Beads of anion-exchange resin are used in the nitric acid plutonium recovery process. The background shows a powder of Reillex™ 402 polymer, which was modified to produce new, highly sorbtive anion-exchange resins.

Photos courtesy of Reilley Industries, Inc.

Molecularly Engineered Resins for Plutonium Recovery

S. Fredric Marsh, D. Kirk Veirs, Gordon D. Jarvinen, Mary E. Barr, and Eddie W. Moody

For several decades, Los Alamos National Laboratory has played a key role in developing ways to reduce the radioactive waste produced in plutonium processing. Recent work has focused on developing molecular-engineered resins to improve the efficiency for removing plutonium from the nitric acid processing streams at the Los Alamos Plutonium Facility and at other plutonium facilities in the Department of Energy (DOE) complex.

Nitric acid processing is used to recover plutonium in a purified form. Plutonium-contaminated residues and waste items such as glass containers, graphite casting molds, and magnesium oxide crucibles can be leached with nitric acid to dissolve the contaminants, and impure scraps of plutonium (typically converted to plutonium oxide) can be dissolved in fluoride-catalyzed nitric acid. The plutonium can then be selectively removed from the nitric acid by an organic polymer known as an anion-exchange resin.

Each polymer unit of the resin contains a cationic site that can retain an anionic complex. In nitric acid, the omnipresent nitrate anions, NO_3^-, will initially sorb to the resin. But plutonium is one of the few metals that form stable anions in nitric acid solutions, forming the Pu(IV) complex $Pu(NO_3)_6^{2-}$. Most metals form cationic or neutral nitrate complexes under such conditions. At an acid concentration of about 7 molar (M), the Pu(IV) anion will preferentially sorb to the resin by displacing, or exchanging with, nitrate anions. All other elements effectively stay in solution.

In the nitric acid process, porous beads made from resin are packed into a column through which the 7-M nitric acid solution is flowed. The plutonium sorbs to the resin while impurity elements wash away. Once the resin has been sufficiently loaded with plutonium, the solution conditions are changed. The plutonium releases from the resin and goes back into solution and is eventually recovered as purified plutonium dioxide. (More information about the recovery process is given in the article "A Vision for Environmentally Conscious Plutonium Processing" on page 436.) Over the last 20 years, the nitric acid process has been used to purify and recover tonnes of plutonium at Los Alamos alone.

Increasing the efficiency of the nitric acid process is key to enhancing plutonium recovery and minimizing radioactive wastes. Such improvements have been the goal of our efforts to engineer new anion-exchange resins.

Improving the Efficiencies of Anion-Exchange Resins

As early as 1959, Jack Ryan, a researcher at Pacific Northwest Laboratory, recognized that the sorption of Pu(IV) on gel-type anion-exchange resins was very slow (Ryan and Wheelwright 1959). Little was done, however, to alter those sorption characteristics. A 1984 report stated that more than three weeks would be required for Pu(IV) to reach equilibrium with a single 1-millimeter-diameter, gel-type resin bead in 7.5-M nitric acid. In the Lab's plutonium facility, the contact time between the solution and the resin in an exchange column was only about 5 to 10 minutes. The slow sorption meant that excessive amounts of resin were needed to recover relatively small amounts plutonium from the nitric acid.

In about 1985, Los Alamos researchers began to address this shortcoming. From their initial studies, they concluded that resin porosity and bead size had the largest effects on the rate of plutonium sorption. Small beads of macroporous resin were found to dramatically increase Pu(IV) sorption kinetics. (Beads made of macroporous materials have extra-large pores that greatly increase the effective surface area of each bead as solutions flow through it.) As a result, the Los Alamos Plutonium Facility switched to a macroporous resin made from a polystyrene-divinylbenzene polymer. Positive results here also led the Rocky Flats Plant to adopt the improved anion-exchange resin.

This improvement, however, was quickly superseded by another one. In the 1960s, Ryan had reported that a polyvinylpyridine resin offered superior sorption and desorption kinetics. In addition, the resin offered a greater capacity for plutonium and greater resistance to nitric acid and radiation damage than polystyrene-divinylbenzene polymers. Although the resin Ryan championed was not commercially available at the time of the Lab's macroporous resin studies, shortly thereafter, we began to collaborate with Reilly Industries, Inc., a supplier of vinylpyridine polymers. One result of this collaboration was the development of a macroporous polyvinylpyridine resin, later designated as Reillex™ HPQ. This new resin was comparable or superior to the best commercial resins then available. We quickly incorporated Reillex™ HPQ in some of the full-scale plutonium processes at Los Alamos and, based on highly favorable results, soon replaced the resin in all remaining processes with Reillex™ HPQ. The company began marketing the resin in 1988.

As of 1997, Reillex™ HPQ had outperformed all of the dozens of other commercial resins we had tested. The resin survives the processing stream's brutal combination of nitric acid and ntense radiation for at least three years and has become the standard for plutonium anion exchange in nitric acid throughout the nuclear industry. Its development did not mark the end of resin research, however. We have continued to look for ways to improve both the sorption speed and capacity of resins. Based on a variety of analytical, modeling, and chemical synthesis techniques, this research has led to a fuller understanding of how plutonium nitrate complexes bind to resins and to the development of promising new bifunctional resins.

Molecular Studies of the Pu(IV) Nitrate Complexes

The advances in anion-exchange resins made during the 1980s were based on comparatively simple experimental evaluations of the effects of the resins' bead size, porosity, and composition. In a sense, these were trial-and-error experiments guided by intuition and earlier experimental results. By 1990, we realized that further
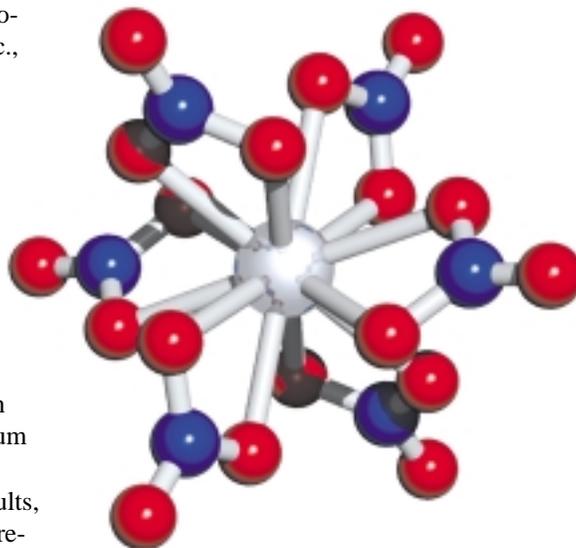
Figure 1. Molecular Model of the Pu(IV) Hexanitrato Complex
The hexanitrato complex is believed to be the one that sorbs to anion-exchange resins. A plutonium ion (silver) is at the center. Each nitrate ligand (NO_3^-) has three oxygen atoms (red) bonded to the nitrogen (blue). The nitrate bonds in a bidentate fashion, that is, two atoms from the ligand bond to the central plutonium ion.

improvements in the anion-exchange process would require a better understanding of what was occurring at the molecular level.

