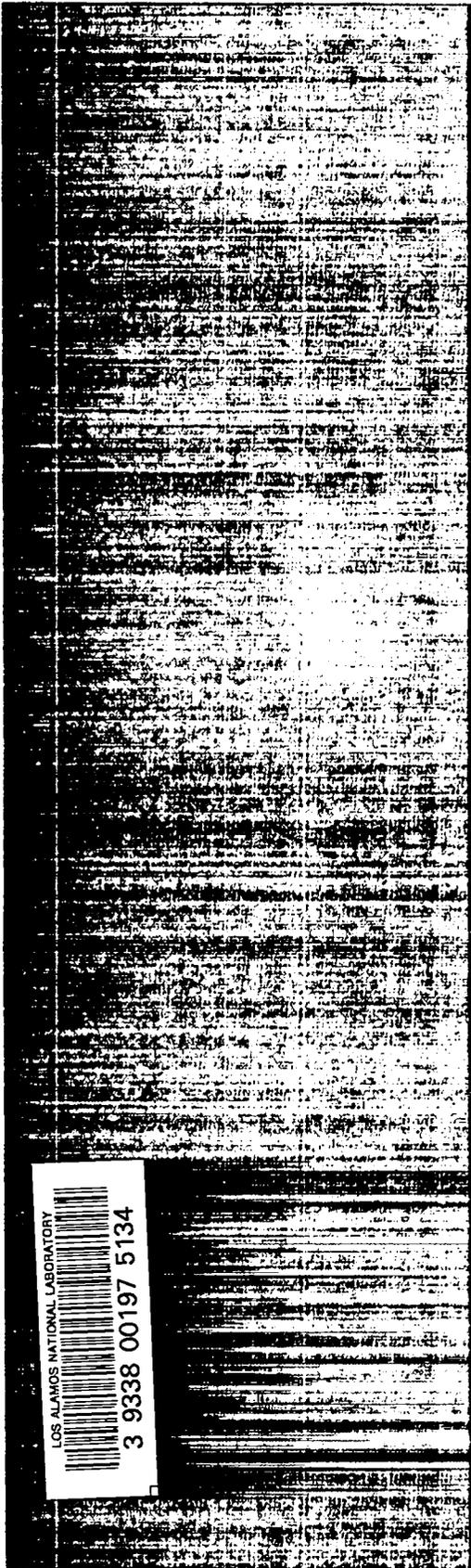


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Plutonium Using Nitrate Anion Exchange*

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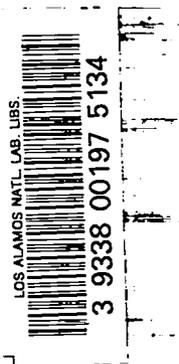
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*Evaluation of a New, Macroporous
Polyvinylpyridine Resin for Processing
Plutonium Using Nitrate Anion Exchange*

S. Fredric Marsh



EVALUATION OF A NEW, MACROPOROUS POLYVINYLPIRIDINE RESIN FOR PROCESSING PLUTONIUM USING NITRATE ANION EXCHANGE

by

S. Fredric Marsh

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 Buchanan¹ (Fig. 1) show why this system is nearly ideal for processing 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 study² identified resin porosity and bead size as the two properties that most influence plutonium sorption kinetics. Based on these findings, the gel-type DowexTM 1×4 resin previously used at Los Alamos was replaced with macroporous

LewatitTM MP-500-FK resin, which resulted in a dramatic improvement in process efficiency.³

Nearly 30 years ago, PermutitTM SK, a gel-type resin no longer produced, was reported to offer better sorption and desorption kinetics⁴ and capacity⁵ for plutonium than other resins available at that time. PermutitTM SK consisted of poly-2-methyl-5-vinylpyridine, rather than the polystyrene used for DowexTM, LewatitTM, and most other strong-base anion exchange resins. In addition to the reported performance benefits of PermutitTM SK, polyvinylpyridine anion exchange resins have been reported to offer greatly increased stability to chemical attack⁶ 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

