STUDIES ON THE SEPARATION OF MINOR ACTINIDES FROM HIGH-LEVEL WASTES BY EXTRACTION CHROMATOGRAPHY USING NOVEL SILICA-BASED EXTRACTION RESINS

REPROCESSING

KEYWORDS: *minor actinides, silica-based extraction resins, Cyanex 301*

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To develop an advanced partitioning process by extraction chromatography using a minimal organic solvent and compact equipment to separate minor actinides such as Am and Cm from nitrate acidic high-level waste (HLW) solution, several novel silica-based extraction resins have been prepared by impregnating organic extractants into the styrene-divinylbenzene copolymer, which is immobilized in porous silica particles (SiO_2-P). The extractants include octyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide (CMPO), di(2-ethylhexyl)phosphoric acid (HDEHP), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301). Compared to conventional polymer-matrix resins, these new types of extraction resin are characterized by rapid kinetics and significantly low pressure loss in a packed column.

The results of separation experiments revealed that trivalent actinides and lanthanides can be separated from other fission products, such as Cs, Sr, and Ru in simulated HLW solution containing concentrated nitric acid by extraction chromatography using a CMPO/SiO_2-P resin-packed column. Satisfactory separation between Am(III) and a macro amount of lanthanides from simulated HLW solution with pH 4 was achieved by using a newly purified Cyanex 301/SiO_2-P resin. However, the Am(III) separation was very sensitive to the purity of Cyanex 301, and the improvement of its stability is an important task for practical utilization.

INTRODUCTION

In the PUREX process, the long-lived minor actinides (MA) such as Am and Cm are generally produced together with various fission product elements (FPs) as high-level waste (HLW) containing concentrated nitric acid. As a final disposal method for HLW, the geologic disposal concept of vitrified HLW has been proposed and investigated worldwide. On the other hand, from the viewpoints of minimizing the long-term radiological risk and facilitating the management of HLW, an isolation of the long-lived MA from HLW is much more desirable. For this purpose, a number of partitioning processes (e.g., TRUEX, TRPO, DIDPA, and DIAMEX) have been developed in recent years.[1–7] However, all these processes essentially utilize liquid-liquid extraction technology by using a mixture of an organic extractant and a hydrocarbon diluent. A large amount of the so-called secondary waste, which is difficult to treat and dispose of, will be generated by the extraction process. In addition, the liquid-liquid extraction process is basically only beneficial for a large-scale process.[8,9] Compared to U and Pu, the minor actinides are significantly less abundant in the spent fuel, so the scale of the separation process for minor actinides

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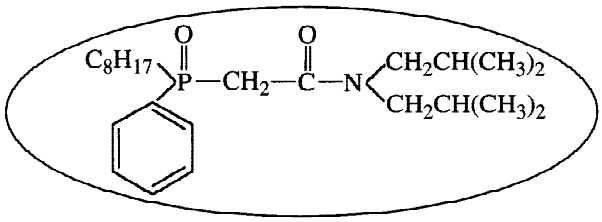
from HLW should be considerably smaller than that of the PUREX process.

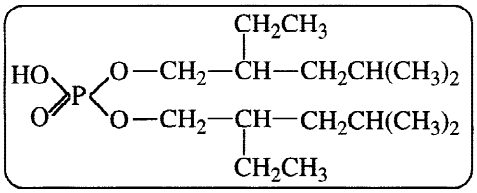
As an alternative method of reprocessing spent nuclear fuels, in recent years we have been investigating an advanced ion exchange process using a novel silica-based anion exchanger.[10–13] In the column separation experiments using simulated spent-fuel solutions, Am(III) and Cm(III) showed no adsorption onto the anion exchanger and leaked out together with most of the FPs, such as Cs(I), Sr(II), and trivalent lanthanides [Ln(III)]. This HLW stream contains approximately 3 to 6 M ($1\,M$ = mol/dm^3) HNO_3.

