**Actinide ion exchange technology in the back end of the nuclear fuel cycle**

**Abstract** Ion exchange is used extensively in nuclear power technology, especially for uranium ore processing, removal of contaminants from power reactor waters and in the back end of the nuclear fuel cycle. In nuclear fuel reprocessing plants, ion exchange is used for the purification of actinide elements for further use, for the solidification of low- and medium-active waste solutions, and for the partitioning of high-level wastes. This paper reviews selected technological uses of ion exchange in these operations for recovery, separation and purification of selected actinides (Pu, U, Np, etc.). Recent research and development on ion exchange technologies for actinides are also summarized.

**Key words** actinide separation and purification • adsorption and elution • ion exchange resin • reprocessing • separation process • spent nuclear fuel

**Introduction**

Ion exchange technology is used in many areas of the nuclear power industry. Nuclear reactor stations employ ion exchange resins for the removal of contaminants from the primary circuit, condensate and fuel storage waters, and for solidification of low- and medium-activity waste solutions [35]. In the back end of the nuclear fuel cycle, ion exchange is used for the solidification of waste solutions, as well as for the partitioning of radioactive elements for further use or disposal [43]. The application of ion exchangers for the separation and purification of radionuclides from nuclear process and waste solutions has increased significantly during the past two decades [17].

Irradiated or spent fuel discharged from nuclear reactors contains U, Pu, and fission products. Reprocessing technology is used to recover fissile values of these elements for reuse as nuclear fuel [18]. After storage and disassembly, the spent fuel is dissolved in nitric acid. The nitric acid concentration of the dissolver solution is then adjusted and the Pu(IV) oxidation state is stabilized by addition of sodium nitrite prior to tri-n-butyl phosphate (TBP) extraction (abbreviated Purex, representing Pu-U-Recovery-EXtraction). The Purex process is used to separate U and Pu from fission products [32].

The initial cycle of the Purex process co-extracts both Pu and U into TBP leaving the fission products, Np, Am and Cm, and small amounts of Pu and U in the raffinate or waste stream [36]. The second cycle, used to partition or separate the U from the Pu, consists of scrubbing the loaded TBP with a stripping solution containing a reducing agent to reduce Pu(IV) to the non-extractable Pu(III). Dilute nitric acid is then used to strip the U from the TBP.
The separated U and Pu streams are purified further by another cycle of the Purex process. Final purification of the U stream is accomplished by either a third cycle of the Purex process or more commonly by silica-gel adsorption. Purex, cation exchange and anion exchange have also been used as the tail-end purification step for Pu.

As alternative technologies for reprocessing spent fuel, several ion exchange processes have been reported in the recent years [10, 26, 39, 41]. For example, one complete flow sheet as shown in Fig. 1 uses a new type of anion exchanger, AR-01, where the resin, with benzimidazole groups as exchange sites, is embedded in porous silica particles [39, 41]. Compared to conventional anion exchange resins with polymeric matrix, this novel anion exchanger is characterized by rapid adsorption/elution kinetics, excellent stability in nitric acid media and significantly lower pressure loss in a packed column. Adsorption performance of U, Pu, Np and various fission products onto this anion exchanger from HNO₃ solution was investigated. In addition, the separation behavior of U and Pu from simulated spent nuclear fuel solutions was examined by column chromatography [39, 41].

This review discusses in detail both the cation and anion exchange processes for Pu separation and purification from Purex solutions. In addition, a brief overview is given of the exchange processes for Pu separation and purification from HNO₃ solution was investigated. In addition, the separation behavior of U and Pu from simulated spent nuclear fuel solutions was examined by column chromatography [39, 41].

Separation and purification of plutonium

History

All existing nuclear fuel reprocessing operations include recovery and purification of Pu free of U, fission products and other impurities. Methods such as evaporation, precipitation, solvent extraction and ion exchange have been proposed to accomplish the concentration and isolation of Pu. However, evaporation does not provide any decontamination, and even concentrates impurities, and precipitation yields high losses of Pu and poor decontamination. On the other hand, both solvent extraction and ion exchange have been used successfully and the latter method has the advantages of more compact equipment, simpler operation and less waste generation.

Both cation exchange and anion exchange can be used to separate Pu from fission products, U and other impurities [14, 29]. Of the two processes, anion exchange is more efficient and provides pure product solution readily handled in subsequent processing steps. Moreover, it was found that a combination of cation and anion exchange processing is most effective.

