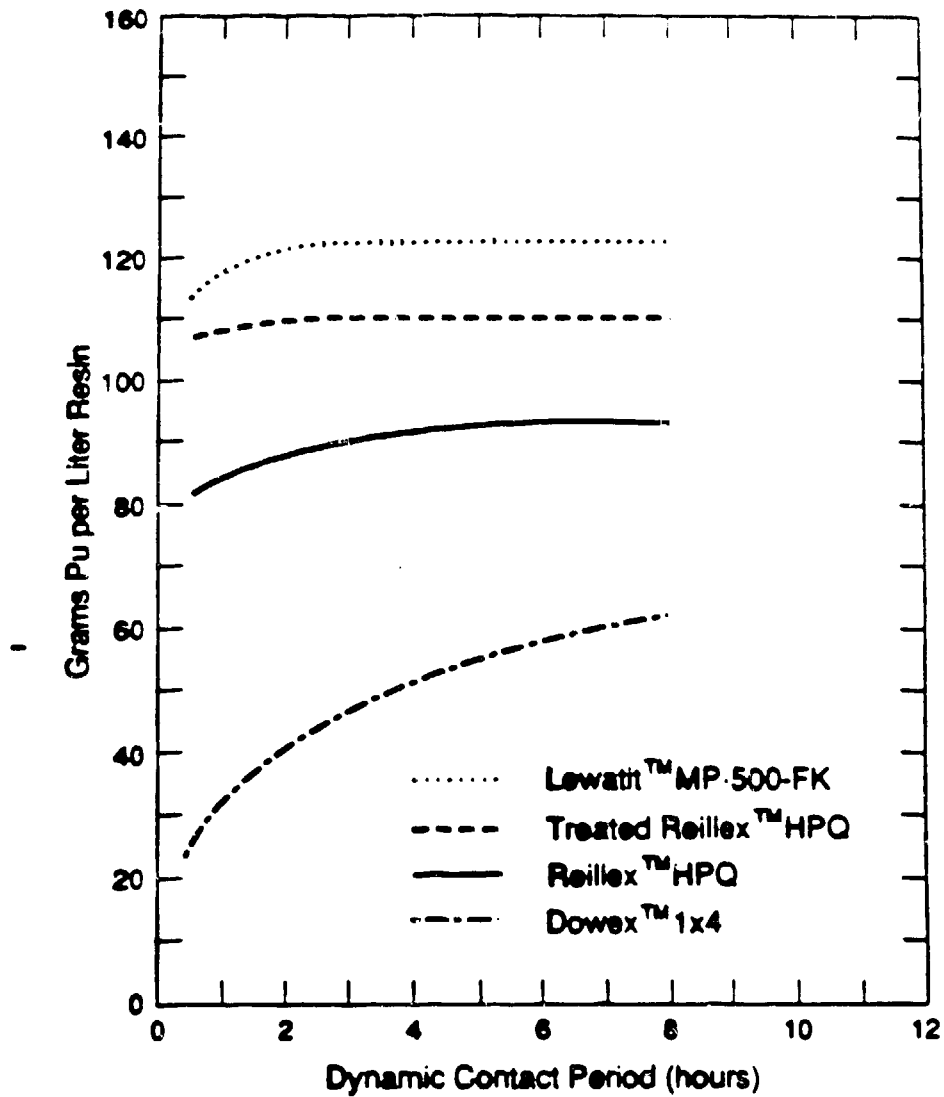


FIGURE 5. Measured capacities of various anion exchange resins for Pu(IV) from 7 M nitric acid.

Because this increase in resin capacity was unexpected, we repeated the Pu(IV) sorption kinetics studies using resin that had been refluxed in concentrated nitric acid. Figures 6 through 11 present comparative distribution coefficients of Pu(IV) from 7 M nitric acid on Dowex™ 1x4, Lewatit™ MP-500-FK, and treated and untreated Reillex™ HPQ for total plutonium loadings of 10, 20, 40, 60, 80, and 100 grams per liter resin, respectively.