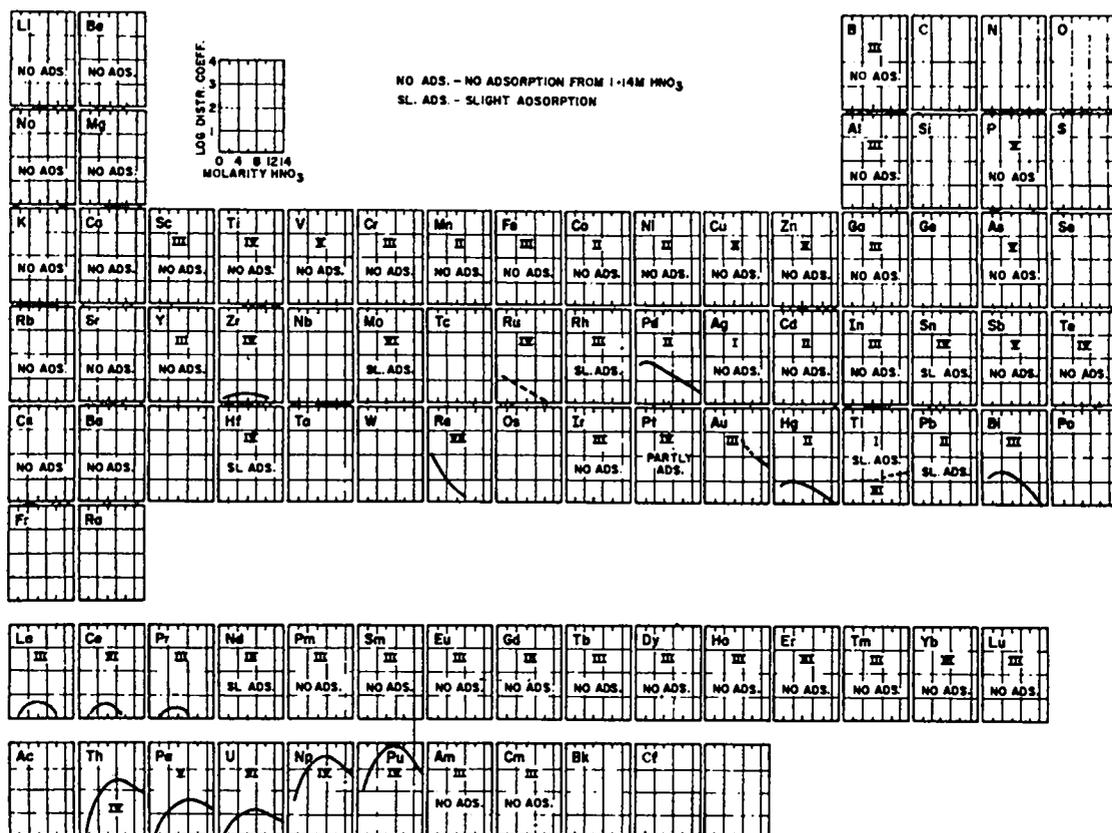


Fig. 1. Distribution of elements from nitric acid onto strong-base anion exchange resin.¹

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

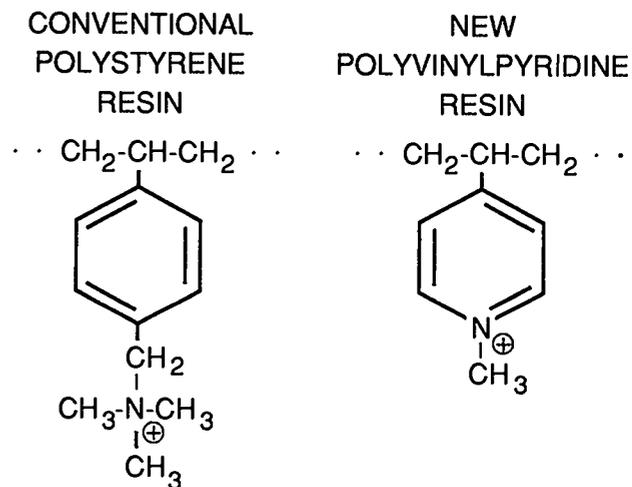


Fig. 2. Comparative structures of conventional polystyrene resin and new polyvinylpyridine resin.

REAGENTS

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

DowexTM 1×4 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.)

LewatitTM 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.)