During the Manhattan Project, ion exchange was considered an alternative to the bismuth phosphate precipitation process used at Hanford for nuclear fuel reprocessing. A flow sheet, developed in 1943, used deep beds of newly developed organic cation exchange resins containing sulfonic acid groups [35]. The process consisted of loading Pu(IV) from a nitric acid solution onto the resin while uranyl nitrate and fission products passed through the column. The column was then washed free of residual U and fission products with dilute sulfuric acid and oxalic acid, respectively. Thereafter, the Pu was eluted with 0.4 M (M = mol/dm³) oxalic acid or 1.25 M sodium hydrogen sulfate. However, the newly developed organic cation exchangers were not adopted for primary fuel reprocessing because of low decontamination factors for fission products and satisfactory operation of the bismuth phosphate process. Later, once the bismuth phosphate precipitation process was replaced by solvent extraction, improved cation exchange resins with higher capacities did provide an alternative process for concentration and isolation of Pu from dilute product streams in solvent extraction processes.

A decade later, Durham and Mills [4] showed that Pu(IV) could be adsorbed on Dowex 1 anion exchange resins from 7–8 M nitric acid. Based on this work, Ryan and Wheelwright [29] evaluated process variables and various resins which provided operating conditions for subsequent utilization of anion exchange at Hanford and other sites [25, 43].

Cation exchange

Cation exchange, used to concentrate and recover Pu from the dilute product stream of the Purex process, is usually accomplished by adding sulfamic acid to the dilute nitric acid solution containing Pu to prevent the oxidation of Pu(III) to Pu(IV). It should be noted, however, that the redox process can cause gas bubbles of nitrogen oxides to form in the ion-exchange column and create channeling of the solution resulting in inefficient operation. The distribution coefficients (g Pu/g resin per g Pu/g solution) for Pu(III) and Pu(IV) are approximately 4,000 and 30,000, respectively. Although Pu(IV) has significantly higher distribution coefficients, loading Pu(III) takes less resin and complexes less with sulfate ion, thus lowering Pu losses during the U elution step. This is accomplished by passing the feed solution through the column of cation exchange resin, adsorbing Pu(III). Anions and most of the monovalent and divalent cationic impurities report to the effluent stream. U is washed from the resin with dilute sulfuric acid. The Pu is...
eluted from the resin with strong nitric acid, which yields a Pu concentration of 40–60 g/dm$^3$ in 5–6 M nitric acid.

As mentioned above, cation exchange does not yield good decontamination of some elements, and fission product decontamination factors are poor [36]. During loading, about 40% of the Ru reports to the effluent. The wash solution removes only small amounts of Ru and rare earths along with the U. Decontamination factors of beta and gamma products from Pu have been reported as 3 and 6, respectively. The primary benefit of cation exchange is product concentration. However, the high nitric acid concentration must be reduced to provide feed adaptable to liquid-to-solid conversion processes, such as peroxide, trifluoride or oxalate precipitation. The eluate solution is readily acceptable as feed to anion exchange. For this reason, a combination process using both cation and anion exchange is advantageous.

In most cases, Dowex 50-x12, 50–100 mesh resins were utilized. (Dowex 50 is a microreticular or gel type resin with 12% crosslinkage.) Newer macroreticular or macroporous (porous gel resins) cation exchange resins (20–50 mesh) have been evaluated for Pu loading and elution kinetics [34]. Dowex MSC-1 was found to have much faster Pu elution kinetics and better decontamination properties than Dowex 50.

In the United States, cation exchange was used routinely at the Savannah River Site for concentration of Pu [8]. Since anion exchange provides better product decontamination than cation exchange, it has been more commonly used since its introduction in 1959 [43].

Anion exchange

In the anion-exchange process, Pu is adsorbed on anion-exchange resin from a strong nitric acid solution and eluted with dilute nitric acid. In strong nitric acid solutions, Pu(IV) forms a hexanitrato anionic complex which strongly adsorbs on the resin. The maximum distribution coefficient for Pu(IV) is obtained in approximately 7 M nitric acid. As the nitric acid concentration increases between 6 and 10 M, acid species of the Pu(IV) complex are formed which are not adsorbed as strongly as the hexanitrato species. Furthermore, nitrate ions start competing with the Pu(IV) complexes for resin sites. Both these effects decrease the Pu(IV) distribution ratios at high nitric acid concentrations. Adding metal nitrates, such as aluminum or calcium nitrate, to low nitric acid feeds overcomes the former inadequacy and significantly increases the distribution coefficient for Pu. Fig. 2 shows the Pu(IV) adsorption behavior onto the anion exchanger, Dowex 1-x4 [29].