To develop an advanced partitioning process by extraction chromatography, which utilizes a minimal organic solvent and compact equipment to separate the minor actinides from the nitrate acidic HLW, we have prepared several novel silica-based extraction resins by impregnating an organic extractant into the styrene-divinylbenzene copolymer, which is immobilized in porous silica particles. Compared to the conventional polymeric matrix resins, these new types of extraction resin are characterized by rapid adsorption-elution kinetics, high mechanical strength, and significantly low pressure loss in a packed column. The extractants employed were octyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide (CMPO), di(2-ethylhexyl)phosphoric acid (HDEHP), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301). Figure 1 shows the chemical structures of these extractants. CMPO has been reported to have a strong extracting ability for trivalent actinides and lanthanides from highly acidic solution.[14,15] HDEHP is well known as a selective extractant for the separation of lanthanides. Cyanex 301 is a commercial extractant,[a] and its purity is 75 to 85%. Recently Zhu et al.[16,17] reported that the purified Cyanex 301, which contains sulfur atoms as the soft donor, is an excellent extractant for the separation of Am(III) from Ln(III).

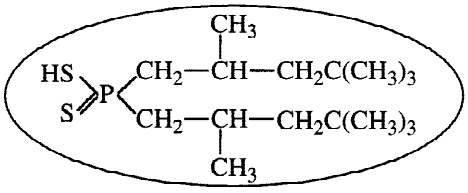
This paper describes the preparation procedure for the novel silica-based extraction resins and their adsorption characteristics for Am(III) and Ln(III) in nitrate acidic solutions. Furthermore, the separation behavior of Am(III), Ln(III), and other typical FPs from simulated HLW solutions is demonstrated by column chromatography. Based on the experimental results, an advanced partitioning process is proposed for the isolation of the minor actinides from a nitrate acidic HLW stream using these new types of extraction resin.



CMPO (octyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide)



HDEHP (di(2-ethylhexyl)phosphoric acid)



Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid)

Fig. 1. Chemical structures of the extractants.

EXPERIMENT

Preparation of Silica-Based Extraction Resins

Spherical silica particles[b] with a diameter of 40 to 60 μm, a mean pore size of 600 nm, and a pore fraction of 0.69 were used. To support the extractants, an inert copolymer of formylstyrene and divinylbenzene was synthesized and embedded in the pores of the silica particles. The preparatory flow sheet of the polymer-immobilized silica particles (SiO_2-P) is illustrated in Fig. 2. The silica particles were put into a glass flask placed in a rotary evaporator. The flask was evacuated by a vacuum pump, and a mixture of the monomers (85 wt% m/p-formylstyrene and 15 wt% m/p-divinylbenzene), initiators (α,α-azobisisobutyronitrile and 1,1′-azobiscyclohexane-1-carbonitrile), and diluents (1,2,3-trichloropropane and m-xylene) was sucked into the flask through a rubber tube. The flask was rotated continuously so that the mixture would soak completely into the pores of the silica particles and then filled with N_2 gas. The flask was maintained in a silicone oil bath and then heated at 363 K for 20 h. The grafted material (SiO_2-P) was washed with acetone and water and then dried overnight at 323 K. The content of the inert copolymer, formylstyrene-divinylbenzene, in the SiO_2-P particles obtained was 17.6 wt% measured by means of thermogravimetric analysis (TGA).

The extractants, CMPO, HDEHP, and Cyanex 301, were impregnated into the SiO_2-P particles. CMPO and HDEHP were used as commercially available products without further purification. A commercial Cyanex 301 product (purity 77.2%) was purified as previously

[a] From Cytex Canada.
[b] From Asahi Chemical Industry.