At each of these six levels of plutonium loading, the treated resin exhibits equivalent or faster sorption kinetics for Pu(IV) than was obtained with untreated resin. Furthermore, in almost every case the sorption kinetics of Pu(IV) on treated Reillex™ HPQ resin is superior to the kinetics of the other three resins tested. This is particularly significant because Lewatit™ MP-500-FK resin was found to offer the fastest kinetics of more than 30 resins evaluated in a previous study.(2)

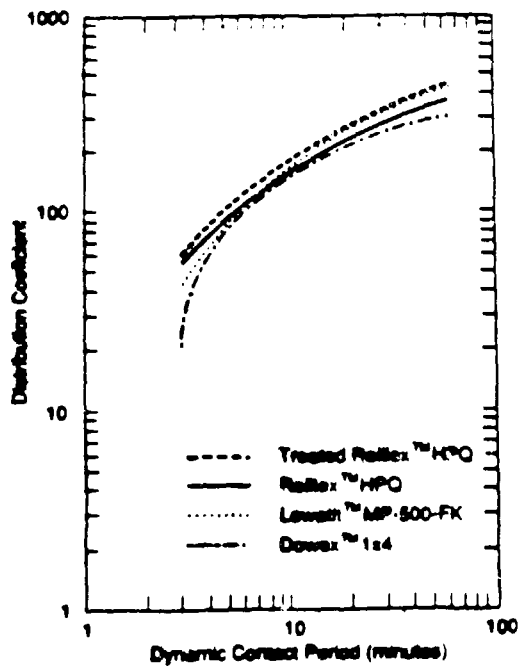


FIGURE 6. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 10 grams per liter resin).

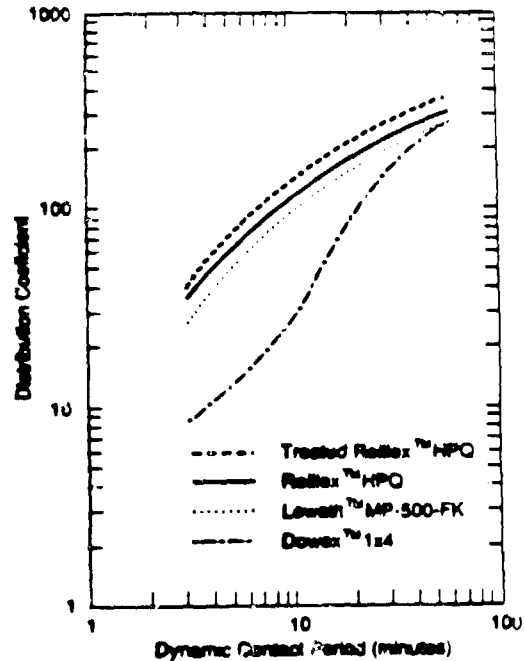


FIGURE 7. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 20 grams per liter resin).

#### Explanation for Improved Performance

The unexpected improvement in resin capacity and sorption kinetics was discussed with Charles Marston, the senior research chemist who developed this resin in collaboration with Donald McQuigg at Reilly Industries, Inc. Marston suggested that refluxing HPQ resin in concentrated nitric acid could cause oxidative cleavage of some alkyl aromatic cross-linking groups, as evidenced by the production of NO<sub>2</sub>. Cleavage of some of the divinylbenzene cross-linking groups would relax the resin network structure by lowering the cross-linking density and allow the resin beads to expand.

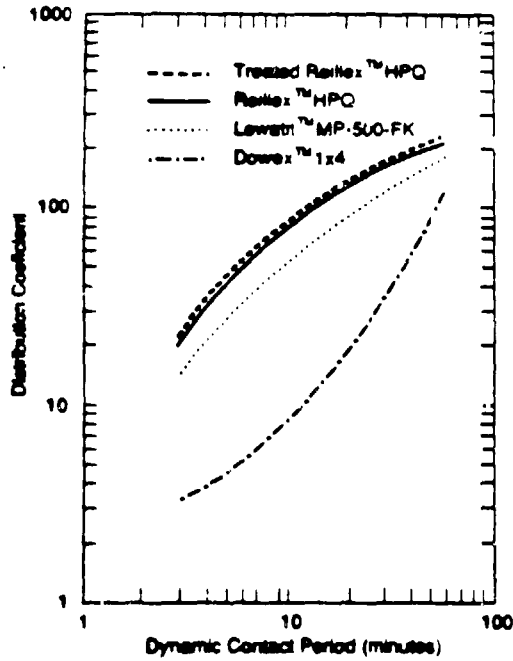


FIGURE 8. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 40 grams per liter resin).