The earliest spectrophotometric studies of plutonium nitrate complexes, both in solution and on anion-exchange beads, were published in 1953 (Durham and Mills). Based on these light-absorption measurements of loaded resin beads and other data, Ryan concluded in 1960 that the Pu(IV) nitrate complex that sorbs on anion-

In 1990, we sought to obtain improved absorption spectra using modern instruments and data-processing techniques. We wanted not only to verify the structure of the sorbed species but also to determine the identity of the Pu(IV) complex *in solution* that most readily reacts with the anion-exchange
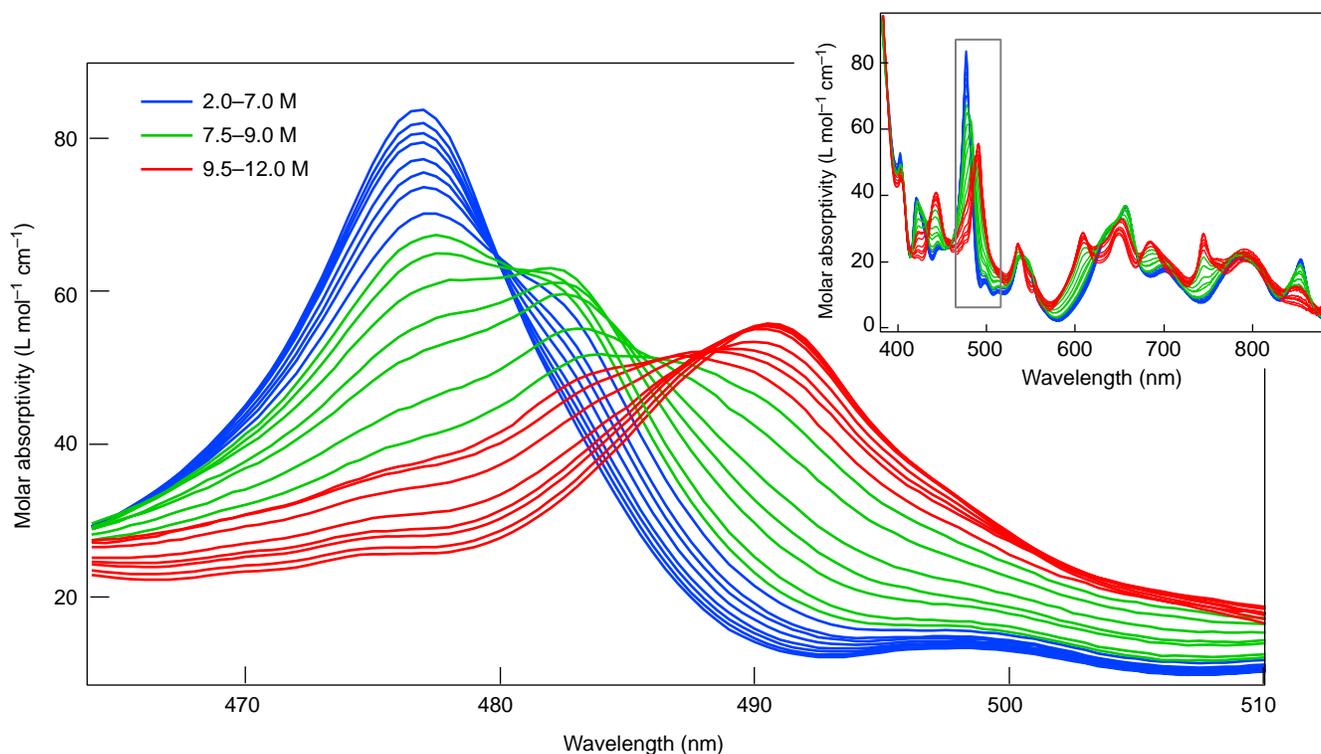
Figure 2. Absorption Spectra of Plutonium Complexes in Nitric Acid
The inset shows the absorption spectra of Pu(IV) in 2- to 12-M nitric acid solutions. The large graph is an expanded view of the region in the gray box. The blue peak at 477 nm can be assigned with confidence to the dinitrato cation $Pu(NO_3)_2^{2+}$; and the red peak at 490 nm, to the hexanitrato anion $Pu(NO_3)_6^{2-}$. The green peak at 483 nm is due to a third complex, most likely a tetranitrato neutral complex. Sequences of curves that cross at the same point (for example, the blue curves at about 480 nm and the red curves at about 488 nm) indicate that changes from one spectrum to the next are dominated by a shifting equilibrium between two plutonium complexes. The lack of such crossings for some series, such as most of those in green, indicate that three or more species are contributing to the spectra. (Graphics courtesy of J. Berg, Los Alamos National Laboratory.)

resin before becoming the sorbed hexanitrato complex. The fact that the highest concentration of this hexanitrato complex occurs at a nitric acid concentration of about 13 M but that Pu(IV) sorption is highest between 7 and 9 M indicated that the hexanitrato complex was not being sorbed directly onto the resin. Instead, it was possible that the complex was the product of a transformation that occurred during sorption.

We began studies, therefore, to produce a database of absorption spectra of Pu(IV) in varying concentrations of nitric acid, with the goal of identifying all of the plutonium species that were present. Our spectrophotometric measurements ranged from the near ultraviolet through the near infrared (300 to 1200 nanometers).

Ryan had identified two major Pu(IV) species in nitric acid concentrations of 1 to 13 M: the positively charged dinitrato complex, $Pu(NO_3)_2^{2+}$, and the divalent hexanitrato complex, $Pu(NO_3)_6^{2-}$. For the most part, our studies agreed with Ryan's observations. We found that in dilute nitric acid, the most abundant complex was the plutonium dinitrato cation, whereas at high concentrations of nitric acid, the most abundant complex was the plutonium hexanitrato anion. We also confirmed Ryan's conclusion that the hexanitrato anion is the sorbed species.

