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Separation of actinides from simulated spent fuel solutions by an advanced ion-exchange process

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Abstract

In order to develop an advanced ion-exchange process to recover U, Pu and other actinide elements from the spent fuels of light-water reactors (LWR), we have manufactured a new type of anion-exchanger characterized by a rapid adsorption–elution rate, high mechanical strength and relatively excellent radiation-resistance. The separation behavior of some actinide elements from simulated spent fuel solutions containing concentrated nitric acid was examined experimentally by ion-exchange chromatography using dilute nitric acid, uranous and thiourea as eluents. U(VI), Np(V), Np(IV) and Np(VI) showed similar adsorption–elution behavior and could be separated from most fission product elements (FPs) such as Cs(I), Sr(II), Mo(VI), Rh(III), Pd(II) and Tc(VII) and trivalent rare earths. Pu(IV) was strongly adsorbed by this anion-exchanger and was effectively eluted as Pu(III) using U(IV)–N_2H_4 as reductive eluent. Am(III) was not adsorbed and mixed with the non-adsorptive FPs. © 1998 Elsevier Science S.A.

Keywords: Actinides; Adsorption; Elution; Ion-exchange; Separation; Spent nuclear fuel

1. Introduction

Since ion-exchange possesses many attractive advantages, such as simple operating procedure, organic solvent free and compact equipment, it has great potential in the application of the reprocessing of spent nuclear fuels. However, during the past decades ion-exchange technology has found very limited application in nuclear fields such as the concentration and purification of actinide elements [1,2]. A slow adsorption–elution rate and an unsatisfactory decontamination factor are considered to be the major reasons for the limited industrial application.

In order to develop an advanced ion-exchange process for recovery of U, Pu and other actinide elements from the spent fuels of LWRs, we have developed a novel anion-exchanger with the resin embedded in porous silica beads. Compared to commercial polymer bead anion-exchangers, this anion-exchanger is characterized by a rapid adsorption–elution rate, high mechanical strength and relatively excellent radiation-resistance [3,4]. Fundamental studies on the adsorption and elution behavior of some actinides and various FP elements with this anion-exchanger have been performed [4–8]. It was found that, in HNO_3 solution, FPs mostly exist in cations with no or very weak adsorption onto the anion-exchanger, while actinides such as U(VI), Np(IV, V, VI) and Pu(IV) exhibit distinct adsorption with the formation of anionic nitrato-complexes. In this work, the separation behavior of U, Np, Pu, Am and typical FP elements from simulated nitric acid solutions of spent LWR fuel was examined by ion-exchange chromatography using dilute nitric acid, uranous and thiourea as eluents.

2. Experimental

The novel anion-exchanger, called AR-01, with macroreticular resin embedded in porous silica beads was used. Its structure and properties are shown in Table 1. The anion-exchanger contains *N*-methylbenzimidazole and *N*,*N′*-dimethylbenzimidazolium groups as exchange sites. The diameter of the silica beads is 40–60 μm, which is about 1/10 of conventional resin beads and provides a rapid ion-exchange rate.

Table 2 illustrates the composition of the simulated spent fuel solutions employed in the separation experiments. The separation experiments were carried out using Pyrex glass columns of 10–20 mm inner diameter and 1000 mm length. Fig. 1 shows a schematic diagram of the column apparatus. The AR-01 anion-exchanger was

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Table 1
Structure and properties of the AR-01 anion-exchanger

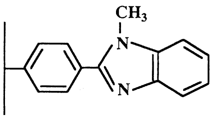
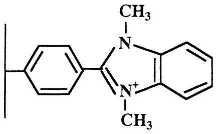
Functional group	
4-(1-Methylbenzimidazole-2-yl)phenyl	4-(1,3-Dimethylbenzimidazolium-2-yl)phenyl
	
Carrier bead	Porous SiO_2
Bead diameter (μm)	40–60
Mean pore size of beads (nm)	600
Pore fraction in beads	0.69
Matrix structure of resin	Macroreticular polystyrene
Resin content (wt%)	24.4
Total capacity (meq/g resin)	3.4
Quaternary capacity (meq/g resin)	2.0