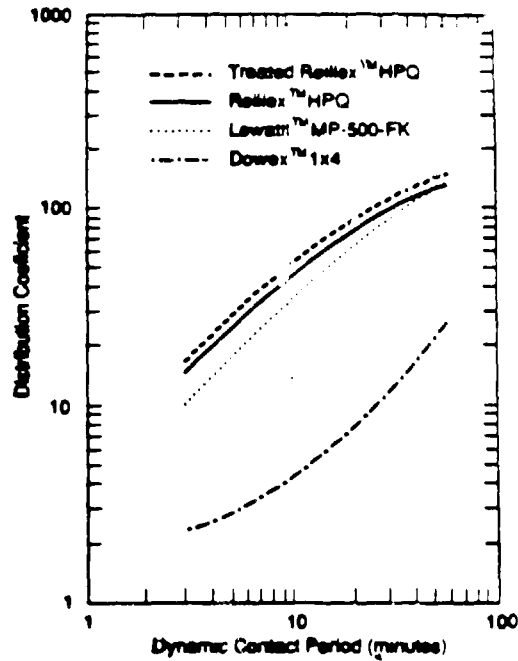


FIGURE 9. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 60 grams per liter resin).

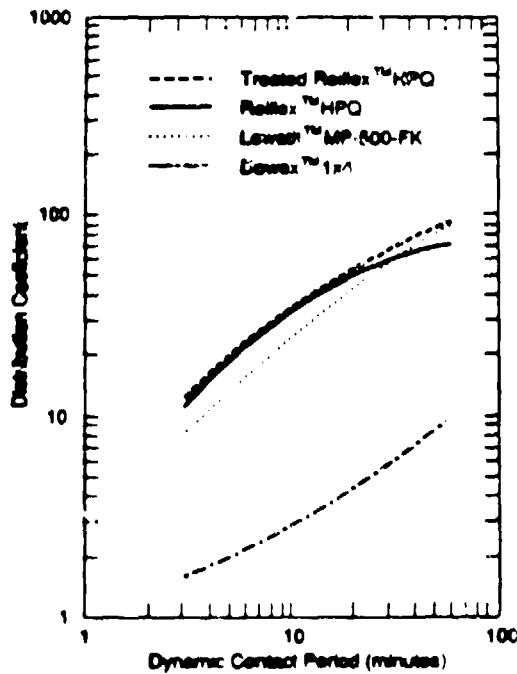


FIGURE 10. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 80 grams per liter resin).

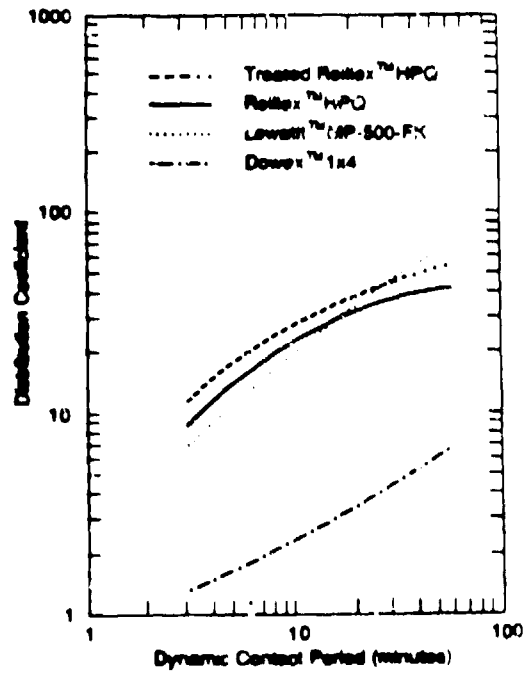


FIGURE 11. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 100 grams per liter resin).

This explanation is in accord with an observed increase in wet resin volume of approximately 10%. The more open structure of expanded beads should make interior anion exchange sites more accessible, which would explain the increased resin capacity and improved sorption kinetics.

### Elution Kinetics

Because Reillex™ HPQ resin exhibits Pu(IV) sorption kinetics comparable or superior to that of Lewatit™ MP-500-FK, we also compared the elution of Pu(IV) from these two resins using dilute nitric acid as the eluant. In all cases, 1-milliliter portions of resin were tested in columns of 7-millimeter diameter, using gravity flow for loading and elution.

Figure 12 presents Pu(IV) elution profiles from Reillex™ resin using eluants of 0.35, 0.40, 0.45, 0.50, and 0.60 M nitric acid. The elution profile