But careful analysis of our spectrophotometric data revealed that at intermediate nitric acid concentrations of approximately 7 M, a third, previously unstudied plutonium nitrate complex reached its peak concentration (see Figure 2). Although we could not identify this third complex, it was especially interesting because as we varied the concentration of nitric acid, the absorption spectrum of the new complex in solution correlated closely with the sorption profile of Pu(IV) onto an anion-exchange resin. We therefore proposed that this new complex might be directly involved in the sorption process. Our results were presented in a Los Alamos report (Marsh et al. 1991).

Before we could confirm and perhaps exploit this hypothesis, however, we needed to identify the third plutonium species in solution that correlated so strongly with the Pu(IV) sorption profile. Unfortunately, we were unable to identify this species by our spectrophotometric measurements. Such information could only be obtained

with other spectroscopic techniques.

Previously, Fratello had used nuclear magnetic resonance (NMR) spectra of carbon, nitrogen, and oxygen in non-complexing organic liquids to observe the speciation of metal ions. Such data could then be used to infer the ions' speciation in aqueous solution. However, his technique could be used only for strongly bound ligands; weakly bound ligands exchange with the water ligands more rapidly than the timescale of NMR measurements, making it difficult to interpret the resulting signal. This problem can sometimes be overcome by acquiring NMR signals in organic solvents cooled to well below the freezing point of water, so that the rates of ligand exchange are significantly slower.

Our first NMR measurements of actinide nitrate complexes, begun in 1992, used nitric acid enriched with ^{15}N to titrate thorium in an organic solvent (deuterated acetone and $CFCl_3$) cooled to –100°C. We used thorium rather than plutonium because it was less hazardous and therefore easier to study and because Th(IV) has a similar chemical behavior to Pu(IV). For example, Th(IV) was known to form hexa-nitrato complexes, and the crystal structures of the thorium tetranitrato and hexanitrato salts were known to be similar to those of the comparable Pu(IV) salts. By measuring the NMR signal of ^{15}N, we observed four distinct thorium species containing—as the nitric acid concentration increased—one, two, four, and six nitrates (Figure 3). However, we observed no species containing three or five nitrates.

When we made similar NMR measurements using Pu(IV) nitrate complexes, the signal for ^{15}N indicated the presence of the hexanitrato species. The NMR signals for the other species were degraded to undetectable levels by the paramagnetism of plutonium. However, with decreasing nitrate concentration, the behavior of the NMR signal for the Pu(IV) hexanitrato complex was identical to what we had observed for Th(IV) hexanitrato. This par-
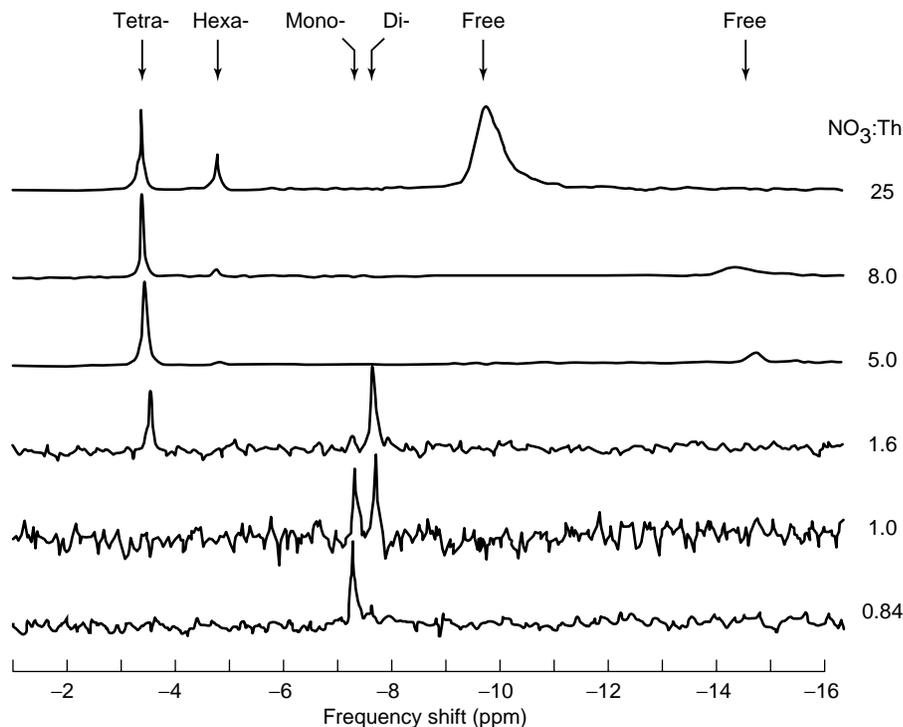
Figure 3. The NMR spectra of ^{15}N-labeled Thorium Nitrato Complexes
Using thorium as a surrogate for plutonium, we were able to detect Th(IV) nitrato complexes as they formed in solution with ^{15}N-labeled NO_3^- ligands. The NMR spectra show the presence of four complexes: mononitrato (shift at –7.2 ppm), dinitrato (–7.6 ppm), tetranitrato (–3.4 ppm), and hexanitrato (–4.8 ppm). The peaks appear in order as the nitrate-to-thorium ratio increases. The thorium mononitrato complex first appears at low concentrations of nitric acid, the thorium dinitrato complex appears at higher concentrations, and so forth. Free nitrate first appears at a nitrate-to-thorium ratio of 5.0 at –14.9 ppm and shifts to –9.6 ppm as the ionic strength of the solution increases. No complexes with three or five nitrates are observed.

allelism reinforced the idea that thorium mimicked the behavior of plutonium in our solutions. Since the neutral thorium tetranitrato species $Th(NO_3)_4$ was abundant in 7-M nitric acid, we tentatively identified our third plutonium species in solution as the electrically neutral plutonium tetranitrato complex, $Pu(NO_3)_4$.

These experimental results, combined with related Raman spectroscopy done at Los Alamos and data from the literature, suggested the following Pu(IV) speciation pattern: the hexanitrato anion was the major species present in 13-M nitric acid; the dinitrato cation had the highest concentration in 2-M nitric acid; and the dinitrato, tetranitrato, and hexanitrato complexes were present at roughly equal concen-

trations in ~7-M nitric acid. Later, more-sensitive experiments also supported this pattern.