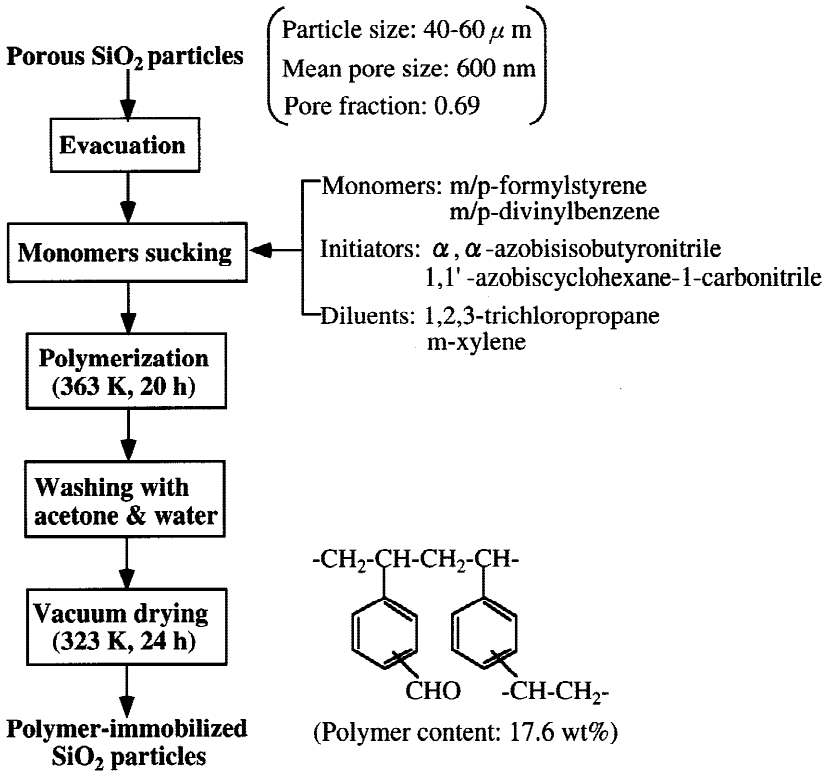


Fig. 2. Preparatory flow sheet of the polymer-immobilized silica particles (SiO_2-P).

described,[18,19] and the purity of the Cyanex 301 obtained was 99.5%. The impregnation procedure of the extractants into the SiO_2-P particles is as follows: ~5 to 7 g of an extractant (CMPO, HDEHP, or Cyanex 301) was placed in a glass flask and dissolved using 20 cm^3 of dichloromethane as a diluent. Subsequently, 10 g of the dried SiO_2-P particles was added to the solution and was shaken mechanically for 2 h at 298 K. The resulting mixture was filtered and washed with a large amount of water over a sintered glass funnel to remove the diluent. The filter cake was then dried in vacuo overnight at 323 to 333 K, and the silica-based extraction resin was obtained. The amount of impregnated extractant was measured by TGA, and the values were found to be 0.4 to 0.6 g/g SiO_2-P. To obtain a polymer-based extraction resin for the comparison experiments to evaluate the adsorption kinetics, the HDEHP extractant was impregnated into a polymeric beads material, Amberlite XAD-7 (mean particle size: 450 μm), which has been widely employed as a support of extraction resins,[15,20] by the aforementioned impregnation procedure.

Adsorption Experiment

All distribution coefficients (K_d) were measured by batch adsorption experiments, and the K_d values for radionuclides were determined radiometrically. In a batch adsorption experiment, a weighed amount of extraction resin (typically, 0.25 g) was combined in a glass vial with Teflon stopper with a measured volume (typically, 5 cm^3) of an aqueous solution spiked with a trace amount ($\sim 10^{-7} M$) of the radionuclides, ^{241}Am, ^{153}Gd, ^{152}Eu, and ^{139}Ce. The resultant mixture was shaken mechanically for more than 1 h. The mixture was then centrifuged until the supernatant was free from suspended extraction resin and 1-cm^3 aliquots of the liquid were sampled for analysis. The gamma activity of the radionuclides was determined by a gamma-ray spectrometer with a Ge detector (Ortec). The lines at energies of 59, 97, 122, and 166 keV were used for evaluating the ^{241}Am, ^{153}Gd, ^{152}Eu, and ^{139}Ce, respectively. Care was taken during measurements to ensure that the pulse rates were generally at least 10 000 to maintain the statistical error of individual measurements on the order of 1%. The distribution coefficient was calculated by

$$K_d = \frac{C_0 - C_S}{C_S} \times \frac{V_S}{W_R}$$

$$= \frac{A_0 - A_S}{A_S} \times \frac{V_S}{W_R} \ (\mathrm{dm^3/kg}) \ , \qquad (1)$$

where

$C_0(A_0)$ = nuclide concentration (activity) in the aqueous phase before adsorption

$C_S(A_S)$ = nuclide concentration in the aqueous phase after adsorption

W_R = weight of the dry extraction resin (kg)

V_S = volume of the aqueous phase (dm^3).

The details of distribution coefficient measurements for stable nuclides were given in previous articles.[10,12]