ReillexTM 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 as follows:

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. The unquaternized pyridine rings are readily protonated 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 ReillexTM 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 approximately 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 ²³⁹Pu 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 Kd 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 Kd values decrease as the plutonium mass per volume of resin increases (Fig. 3). (A solution-to-resin volume ratio of 10 was used for these 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

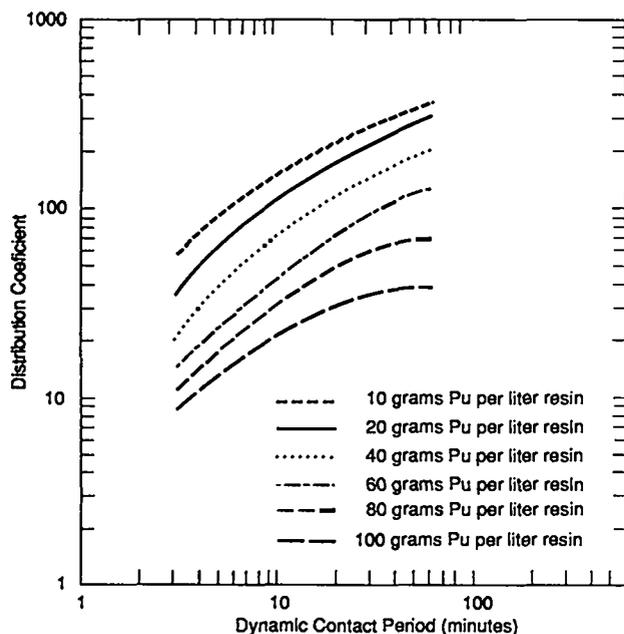


Fig. 3. Sorption of Pu(IV) on ReillexTM HPQ anion exchange resin from 7 M nitric acid as a function of plutonium loading.

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 K_d curves for different resins are therefore valid only when quantities of plutonium per resin volume are identical. We have accordingly measured and reported the sorption kinetics of Pu(IV) from 7 M nitric acid on ReillexTM HPQ, LewatitTM MP-500-FK, and DowexTM 1×4 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. Marston⁶ 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 ReillexTM 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 (1) high concentrations of nitric acid and (2) 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 ReillexTM HPQ resin to boiling, concentrated nitric acid for 3 hours. Although a small amount of NO₂ 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 boiling the resin in concentrated nitric acid caused the initially white ReillexTM HPQ resin to acquire a slight yellow color, there was no significant change in the surface appearance at 10,000X, as shown in scanning electron micrographs of both (Figs. 4 and 5). The thermal decomposition profiles of acid-boiled and untreated ReillexTM HPQ resin (both air-dried in nitrate form), as determined by thermogravimetric analysis in an argon atmosphere, were found to be nearly identical (Fig. 6).

The similar thermal decomposition profiles further confirm the absence of any significant resin alteration by the treatment. The thermal decomposition profile of LewatitTM MP-500-FK resin also was determined and is included in Fig. 6. The initial decomposition of ReillexTM resin at a lower temperature than LewatitTM 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.

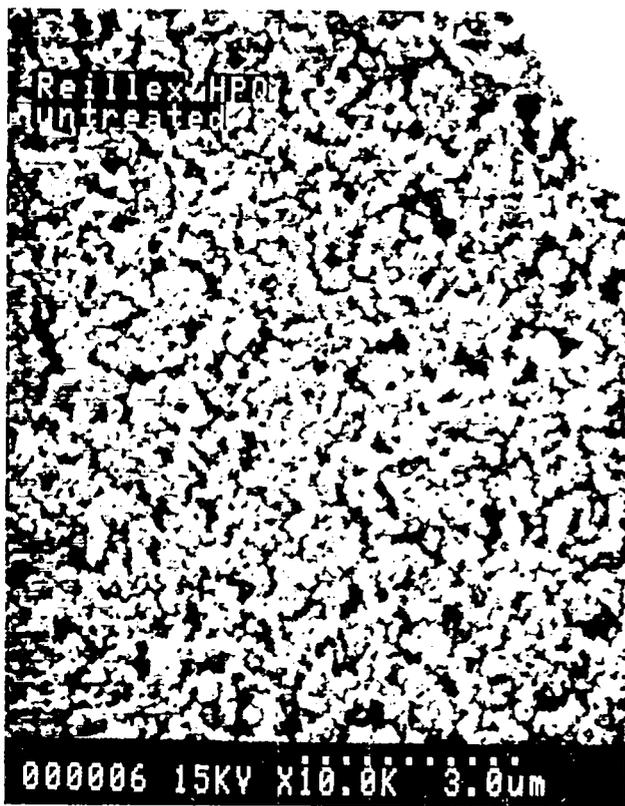


Fig. 4. Scanning electron micrograph (10,000X) of the surface of untreated ReillexTM HPQ anion exchange resin.