As already discussed, the sorption of plutonium onto an anion-exchange resin and the concentration of the neutral tetranitrato complex both peak at ~7-M nitric acid. Furthermore, the sorption of Pu(IV) as a function of nitric acid concentration parallels the concentration of the tetranitrato species. But it appeared that only the hexanitrato complex sorbed to the resin. For anion exchange to occur, then, the neutral Pu(IV) tetranitrato complex would have to acquire two more nitrate groups to become the divalent hexanitrato anion.

The spectroscopic data suggested that a pentanitrato complex was rela-

(a)

(b)
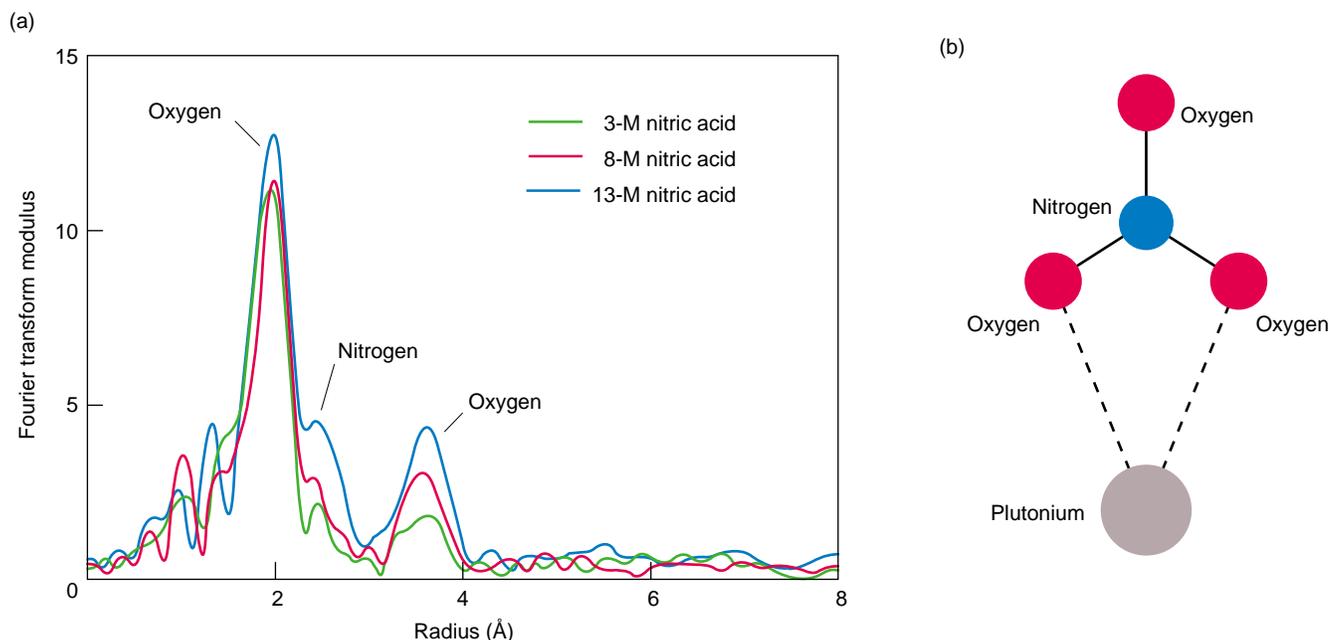
Figure 4. XAFS Studies of Pu(IV) Nitrato Species

(a) The Fourier transforms (FTs) of XAFS data reveal the relative positions and number of nearest-neighbor atoms around a central atom (in this case, plutonium). The largest peak corresponds to oxygen atoms that are located about 2.41 Å from the plutonium atom. (Because of the XAFS phase shift, peaks in the FTs are shifted to lower radii than actual distances from the plutonium ion.) The second and third peaks correspond to nitrogen atoms located about 2.97 Å from the plutonium and to a second set of oxygen atoms located about 4.15 Å from the plutonium. These distances are entirely consistent with a bidentate bonding arrangement, as illustrated in (b). The number of nitrate or water ligands that bind to the plutonium ion for different nitric acid concentrations can be obtained by comparing the intensities of the various peaks in the FT. The intensities of the third peak, for example, are in a ratio of 6:4.4:2.6 for 13-, 8-, and 3-M nitric acid, respectively. With the distribution of plutonium nitrato species obtained from XAFS absorption spectra, the expected ratio would be 6:4.3:2.5. Thus the XAFS and light-absorption data are in complete agreement.

tively unstable, which meant that the tetranitrato complex was unlikely to acquire the additional nitrates via a two-step process. Instead, the conversion requires the simultaneous convergence of the neutral $Pu(NO_3)_4$ complex and two nitrate ions, a highly unlikely event. (This unfavorable complexation reaction might explain the notoriously slow kinetics for sorbing Pu(IV) on anion-exchange resins from nitric acid.) The question was how we might facilitate the required conversion of the Pu(IV) tetranitrato complex to the Pu(IV) hexanitrato complex.

An intriguing possibility was to develop a "bifunctional" resin in which each repeating polymer unit would contain two cationic sites that were separated by a fixed distance. Such an arrangement would improve adsorption in two ways. First, two nitrate ions, bound initially to the cationic sites,

could be positioned in close proximity to each other. The neutral tetranitrato species could readily react with them to form the sorbed hexanitrato species. And second, the two positive charges on the polymer unit would hold the divalent hexanitrato complex more strongly. These properties should produce faster kinetics and higher K_d values.[1] But how should the two anion-exchange sites be spaced to achieve the best performance?

To answer that question, we needed structural information about the Pu(IV) nitrate complexes, which was minimal at the time. We were faced with a number of questions: Did one or both oxygens on each nitrate ligand bind directly to the plutonium ion? What was the coordination number for each Pu(IV) species, that is, how many nitrates and waters were coordinated with each plutonium ion? What were the

bond distances from the plutonium ion to the nitrate oxygens? Were the shapes of the bound nitrate ligands distorted from those of the free nitrate? What were the similarities and differences between the Pu(IV) hexanitrato species in solution and in the solid state?