Separation Experiment

Separation experiments for simulated HLW solutions were carried out using a Pyrex-glass column with 10-mm inner diameter and 200-mm length. Figure 3 shows a schematic of the column apparatus. An extraction resin (dry weight: 7.0 to 7.5 g) was transferred to the column in the slurry state under 2 to 3 bars of N_2 pressure. The volume of the resin bed (BV) was ~11.5 to 12.0 cm^3. The column and the throughput solutions were kept at a constant temperature with heated water jackets. Prior to the chromatographic operation, the extraction resin was conditioned by passing 100 cm^3 of a blank solution with the same pH (acid concentration) as in the simulated HLW solution through the column. In the separation experiments using Cyanex 301–impregnated extraction resin, 20 cm^3 of a simulated HLW solution (pH 4.0) containing trace amounts of ^{241}Am, ^{153}Gd, ^{152}Eu, and ^{139}Ce, 1 M $NaNO_3$, and a macro amount of Eu(III) (10^{-2} M) was applied to the column at a constant flow velocity of 1.0 cm^3/min (0.76 m/h) by a high-performance liquid chromatography metering pump. The 20 cm^3 of HNO_3 acidic solution with pH 4.0 was fed to the column as the rinse solution to wash the column and the extraction resin. Subsequently, 30 cm^3 of 0.1 M HNO_3 was supplied to the column as the eluent solution. The effluents from the column were collected by an autofractional collector in 3-cm^3 aliquots. The gamma activity of the radionuclides in each fraction was counted by the gamma spectrometer as previously described. In the separation experiments using CMPO-impregnated extraction resin, a simulated HLW solution containing 5×10^{-3} M of Ln(III), some typical FPs, and 3 M HNO_3

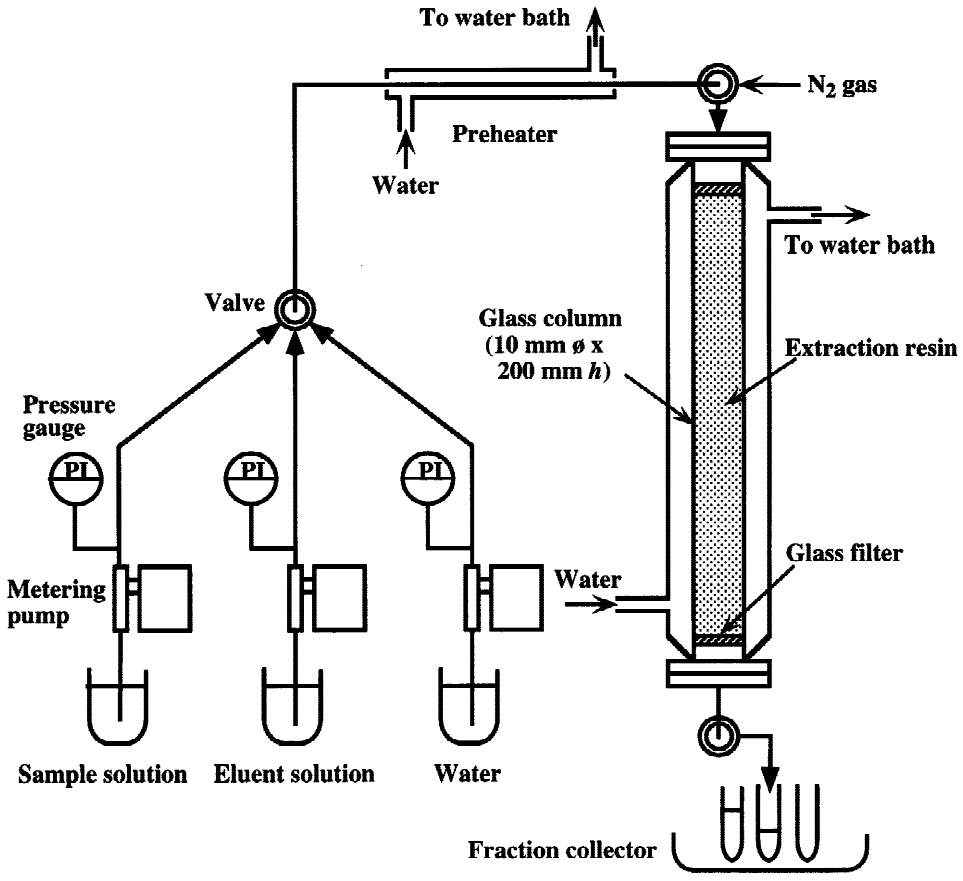


Fig. 3. Schematic of the column apparatus for separation experiments.

was used. Distilled water was utilized as the eluent. The metal concentrations in the effluents were determined by inductively coupled argon plasma spectroscopy (Shimadzu ICPS-1000III).