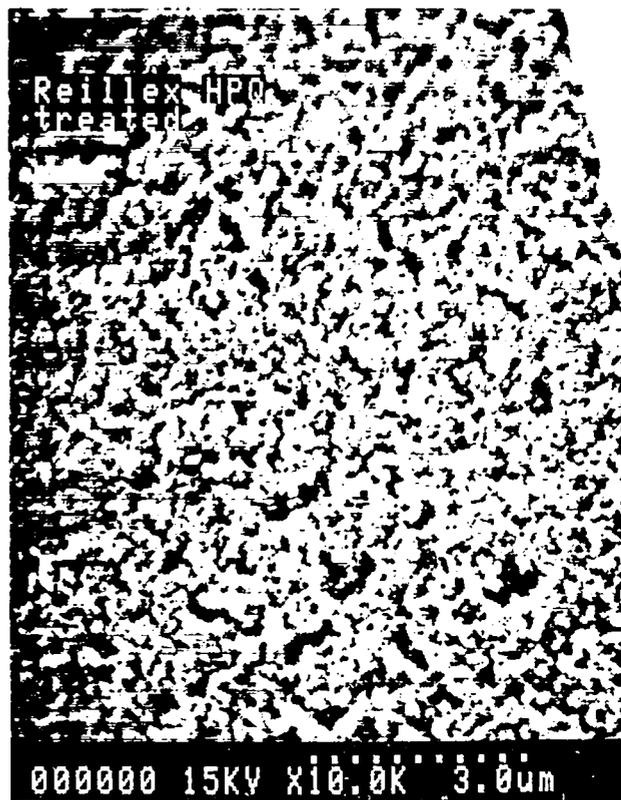


Fig. 5. Scanning electron micrograph (10,000X) of the surface of ReillexTM HPQ anion exchange resin that had been boiled in concentrated nitric acid for 3 hours.

Resin Capacity

To further determine whether the 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 total quantity of Pu(IV) (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 7 shows the measured capacities of DowexTM 1×4, LewatitTM MP-500-FK, and ReillexTM 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!

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 8 through 13 present comparative distribution coefficients of Pu(IV) from 7 M nitric

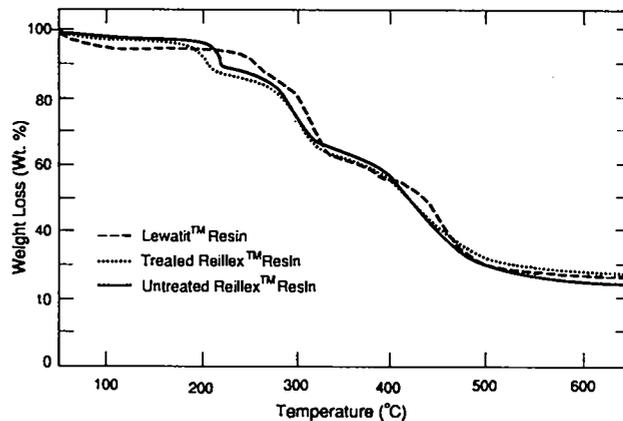


Fig. 6. Thermal decomposition profiles of nitric acid-boiled ReillexTM, untreated nitrate-form ReillexTM HPQ resins, and nitrate-form LewatitTM MP-500-FK resin.

acid on DowexTM 1×4, LewatitTM MP-500-FK, and treated and untreated ReillexTM HPQ for total plutonium loadings of 10, 20, 40, 60, 80, and 100 grams per liter resin, respectively.