X-ray absorption fine structure (XAFS) spectroscopy could help answer these questions, but at the time no synchrotron x-ray facility (where XAFS experiments are done) allowed plutonium-containing materials on-site. Fortunately, the forward-looking man-

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[1] K_d gives a measure of the sorption affinity of the resin. It is defined as: $K_d = (1 - [B]/[A])V/M$, where $[B]$ is the concentration of the element, here Pu(IV), in solution after contact with the resin, $[A]$ is the concentration of the element in solution before contact with the resin, V is the volume of the solution in contact with the resin (in milliliters) and M is the weight (in grams) of the dry resin. The higher the K_d, the greater the sorption.

agement at the Stanford Synchrotron Radiation Laboratory (SSRL) agreed to embark with Los Alamos on an exhaustive study of the hazards involved in conducting XAFS experiments with actinides. As a result of that effort and the safe operating procedures that were developed, research groups from DOE laboratories at Los Alamos, Berkeley, Livermore, Argonne, and Richland (Washington) as well as from Australia and France now regularly study actinides at SSRL. Moreover, similar capabilities have also been developed for handling actinides at synchrotron facilities at both Berkeley and Argonne.

By 1995, XAFS spectroscopy provided all of the bond lengths and angles for the Pu(IV) hexanitrato species. Our studies of plutonium in nitric acid at concentrations of 3, 8, and 13 M dramatically confirmed the presence of inner-sphere nitrate species, yielded stoichiometries consistent with other methods, and provided precise bond distances and coordination numbers (see Figure 4). The Pu(IV) hexanitrato species in solution was found to have essentially the same structure as the hexanitrato species in the solid state. Moreover, extended x-ray absorption fine structure (EXAFS) showed that the plutonium complex sorbed on an anion-exchange resin was structurally identical to the solution species that had the highest concentration in 13 M nitric acid, that is, the hexanitrato anion, in agreement with the earlier light-absorption measurements.

First Bifunctional Anion-Exchange Resins

At this time, bifunctional anion-exchange resins were not commercially available nor, to our knowledge, had they ever been prepared in even experimental quantities. In 1996, therefore, we began to collaborate with Prof. Richard Bartsch at Texas Tech University, who was interested in developing a polymer synthesis program that could help prepare such resins. All bi-

functional resins described below were prepared at Texas Tech to our specifications.

We had several objectives for the first bifunctional resins. We wanted to (1) synthesize the new resins by modifying an existing, commercially available (hence low-cost) resin that offered superior resistance to acidic and radiolytic degradation, (2) evaluate the effect of placing different chemical groups at the second ion-exchange site, (3) vary the separation distance between the two exchange sites, that is, vary the number of hydrocarbons linking the sites, and (4) vary the rigidity of these hydrocarbon chains.

The first bifunctional resins were prepared for us in 1996 by modifying another Reilly Industries' vinylpyridine polymer resin, Reillex™ 402. This resin, seen in Figure 5(a), is easily derivatized. The new resins were synthesized by attaching different chemical groups to the nitrogen atom of the pyridine with a short hydrocarbon chain. In one resin, the other end of the chain had a trimethylammonium group—$N(CH_3)_3$—as shown in Figure 5(b). The pyridine nitrogen provided one anion-exchange site, the nitrogen within the trimethylammonium group provided the second, and the number of hydrocarbons in the linking chain established the distance between the two sites. We prepared several such resins that differed only in the length of their hydrocarbon chains, which varied from two to six carbons. All resin polymers were cross-linked with divinylbenzene at 2 to 3 percent. (The degree of cross-linking controls the resin's rigidity, porosity, resistance to acidic and radiolytic degradation, and other properties.)

Another series of bifunctional resins was synthesized with a pyridinium group, as shown in Figure 5(c). That series had spacer chains of two to six hydrocarbons. In addition, we prepared a series of resins with a trimethylphosphonium group (with chains of two to five hydrocarbons), as well as a resin that had a trimethylammonium group

attached with an ether chain (two hydrocarbons on either side of an oxygen atom).

The resins' performance was evaluated by measuring the K_d values of Pu(IV) onto the resins in 1-, 3-, 5-, 7-, and 9-M nitric acid over contact times of 0.5, 2, and 6 hours. In all cases, resins formed with the five-carbon chains gave the highest K_d values in 7-M nitric acid. Table I compares the K_d values for several of these resins with those obtained for Reillex™ 402. The K_d values for the bifunctional resins are roughly 2 to 4 times higher than those of the base resin.[2] Another interesting result is that the trimethylammonium resin with the ether chain (column 4) is superior to the trimethylammonium resin with a chain of five hydrocarbons (column 3). This suggests that the increased flexibility of the oxygen spacer may contribute to the resin's improved performance.

We also tested the performance of one of our earliest resins (TTU-4, which had a trimethylammonium group attached to a spacer chain of four hydrocarbons) for removing Pu(IV) from a solution that simulated acid-dissolved sludge from the high-level nuclear waste storage tank 102-SY at the Hanford Reservation in Washington. Although the nitric acid concentration of this solution was only 0.5 M, the high concentration of dissolved nitrate salts provided a total nitrate concentration of 5 M. Our experiments again measured K_d for various solution/resin contact times but compared the results with those for Reillex™ HPQ. In all cases, the plutonium K_d values for the bifunctional resins were dramatically greater than those for Reillex™ HPQ, as evident in Table II. The fact that the K_d values for other

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[2]The K_d values of the new resins were also as much as 14 times greater than those of Reillex™ HPQ resin. But Reillex™ HPQ is cross-linked at 25% (to give the resin mechanical strength), which substantially limits access to the cationic binding sites compared with the 2% cross-linked Reillex™ 402. Simply comparing the K_d values, therefore, is not a valid indicator of the resin's overall performance in an exchange column.