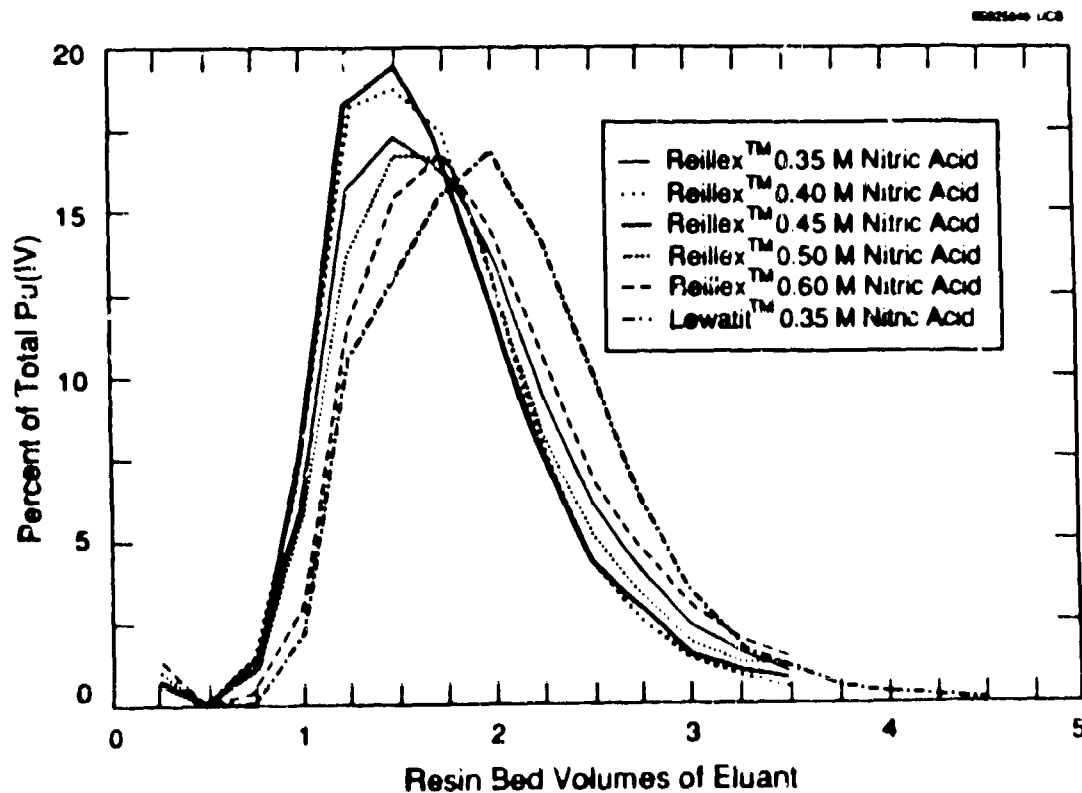


FIGURE 12. Comparison of Pu(IV) elution profiles from Reillex™ HPQ resin using eluants of 0.35, 0.40, 0.45, 0.50, 0.55, and 0.60 M nitric acid, and from Lewatit™ MP-500-FK resin using only an eluant of 0.35 M nitric acid.

of Lewatit™ resin using only 0.35 M nitric acid is presented for comparison. Note that the elution is consistently sharper and more complete in a smaller volume with Reillex™ resin, even when higher concentrations of nitric acid are used as the eluant. This indicates that the purified plutonium product can be recovered at higher concentration in a smaller volume from Reillex™ resin. The improved elution is particularly significant because elution of Pu(IV) with dilute nitric acid is much faster from Lewatit™ resin than from any other resin previously tested.

#### Radiolytic Degradation

Another major safety advantage expected from Reillex™ HPQ resin is increased resistance to radiolytic degradation. According to Gangwer et al.,(7) "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." Our near-term plans include a comparison of the radiolytic stability of Reillex™ HPQ resin with several other macroporous and gel-type polystyrene resins commonly used in the nuclear industry.

#### SUMMARY

A newly available, macroporous anion exchange resin based on a copolymer of 1-methyl-4-vinylpyridine and divinylbenzene has been evaluated. This new resin offers high capacity and rapid sorption kinetics for Pu(IV) from nitric acid, as well as greater resistance to chemical attack by nitric acid. Significantly greater resistance to radiolytic degradation also is expected, based on published studies of similar polyvinylpyridine resins.



## ACKNOWLEDGMENTS

The author gratefully acknowledges the outstanding technical contributions of Charles R. Marston, Donald McQuigg (the original developer of the Reillex<sup>TM</sup> family of polymers), and Richard D. Johnston, all of Reilly Industries, Inc., as well as the exceptional cooperation of Reilly Industries, Inc.\* The collaboration between Reilly and Los Alamos represents a model for effective interaction between our national laboratories and private industry.

The author also is grateful to Anthony C. Muscatello for his assistance during the elution experiments, and to Larry R. Avens for thermogravimetric analyses of various anion exchange resins.

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\* Reilly Industries, Inc., 1500 S. Tibbs Avenue, Indianapolis, IN 40241, was formerly known as Reilly Tar & Chemical Corp.

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