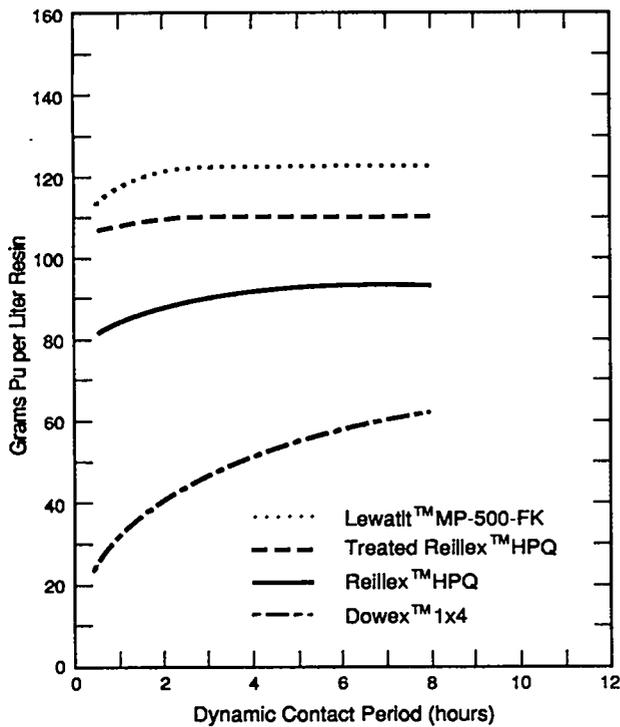


Fig. 7. Measured capacities of various anion exchange resins for Pu(IV) from 7 M nitric acid.

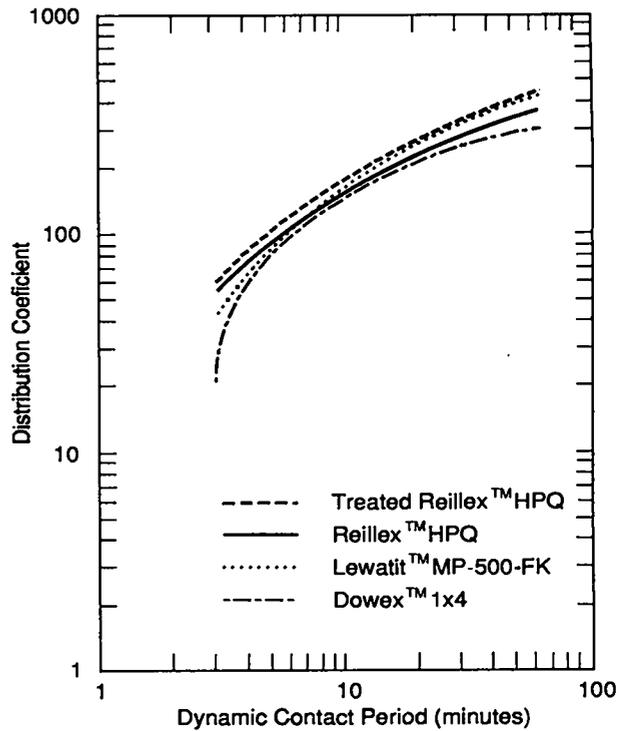


Fig. 8. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 10 grams per liter resin).

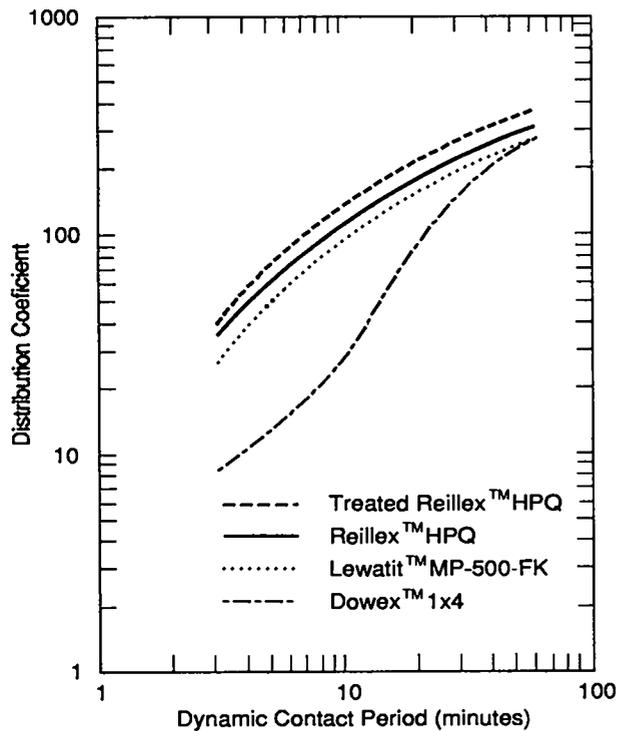


Fig. 9. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 20 grams per liter resin).