Table I. Measured K_d Values for Pu(IV) in 7-M Nitric Acid onto Resins

Contact Time		Spacer and Functional Group of Bifunctional Resin[a]		
(h)	Reillex 402[a]	$(CH_2)_5-N(CH_3)_3$	$(CH_2)_2O(CH_2)_2-N(CH_3)_3$	$(CH_2)_5$–pyridinium
0.5	1258	3500	4800	5700
2	2635	4300	6800	8800
6	2591	3800	6800	11000

[a] K_d values measured in mL/g

(a) Reillex™ HPQ   (b) Reillex™ 402   (c) Trimethylammonium   (d) Pyridinium

(e)
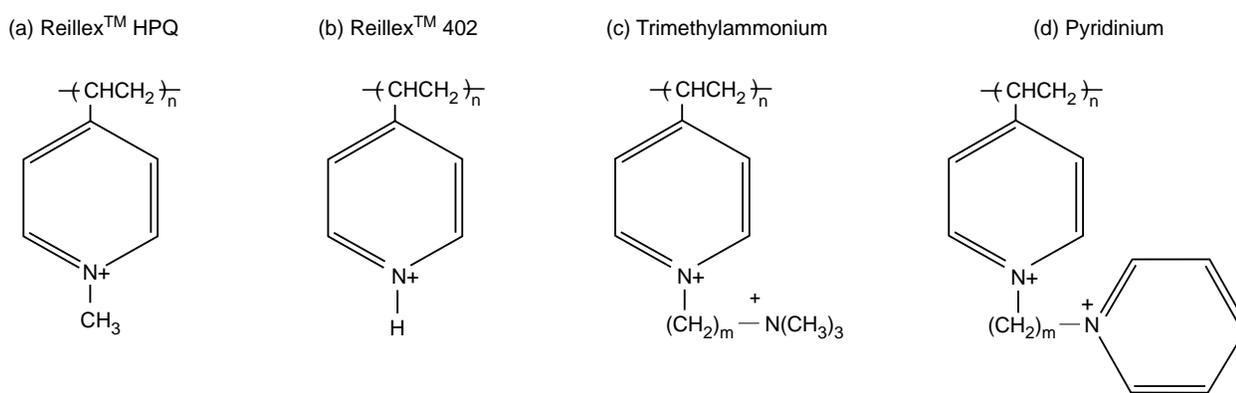
Figure 5. The First Series of Bifunctional Resins

(a) Reillex™ HPQ is a vinylpyridine polymer resin that has a methyl group, CH₃, attached to the nitrogen atom of the pyridine. One polymer unit is shown. As seen in (b), Reillex™ 402 is similar, except that a hydrogen atom is attached to the nitrogen. Collaborators at Texas Tech University replaced that hydrogen with hydrocarbon chains of various lengths, to which were attached different chemical groups, including (c) trimethylammonium and (d) pyridinium. The chains were two to six hydrocarbons long. A plutonium hexanitrato complex should bind to the two positively charged nitrogen sites of these bifunctional resins. (e) In this cartoon, a polymer chain has numerous sites functionalized with trimethyl-ammonium, three of which have Pu(IV) hexanitrato groups (shown as "pin-wheels") sorbed on them. Derivatizing a polymer is not 100% efficient, so we've shown two sites that are not functionalized.
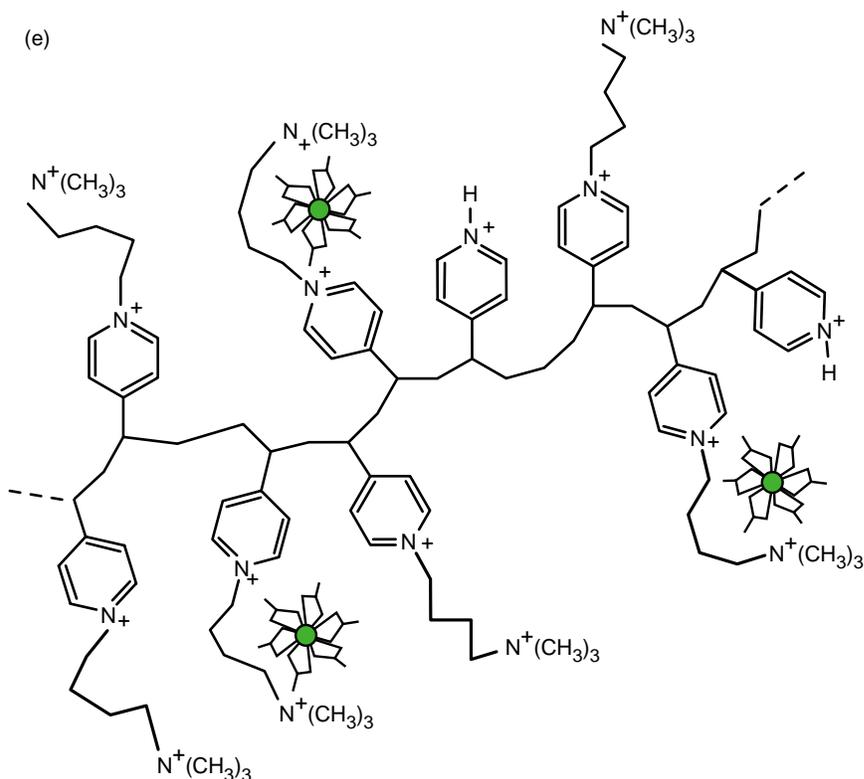
Table II. Approximate K_d Values of Several Elements to Resins in High-Level Waste Sludge

Element	Reillex HPQ[a] (mL/g)	TTU-4[a] (mL/g)
Plutonium	78	1100
Americium	4	6
Cerium	14	23
Chromium	1	1
Cesium	1	1
Iron	1	1
Strontium	1	1
Technetium	76	24
Uranium	17	18
Yttrium	1	1
Zirconium	4	4

[a]Contact time of 0.5 hours

metal ions in solution were about the same for all resins demonstrated that the enhanced sorption was selective for Pu(IV), as we had envisioned.

Molecular Models

In 1998, we began to develop computer models to help us better understand how anion-exchange resins function and to guide our development of new resins. As noted, an important figure of merit for an anion-exchange resin is K_d, which can be shown from thermodynamic arguments to be proportional to what we call the "stickiness factor," or SF.

SF is the sum of the electrostatic forces binding a plutonium hexanitrato complex to the resin's cationic site.[3] To calculate it, we must know how the electronic charge is distributed within the complex and within a polymer unit of the resin. In an exact calculation, we would solve the Schrödinger equation (with relativistic corrections) for all the electrons of all the atoms within the

[3]Our model does not address how the neutral Pu(IV) tetranitrato complex acquires two negatively charged nitrate ions to become the divalent Pu(IV) hexanitrato anion. The model simply examines how the hexanitrato complex binds to the resin.

hexanitrato complex and the resin. This *ab initio* (from first principles) approach would give the continuum charge distributions throughout the complex and the polymer unit, which change as the two species approach and bind to each other. The total electrostatic binding energy would then involve a double integral over the entire charge distribution. At present, however, such a calculation exceeds the capabilities of the world's largest supercomputer!