Table 2
Composition of simulated spent fuel solutions for separation experiments

Solution	Element concentration (mM)
A	U(VI) 100, Cs(I) 5, Sr(II) 5, Y(III) 5, Nd(III) 5, Zr(IV) 2.5, Mo(VI) 2.6, Ru(III) 6, Rh(III) 2.5, Pd(II) 5, 6 M HNO_3
B	U(VI) 500, Np(V,VI) 5, Cs(I) 2, Sr(II) 1, Zr(IV) 5, Nd(III) 3, Tc(VII) 1, 6 M HNO_3
C	U(VI) 1050, Pu(IV) 12.4, Np(V) 4.2, Am(III) 0.12, Cs(I) 7.5, Nd(III) 9.7, Zr(IV) 11.0, Tc(VII) 6.8, 6 M HNO_3

charged into the column as a slurry. The height of the ion-exchanger bed was 850–900 mm. The column and the throughput solutions were maintained at 333 K with heating water jackets. The simulated spent fuel solution was fed into the column at a constant flow rate of 3.8 or 9.0 m h^{-1}. Then the eluent solutions, i.e. HNO_3, U(IV)–N_2H_4 (reductive eluent for Pu(IV)) and thiourea (Tu, H_2NCSNH_2), were applied to the column successively. The effluents from the column were recovered by fractional collectors with a volume of 6–15 cm^3. The element concentrations in each collector were analyzed quantitatively by means of ICP spectroscopy (for Experiments A and B) and γ-spectrometry (for Experiment C). The valence of the actinides in the effluents was measured qualitatively by UV spectrometry.

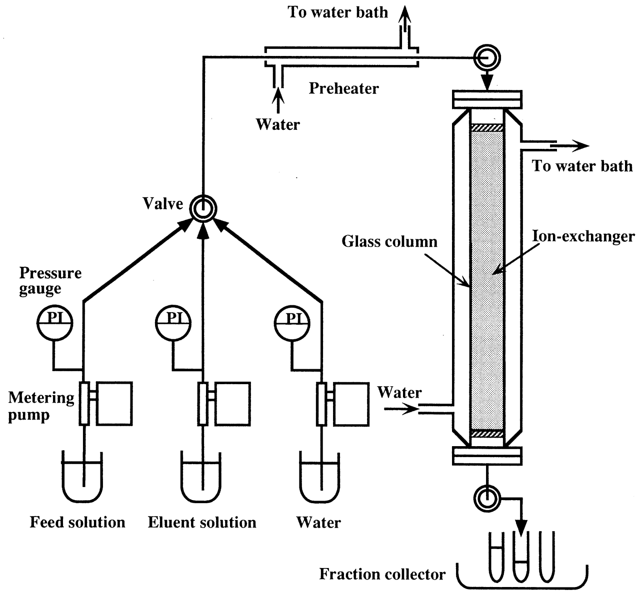


Fig. 1. Schematic diagram of the column apparatus for separation experiments.

3. Results and discussion

To examine the separation behavior of various FPs from U, a column experiment was carried out for simulated spent fuel solution A containing U(VI) and typical FPs. The results are illustrated in Fig. 2. As can be seen, the elements Cs(I), Sr(II), Y(III), Nd(III), Mo(VI) and Rh(III) showed almost no adsorption. These elements leaked out with the feed solution and the 6 M (M=mol dm^{-3}) HNO_3 washing solution. U(VI) was completely adsorbed by the anion-exchanger and eluted by 1 M HNO_3 solution. Perfect separation between U(VI) and the above FPs was achieved. A portion of the Zr(IV) adsorbed onto the anion-exchanger and leaked out with 6 M HNO_3 behind the above non-adsorptive elements. Ru(III) was completely adsorbed and showed a broad elution curve from 6 M to 0.1 M HNO_3 eluent solution. This complicated elution performance may be explained by the HNO_3 concentration dependence of Ru(III) adsorption. Ru(III) exhibits a quite closed distribution ratio in this HNO_3 concentration range [6]. Therefore, the separation method for Ru(III) from