RESULTS AND DISCUSSION

Adsorption Characteristics

According to previous studies,[3,16,21,22] the adsorption reactions of trivalent metal ions onto CMPO-, HDEHP(HA)-, and Cyanex 301(HX)-impregnated extraction resins can be expressed by Eqs. (2), (3), and (4), respectively, which are the same as those for liquid-liquid extraction:

$$M^{3+} + 3NO_3^- + 3CMPO = M(NO_3)_3(CMPO)_3 \ , \quad (2)$$

$$M^{3+} + 3(HA)_2 = M(HA_2)_3 + 3H^+ \ , \quad (3)$$

and

$$M^{3+} + 2(HX)_2 = MX_3(HX) + 3H^+ \ . \quad (4)$$

To evaluate the adsorption kinetics of the silica-based extraction resins, the time evolution of Nd(III) adsorption from 0.1 *M* HNO_3 solution onto the HDEHP-impregnated extraction resin was measured, and the results are illustrated in Fig. 4. As can be seen, the Nd(III) adsorption onto the HDEHP/XAD-7 resin was very slow and still continued after 20 h. On the other hand, with HDEHP/SiO_2-P resin, the adsorption is quite rapid and reached an equilibrium state after ~30 min. The adsorption kinetics of metal ions onto impregnated extraction resins has been investigated by some authors.[23,24] It is well known that in many cases, the adsorption kinetics is limited by the diffusion step inside the resin, and a reduction in the particle size of an extraction resin will lead to more rapid kinetics. The particle size of HDEHP/SiO_2-P resin is 40 to 60 μm, which is $\sim\frac{1}{10}$ of the HDEHP/XAD-7 resin, so the rapid adsorption kinetics shown by HDEHP/SiO_2-P resin is considered to result mainly from the fine particle size.

The leakage behavior of the HDEHP extractant from the extraction resin during the adsorption experiment is also shown in Fig. 4. It is apparent that the leaked amount was very slight (<1%) and did not increase with time.

Figure 5 shows the effect of HNO_3 concentration on the adsorption of ^{241}Am(III), ^{153}Gd(III), ^{152}Eu(III), and ^{139}Ce(III) from nitric acid solution onto HDEHP/SiO_2-P resin. Note that the adsorption of these nuclides significantly decreased with increasing HNO_3 concentration. This is due to the increase of H^+ concentration and can be explained by the equilibrium of Eq. (3). As shown in Fig. 5, the heavy Ln(III), i.e., Gd(III) and Eu(III), presents stronger adsorption, and the separation factor (the ratio of distribution coefficient) between these Ln(III)

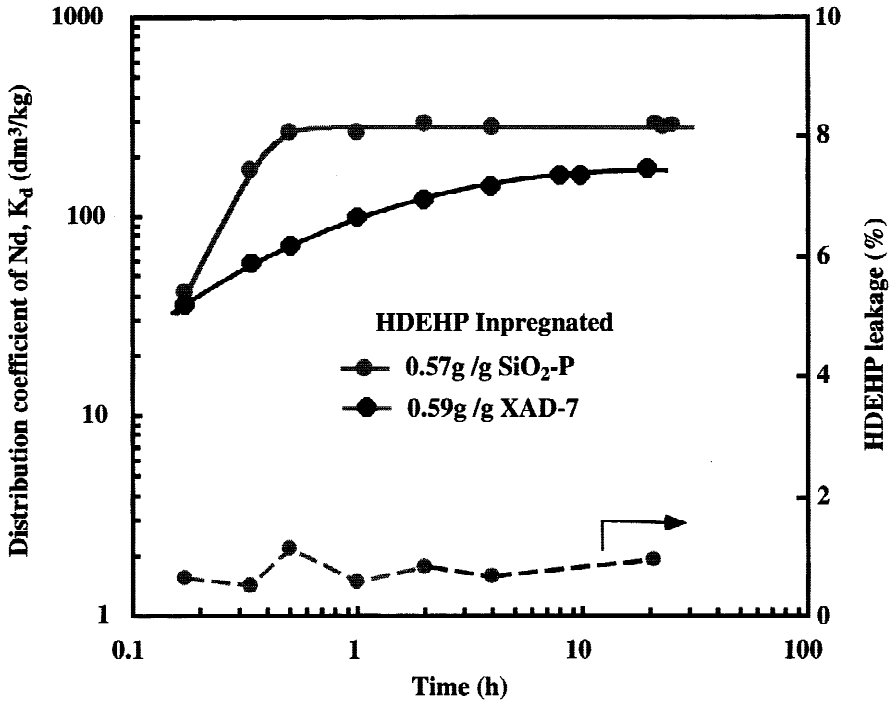


Fig. 4. Time evolution of Nd(III) adsorption from nitric acid solution onto HDEHP-impregnated resin (0.57 g HDEHP/SiO_2-P, 0.1 mol/dm^3 HNO_3, 298 K).