Our approach for obtaining the SF has been to forgo a full quantum mechanical calculation and instead use a "partial charge" model consisting of point charges, which are placed at the centers of the atoms of the complex and of the polymer unit. These charges represent the average charge at each atom. Two charges within either the complex or the polymer unit interact through a linear force as if they were connected by a spring, where the spring constant represents the strength of the chemical bond. This collection of partial charges held together by chemical-bond springs is called a molecular mechanics model.

Our molecular mechanics model has everything needed to calculate the electrostatic interaction of the hexanitrato complex and the resin—that is, it contains the relative positions and magnitudes of the point charges for the entire system. Once these charge distributions are known, we need only calculate the electrostatic energy between a charge in the plutonium hexanitrato and a charge in the resin and then take the sum over all such pairs. Because of the springs, the model is mechanically flexible and to some degree can simulate how the resin's spacers distort to better fit the hexanitrato complex.

Even with this simplified approach, however, we could not estimate the partial charges for the hexanitrato complex within a reasonable amount of computer time. As a result, we have limited ourselves to *ab initio* calculations for $Pu(NO_3)^{3+}$, which can be viewed as a model for one-sixth of the hexanitrato complex (see Figure 6). The results are
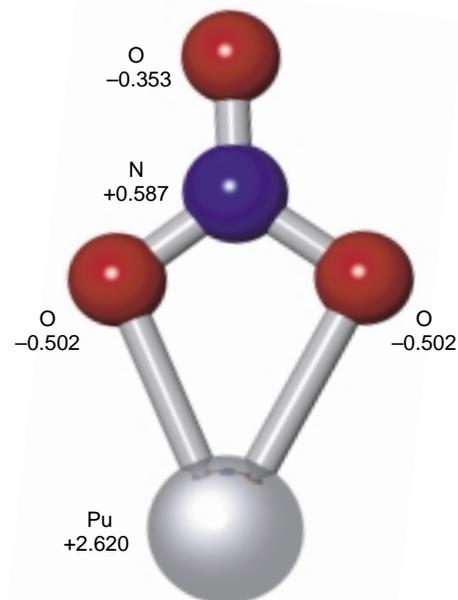
Figure 6. The Partial-Charge Model for the Pu(IV) Hexanitrato Complex Our molecular mechanics model for the hexanitrato complex is based on calculations for the partial charges of $Pu(NO_3)^{3+}$, which can be viewed as one-sixth of $Pu(NO_3)_6^{2-}$. These calculations are then extrapolated to obtain the partial charges of the hexanitrato complex. This modeling procedure seems to be valid because when we compare the estimates of bond lengths and angles from our model with EXAFS data, the differences are quite small.

then extrapolated to $Pu(NO_3)_6^{2-}$. The structure of plutonium hexanitrato as derived from this model has proved to be remarkably accurate. When we overlay our molecular mechanics model of the hexanitrato complex with a ball-and-stick model obtained from EXAFS studies, differences in the positions of the atoms and their bond lengths and angles are quite small.

By using a computer code to calculate the electrostatic forces between the complex and the polymer unit as well as their resulting motions, we can watch the two species interact on a computer screen. The initial separation between the two species is 4 angstroms,

Figure 7. A Bound Complex
The Pu(IV) hexanitrato complex shown here is electrostatically bound to one polymer unit of a bifunctional resin. The chemical structure of this resin—poly(N-alkylene-trimethylammonium 4-vinylpyridine nitrate)—is also shown in Figure 5(c). In the polymer unit, the carbon atoms are bright teal, the cation-exchange sites are the two blue nitrogen atoms, and the small gray spheres are hydrogen atoms. At each exchange site, binding results from the strong electrostatic attraction between one of the polymer's positively charged nitrogen atoms and a negatively charged oxygen atom (red) on the hexanitrato complex.

$Pu(NO_3)_6^{2-}$

Pyridine

Hydrocarbon chain

Trimethylammonium
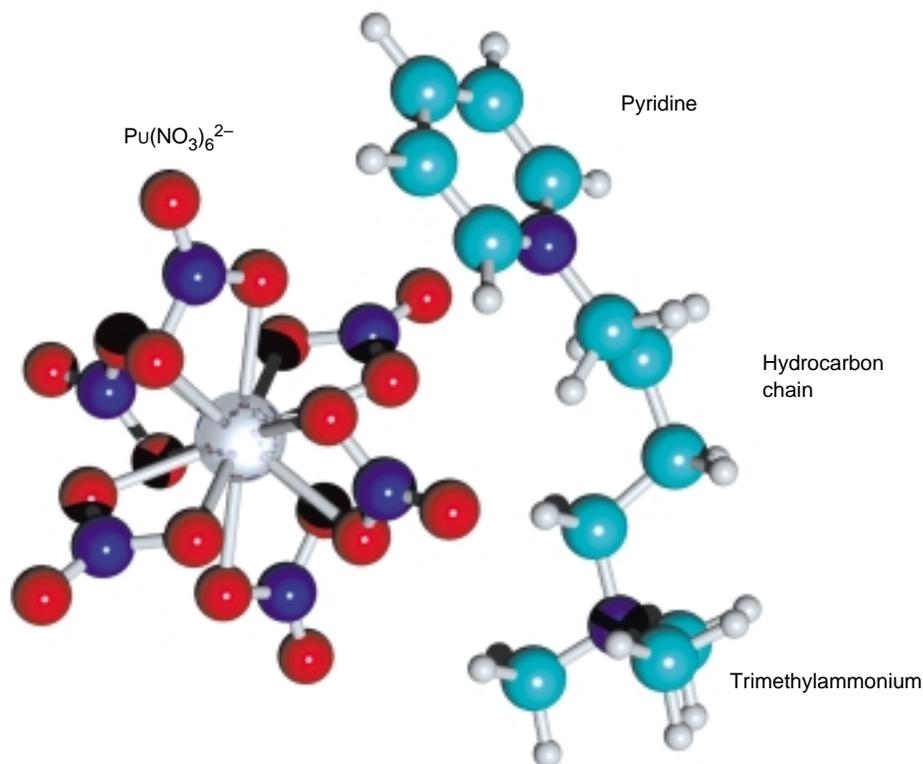
but they soon drift toward each other, rotating and flexing as necessary to minimize the system's energy. Binding is complete when the two species come to rest, and a calculation of the system's electrostatic energy at that point gives the SF. Normally, binding occurs in about a thousand steps, which requires about 15 minutes on a desktop computer. A bound complex is shown in Figure 7.