Pu(IV) adsorption is more strongly influenced by kinetics (which demand higher temperatures) than by equilibrium (which is an exothermic reaction and requires lower temperatures). The large size of the Pu hexanitrato complex presumably causes the ion-exchange rate to be slow. The loading kinetics can be increased by adjusting the temperature of the feed solutions to 333–343 K [29]. In the past, gel or microreticular anion-exchange resins such as Dowex 1-x4 or Permutit SK have been used for Pu purification. However, newer macroreticular or macroporous resins have shown to have better loading and elution kinetics [23]. It is well known that in many cases, the ion exchange kinetics is limited by the diffusion step inside the resin phase, and a reduction in the bead size of the resin will lead to more rapid kinetics. Notwithstanding, the large bead (20–50 mesh) macroporous resins still do not out-perform small bead (50–100 mesh) Dowex 1-x4 except perhaps the new Reillex resins [19]. A newer anion exchanger, AR-01, combining macroporous resins to a unique porous silica particles with a diameter of 50 µm, characterized in Table 1, has shown significantly improved kinetics (Fig. 3) [39, 41].

Continuing with the description of the column operation, after loading, the resin is usually washed with 6–7 M nitric acid to remove weakly adsorbed impurities. Pu can be eluted from the resin with dilute nitric acid because the anionic Pu(IV) nitrato-complex is destroyed. Usually 0.35 M nitric acid is used and lower acid concentrations are avoided to prevent hydrolysis and Pu polymer formation. Eluent solutions containing reducing agents can improve elution kinetics by forming Pu(III). Some reducing agents can add

Fig. 2. Distribution coefficients of Pu(IV) onto Dowex 1-x4 anion exchanger from nitrate solution [29].

Fig. 3. Time evolution of Pu(IV) adsorption from nitric acid solution onto AR-01 anion exchanger (6 mol/dm$^3$ HNO$_3$, 297 K).
impurities, such as iron and sulfate, but the use of hydroxylamine nitrate, occasionally coupled with hydrazine, does not produce additional impurities. The use of ascorbic acid can cause precipitate formation from the reaction products of the reductant. Further, reducing agents can cause gassing problems in the column resulting in channeling of solution and inefficient elution. Wei and co-workers found that Pu(IV) can be eluted rapidly from an anion exchanger by using dilute formic acid as an eluent [42]. Near complete elution of the adsorbed Pu(IV) from the AR-01 anion exchanger was achieved by supplying 0.53 bed volume of 1 M HCOOH to the column (Fig. 4). Pu product concentrations of 50–60 g/dm³ can typically be attained in 2–3 M nitric acid, readily adaptable for liquid-to-solid conversion processes such as oxalate or peroxide precipitation [3].

The anion-exchange process offers excellent product decontamination since few metal ions form anions in 6–7 M nitric acid [2, 7]. Np(IV) and Th(IV) also form hexanitratoo complexes which can load on the resin. The nitrato complexes of the tetravalent actinides have stability constants much higher than the hexavalent actinides. The stability constants for trivalent and pentavalent actinide nitrate complexes are very small. Most elements do not form anionic complexes in nitric acid and the distribution ratio of these elements adsorbed onto anion exchange resin from 1–14 M nitric acid is low [7]. Most fission products can not be adsorbed by anion exchange resin in nitric acid except for some adsorption of Ce(IV), Tc(VII) and platinum group metals such as Pd and Ru [6, 40, 41]. The elements that show weak adsorption can be easily washed from the resin with only one or two bed volumes of 6–7 M nitric acid. Elements such as Hg(I), Ce(III), U(VI) and Bi(III) require more wash solution volume, even as much as 20 bed volumes. The strongly adsorbed platinum group metals can be separated from Pu because they do not elute with dilute nitric acid. Thus, under the proper conditions, use of anion exchange can separate Pu from all elements except Np(IV) and Th(IV).

Anion exchange was used routinely for the third cycle of Pu purification following Purex solvent extraction [3]. Further, Pu was concentrated and purified effectively from irradiated fuel solutions. The resultant gamma decontamination factors for Pu were $2 \times 10^4$ in a single cycle and $4 \times 10^7$ in two cycles; Nb was the limiting activity. The same process was used to recover $^{238}\text{Pu}$ and $^{237}\text{Np}$ in the production of $^{238}\text{Pu}$ for isotopic heat sources [31].