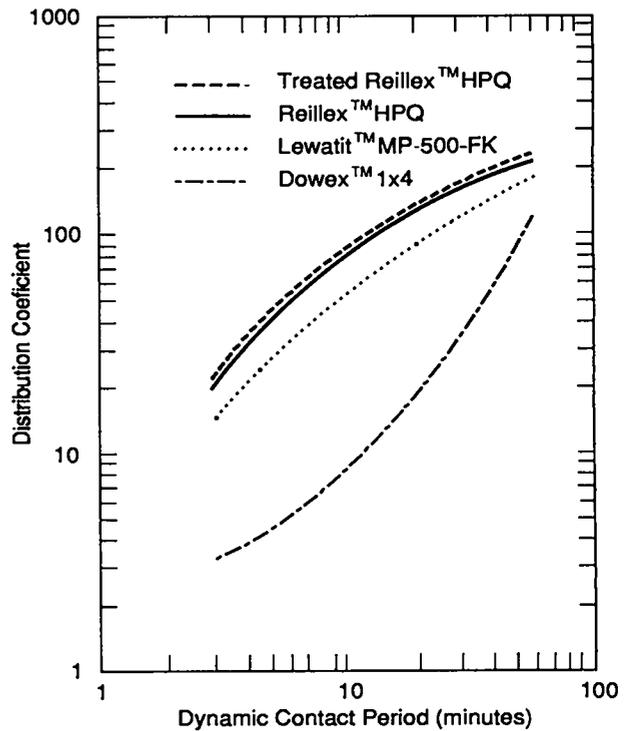


Fig. 10. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 40 grams per liter resin).

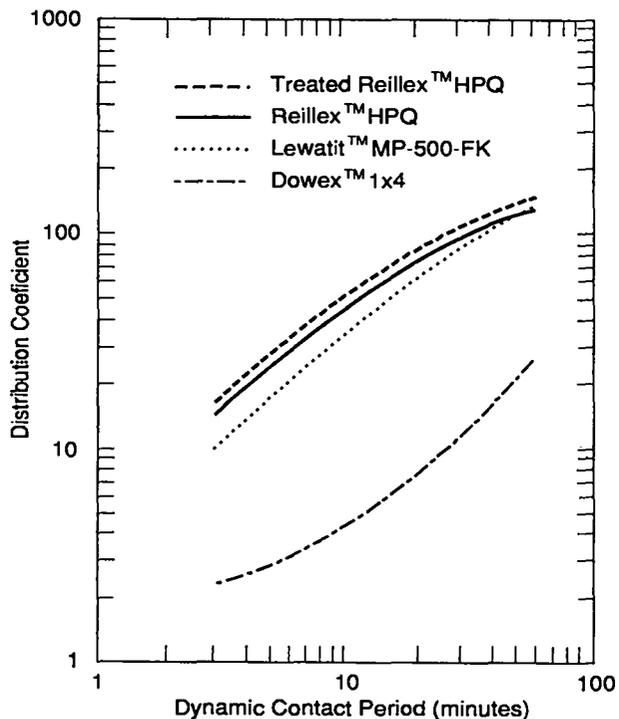


Fig. 11. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 60 grams per liter resin).

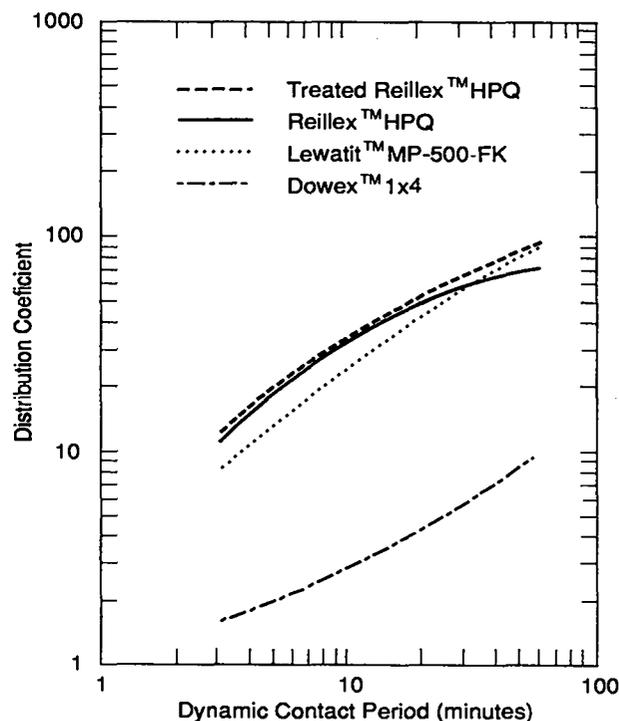


Fig. 12. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 80 grams per liter resin).