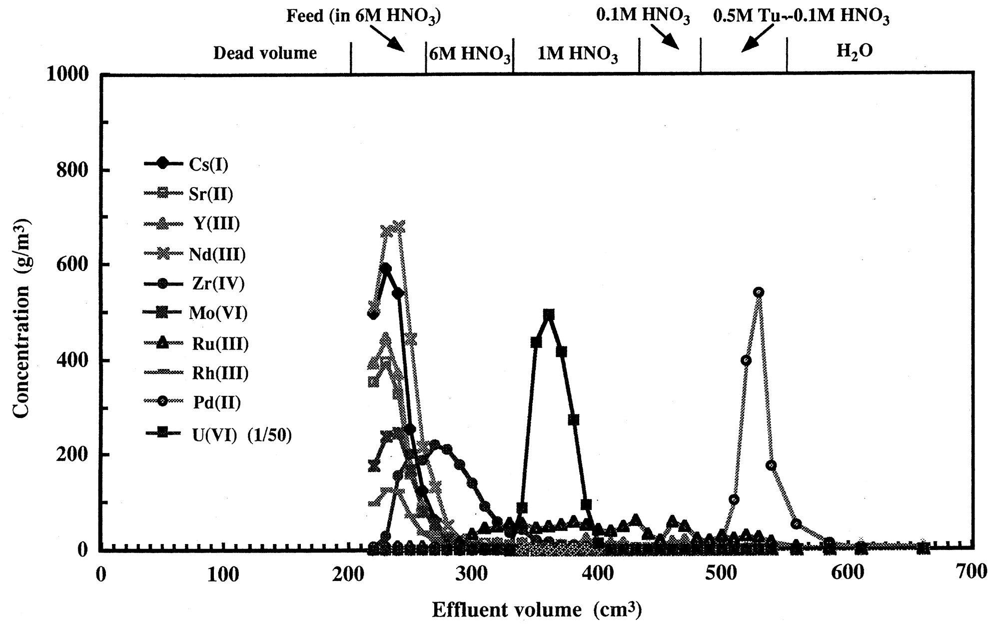


Fig. 2. Elution curves of column experiment for simulated spent fuel solution A (column ϕ 20 mm, h 1000 mm, flow rate 3.8 m h^{-1}, temp. 333 K).

U(VI) necessitates further investigation. On the other hand, Pd(II) was strongly adsorbed by the anion-exchanger and was effectively eluted by thiourea solution. Complete separation of Pd(II) from U(VI) and other FPs was achieved. It was found that the elution order for all the elements is in good agreement with the adsorbability as described in previous reports [6,7].

Fig. 3 shows the results of the column experiment for simulated spent fuel solution B containing Np(IV, V, VI), Tc(VII), U(VI) and several PFs. It was found that the non-adsorptive FPs such as Cs(I), Sr(II) and Nd(III) and the weakly adsorptive Zr(IV) showed almost the same behavior as shown in Fig. 2. U(VI) was eluted by dilute HNO_3 solution behind these FPs. However, a portion of the U(VI) mixed with the tail fraction of the FPs, which probably results from the fact that the U(VI) concentration in the feed was increased from 0.1 M (in Experiment A) to 0.5 M. Both Np(V) and Np(VI) were adsorbed by the anion-exchanger. They were eluted by 1 M HNO_3 and mixed in the U(VI) fraction. Further separation of Np from U is expected by reducing Np(V) and Np(VI) to Np(IV) which has significantly stronger adsorption than U(VI) [8].

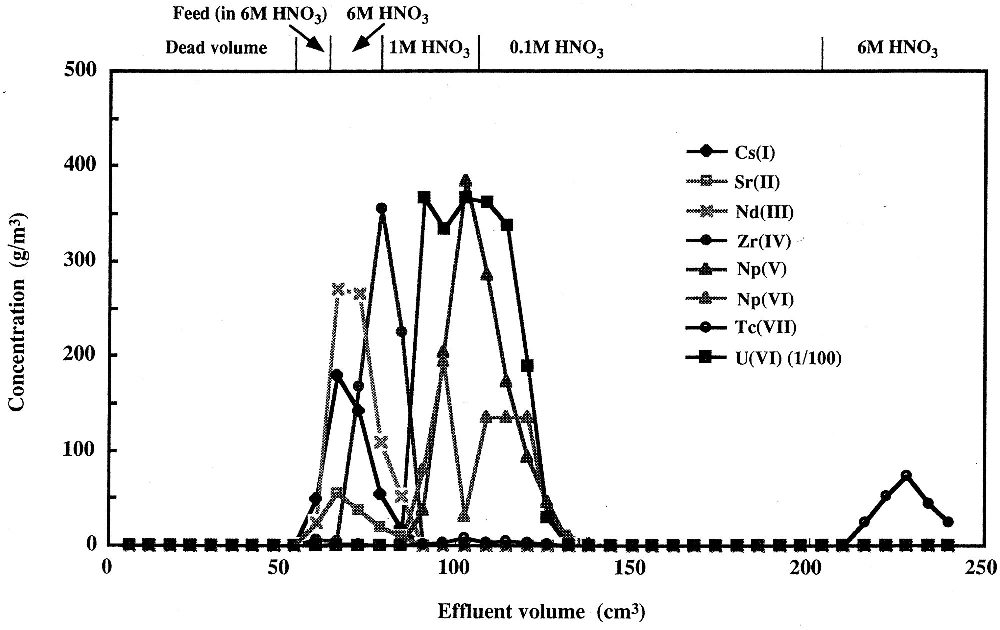


Fig. 3. Elution curves of column experiment for simulated spent fuel solution B (column ϕ 10 mm, h 1000 mm, flow rate 3.8 m h^{-1}, temp. 333 K).