One cycle of Purex was eliminated at Hanford by utilizing anion exchange purification of Pu [14, 36]. The process was operated continuously using a Higgins contactor [28]. The loading and elution sections were both 13 cm in diameter and 2.1 m high. The resin was loaded to a Pu concentration of 30–50 g Pu/dm³. The effluent stream, containing 0.5% of the Pu feed, was recycled to prevent any loss. The process, operated for more than 2 years with an efficiency of about 95%, provided good decontamination of U (10⁵–10⁶), fission product impurities (10⁴ for Ru and 10⁵ for Zr-Nb), and other impurities.

Anion exchange was used for the recovery of Pu from oxalate solutions, however it was discovered that nitric acid concentration of 9 M was required to prevent interference from oxalate [18]. Interference of fluoride ion in anion exchange processing can be overcome by adding aluminum nitrate to complex the fluoride ion.

### Separation and purification of other actinides

Although till now the most important use of actinide ion exchange in fuel reprocessing is the tail-end purification and concentration of Pu following Purex processing, ion exchange has also been utilized for the purification of U and the separation and recovery of individual actinide elements and isotopes. Excellent reviews of ion exchange in
the atomic energy industry have summarized the studies dealing with Th, Pa, U, Np, Pu, Am, Cm and actinide-lanthanide separations, and the heavy actinides Bk, Cf, Es and Fm [11–13]. Other reviews contain various articles on actinide separation, recovery and purification [1, 24].

Uranium

The most common tail-end process for U purification is silica-gel adsorption, where the U nitrate solution is passed through the silica-gel column which removes gamma-emitting impurities by a factor of approximately 20. Ion exchange has also been utilized to a lesser degree. In this regard, U was decontaminated of Ru by a factor of 10 or greater. This was accomplished as follows: uranyl nitrate solution was first heated at 363 K for 1/2 h after adding 2 g/dm³ thiourea. This solution is then passed through a bed of carboxylic acid resin which adsorbs the Ru. The Ru was then stripped from the resin with 6 M nitric acid. U has also been concentrated from a dilute solution by adsorption on sulfonic type cation exchange resins [18].

A new process utilizes the adsorption of tetravalent uranium on anion exchange resin. To enhance the separation factor between U and the adsorptive fission products such as Zr and Ru, Wei and co-workers investigated the electrolytic reduction of UO₂²⁺ to U⁴⁺ which shows considerably stronger adsorption onto the anion exchanger than UO₂²⁺ in HNO₃ solution (Fig. 5) [38, 39]. The electroreduction was successfully performed using a novel flow type cell containing a carbon fiber column electrode. After electroreduction, complete separation of U(IV) from the fission products was achieved by the ion exchange column [38, 39].

Neptunium

Np(IV) can be separated from U, Pu and other common metallic impurities by adsorption on anion exchangers from a 6 M nitric acid solution containing a reducing agent such as ferrous sulfamate to maintain Pu(III) and Np(IV) [31]. The impurities are washed from the column with 6 M nitric acid. The adsorption and elution behavior of Np(IV) was found to be very similar to Pu(IV).

Fig. 5. Distribution coefficients of U(IV) and U(VI) onto AR-01 anion exchanger from nitric acid solution (333 K) [39].

Other actinide elements

Cation exchange, usually in conjunction with other separation processes, has been used to separate and purify Am and heavy actinides [5, 18, 30, 32, 35, 43]. Additional applications of ion exchange in nuclear fuel reprocessing, including low-level waste treatment, continue to be developed [17, 33].

Resin stability and safety considerations

Various studies have been performed on the chemical and radiation stability of ion exchange resins [15, 16, 20, 21, 27, 37]. Some accidents and failures occurred in ion exchange operations have been investigated and reviewed [9, 22]. From a safety standpoint, the most important consideration in actinide ion exchange technology is the prevention of over-pressurization and elevated temperature in the column. Anion exchange resins loaded with Pu nitrate complex contain up to three nitrate ions per exchange site compared to nitrate from resin with only one nitrate ion per site. If the column is not vented and elevated temperature should occur, an exothermic and auto-catalytic reaction can result and a rapid chemical excursion can take place. Furthermore, if the resin loaded with Pu is permitted to dry out, the situation is further aggravated. Precautions are taken to insure that this circumstance does not occur. It is important to note that whenever the anion exchange process is shut down for any period of time exceeding 8 h, a resin bed is left saturated with dilute nitric acid. As an additional safety measure, the resin bed is never left loaded with Pu for more than 8 h at one time. Further, the columns should be fitted with rupture disks to prevent over-pressurization.

References


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