This technique gives us a quick and easy means of evaluating the performance of an anion-exchange resin relative to other resins of similar composition. For example, our molecular mechanics model has been able to reproduce the experimental trends in K_d values as the values vary with spacer length when the same chemical group is used as the second ion-exchange site. (The calculations assume that the hexanitrato complex and the polymer unit are in vacuum, but the K_d values can be scaled to provide liquid-phase results. Because our model calculates only the K_d of one resin relative to another and because the solvent effects are similar for the different resins, the trends we observe should be valid.)

As our molecular modeling becomes more sophisticated, we will be able to compare K_d values across families of resins with different types of second ion-exchange sites and with various combinations of spacer/second-site groups. Modeling will help us select—from a vast range of chemical possibilities—the most promising options for future laboratory synthesis and testing.

Our results for plutonium can also be applied to some extent to other actinide IV species that form hexanitrato complexes, such as thorium and neptunium, because the direct interaction between the plutonium ion and the resin is minimal. Instead, the major interaction is between the outer oxygens of the nitrate ligand and the cationic sites of the resin.

Future Directions for Anion-Exchange Resins

The overall performance of our bifunctional resins bodes well for the future. For the resins described in this article, the only shortcoming is a lack of mechanical strength. But we have recently developed a new series of bifunctional resins that are cross-linked

at about 20 percent. While increasing the mechanical strength, the greater cross-linking decreases the sorption, and at this point in our development project, Reillex™ HPQ remains the resin of choice for nitric acid processing.

However, we can envision different bifunctional resins that could be useful in other applications, for example, scavenging precious metals from what would normally be considered waste solutions, or removing toxic, nonradioactive metals from other industrial waste streams. Our molecular mechanics model allows us to simulate and "test" these different resins on a desktop computer in less than a day, saving the considerable time and expense required to synthesize and test them in the laboratory.

In a concurrent development program, Los Alamos researchers made rods of porous polystyrene foam as possible replacements for the beads now used to pack anion-exchange columns. The rods' porosity can be carefully controlled to provide short, optimal flow paths to functional groups attached to the polystyrene. Their use results in better sorption and better flow characteristics within a pressurized fluid

system, so they are in general a better support medium for column chromatography, including the anion-exchange process. Because the foam can be functionalized to provide two exchange sites, the rods may offer some advantages over resin beads. Initial tests of these rods have shown promising results.

Further Reading

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S. Fredric Marsh began his 39-year career at the Idaho Chemical Processing Plant, where he developed improved radioanalytical procedures for plant-support laboratories. He spent five years at the Babcock & Wilcox Nuclear Development Center near Lynchburg, VA, focusing on radiochemical separations research, before moving on to Los Alamos National Laboratory. He was with the Laboratory for 25 years, first with the Analytical Chemistry Group, and then with the Nuclear Materials Process Development Group. Fred's contributions to plutonium ion-exhange processing were recognized by a DOE Award of Excellence in 1986 and a LANL Distinguished Performance Award in 1988. He is co-inventor of a bifunctional anion-exchange resin that is highly selective for plutonium. This new resin has been licensed to Reilly Industries, which will manufacture it as a commercial prodcuct.

D. Kirk Veirs was born in Watsonville, CA, and received his B.S. in chemistry and environmental science from Northern Arizona University in 1976. He received his Ph.D. in physical chemistry from Pennsylvania State University in 1981. As a Director's-Funded postdoctoral fellow and technical staff member at Los Alamos (1981-1985) he measured rotationally induced changes in the Raman crosssection of hydrogen isotopomers. During a brief tenure at Lawrence Berkeley Laboratory from 1985–1990, he developed a method to spectroscopically image material properties. He returned to Los Alamos in 1990 and is now a Team Leader in the Nuclear Materials Technology Division. He studied the speciation of plutonium in nitric acid and is interested in the chemical changes that occur in stored actinide materials and other related surface processes. He is a member of the NMT Division Science Leadership Council and a corecipient of the 2000 R. D. Baker Award.

Gordon D. Jarvinen received his B.S. in chemistry in 1973 from the Massachusetts Institute of Technology and his Ph.D. in inorganic chemistry in 1979 from the University of California, Los Angeles. He was a resident research fellow at E. I. Du Pont de Nemours & Company during the summer of 1973 and a Postdoctoral Fellow at the Los Alamos National Laboratory for 1979–1981, where he is currently a technical staff member. His research interests include actinide and lanthanide coordination chemistry and separation technology, design and synthesis of ligand systems for improved separation and analysis of metal ions, development of chelating and ion-exchange polymers, and membrane separations. Gordon is a member of the American Chemical Society (ACS) and the American Association for the Advancement of Science, and is Chair of the ACS Separation Science and Technology subdivision of the Industrial & Engineering Chemistry Division for 2000.

Mary Barr received her B.S. in chemistry from the University of the South–Sewanee, TN, graduating with the "Orwellian Class" of 1984. She received her Ph.D. in inorganic chemistry from the University of Wisconsin at Madison in 1991. Her Los Alamos career began in 1991 as a Director's-funded postdoctoral fellow. She has been a staff member in the Nuclear Materials Technology Division since 1993. Her recent projects include the development of improved anion-exchange resins and extractants for actinides from process and waste streams. Her previous activities have ranged from synthesizing and evaluating ion-specific chelation systems to advising the Nuclear Materials Stabilization Task Group for the Defense Nuclear Facilities Safety Board on developing procedures for removing actinides from contaminated soils.

Eddie Moody attended Union University in Jackson, TN, where he received his B.S. in chemistry in 1992. He then attended the University of Memphis, where he received his M.S. in 1994 and his Ph.D. in 1997 in inorganic chemistry. He then went on to join Los Alamos National Laboratory as a postdoctoral fellow in the Nuclear Materials Technology Division, becoming a staff member in 1999. He is primarily interested in theoretical modeling of plutonium chemistry, but is also very interested in modeling the surface interactions of different compounds. His other hobbies are scuba diving and aviation.