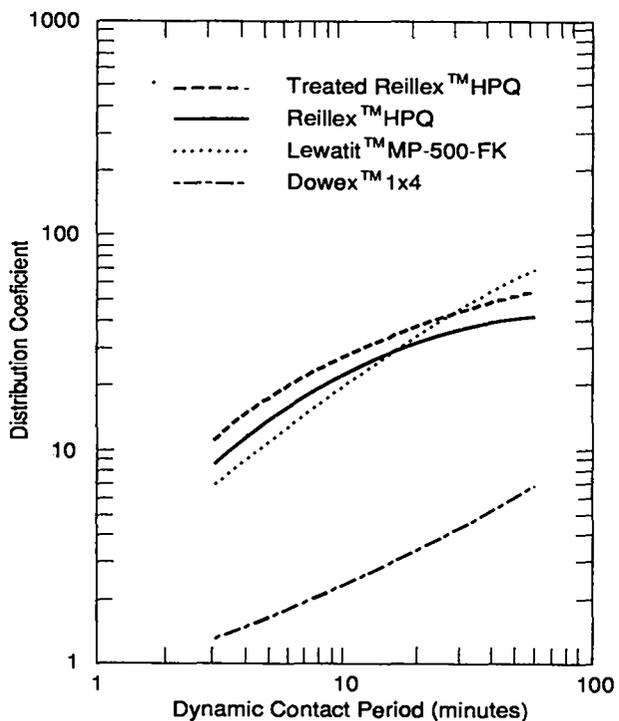


Fig. 13. Sorption of Pu(IV) on various anion exchange resins from 7 M nitric acid (Pu loading = 100 grams per liter resin).

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

Explanation for Improved Performance

The unexpected improvement in 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 NO₂. 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.

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 ReillexTM HPQ resin exhibits Pu(IV) sorption kinetics comparable or superior to that of LewatitTM 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 evaluated in 7-millimeter-diameter columns, using gravity flow for loading and elution.

Figure 14 presents Pu(IV) elution profiles from ReillexTM resin using 0.35, 0.40, 0.45, 0.50, and 0.60 M nitric acid. The elution profile of LewatitTM 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 ReillexTM 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 ReillexTM resin. The improved elution is particularly significant because elution of Pu(IV) with dilute nitric acid is much faster from LewatitTM resin than from any other resin previously tested.

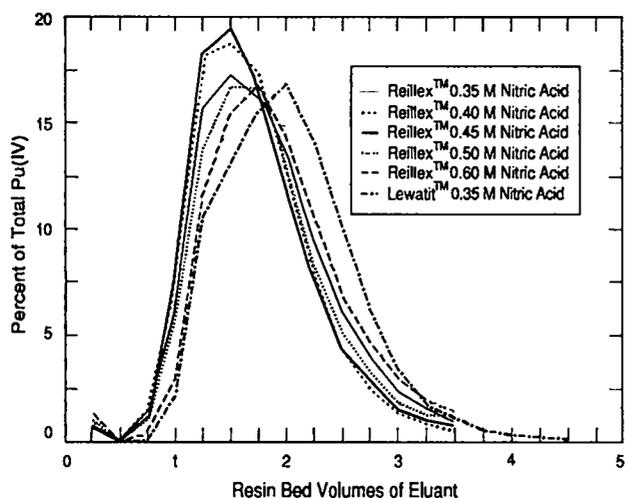


Fig. 14. Comparison of Pu(IV) elution profiles from ReillexTM HPQ resin using 0.35, 0.40, 0.45, 0.50, 0.55, and 0.60 M nitric acid elutriant, and from LewatitTM MP-500-FK resin using only 0.35 M nitric acid eluant.

Radiolytic Degradation

Another major safety advantage expected from ReillexTM 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 an experimental comparison of the radiation stability of ReillexTM 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 ReillexTM 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.

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

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