Tc(VII) was strongly adsorbed by the anion-exchanger and eluted by 6 M HNO_3. Tc(VII) was considered to be adsorbed in the form of TcO_4^- and the adsorption decreased with increasing HNO_3 concentration [8,9].

To investigate the separation behavior of Pu and Am, a column experiment was performed for simulated spent fuel solution C containing Pu(IV), Am(III), U(VI), Np(V) and several PFs. Since Pu(III) presents almost no adsorption onto the anion-exchanger, U(IV)–N_2H_4 solution was utilized as a reductive eluent for Pu(IV) in this experiment. The results of this experiment are shown in Fig. 4. As can be seen, non-adsorptive Cs(I) and Nd(III) and weakly adsorptive Zr(IV) showed the same behavior as illustrated in Figs. 2 and 3. Am(III) also presented no adsorption and mixed with the non-adsorptive FPs. U(VI) and Np(V) showed similar behavior as in Fig. 3, but a portion of the U(VI) was not adsorbed and leaked out together with the FPs mentioned above. This may result from the higher U(VI) feed concentration (1.05 M) and the faster flow rate (9.0 m h^{-1}) employed in this experiment. Pu(IV) was completely adsorbed and showed complicated elution behavior. Most Pu(IV) was effectively reduced by U(IV)–N_2H_4 and eluted as Pu(III). About 95% of Pu was separated from the FPs and U(VI) contained in the feed. However, the excess reductant U(IV) leaked out together with Pu(III) and their separation needs to be investigated further. Only 38% of the adsorbed Np(V) was eluted in this experiment. This may be explained by assuming that the remainder was reduced by U(IV) to the strongly adsorptive Np(IV) which is difficult to elute with 1 M HNO_3. Furthermore, no Tc(VII) was eluted; this is presumed to be due to the complicated catalytic redox reactions with U(IV)–N_2H_4 [10].

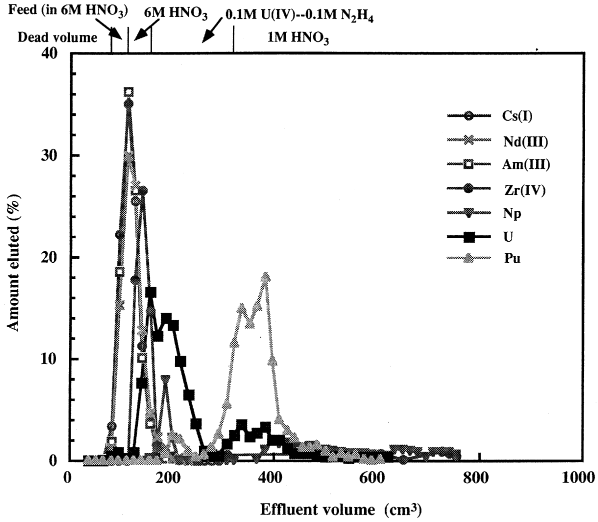


Fig. 4. Elution curves of column experiment for simulated spent fuel solution C (column ϕ 17 mm, h 1000 mm, flow rate 9.0 m h^{-1}, temp. 333 K).

4. Conclusions

The separation behavior of actinides from simulated spent fuel solutions in 6 M HNO_3 was examined by column chromatography using the novel anion-exchanger AR-01. U(VI), Np(V), Np(IV) and Np(VI) showed similar adsorption–elution behavior and could be separated from most FP elements such as Cs(I), Sr(II), Mo(VI), Rh(III), Pd(II) and Tc(VII) and trivalent rare earths. Pu(IV) was strongly adsorbed by the anion-exchanger, and was effectively eluted as Pu(III) by using U(IV)–N_2H_4 as reductive eluent. Am(III) was not adsorbed and mixed with the non-adsorptive FPs.

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