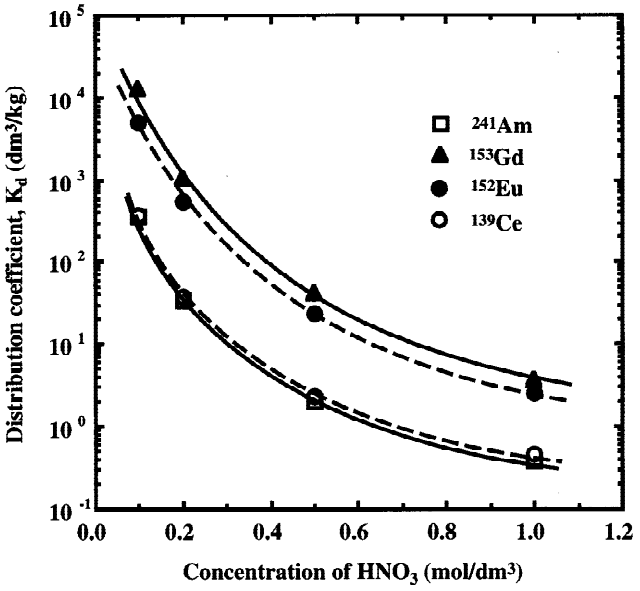


Fig. 5. Effects of nitric acid concentration on the adsorption of Am(III) and Ln(III) onto HDEHP-impregnated resin (0.57 g HDEHP /SiO_2-P, 298 K).

and Am(III) is ~10. However, because the distribution coefficient of Am(III) is almost the same as that of Ce(III), a light Ln(III) in the experimental range of HNO_3 concentration, we conclude that the separation between Am(III) and the light Ln(III), such as La(III), Ce(III), Nd(III), which form the majority of FP lanthanides in the HLW solution, is very difficult by extraction chromatography using the HDEHP/SiO_2-P resin.

Figure 6 illustrates the relationship between the distribution coefficient of ^{241}Am(III), ^{153}Gd(III), ^{152}Eu(III), and ^{139}Ce(III) plotted against the pH value with Cyanex 301/SiO_2-P resin. It was found that Am(III) showed quantitative adsorption from pH ~3.0 onward, and the adsorption increased dramatically with increasing pH value. However, the trivalent lanthanide nuclides showed only slight adsorption at all the experimental pH values, and the separation factor for Am(III)/Ln(III) is up to nearly 1000 at pH 4 to 4.5. This indicated that the Cyanex 301/SiO_2-P resin shows significantly high adsorption selectivity for Am(III) compared to trivalent lanthanides, and the results agreed well with those reported in liquid-liquid extraction.[16,18] On the other hand, the previous experiments indicated that ^{244}Cm(III) can also be extracted by purified Cyanex 301 and showed an extraction behavior similar to Am(III) (Ref. 18). From these results, it is expected that Am(III) and Cm(III) can be effectively separated from Ln(III) by means of column chromatography using the Cyanex 301/SiO_2-P resin. The mechanism for the highly selective adsorption of Am(III) and Cm(III) in comparison to Ln(III) has not yet been clarified and is assumed to result partly from the relatively stronger complex formation (metal-ligand covalent bonding) between the transplutonides and the soft donor (S) (Ref. 18).

Separation Behavior

Since CMPO, a bifunctional organophosphorus compound, can efficiently extract trivalent actinides and lanthanides from aqueous solution containing concentrated nitric acid, it has been extensively studied for the coextraction of MA-Ln from HLW solutions.[1–3,14] To examine the separation behavior of Ln(III) from other FPs, a separation experiment for a simulated HLW solution containing typical Ln(III) and FPs was carried out using a CMPO/SiO_2-P packed column. Figure 7 shows the elution curves of the column chromatography for the sample solution containing $\sim 5 \times 10^{-3}$ *M* of Nd(III), Gd(III), Y(III), Cs(I), Sr(II), and Ru(III) and 3 *M* HNO_3. As can be seen, Cs(I) and Sr(II) showed no adsorption. These elements leaked out with the sample solution and the 3 *M* HNO_3 rinse solution. Most of the Ru(III) was not adsorbed by the extraction resin either and showed a behavior similar to Cs(I) and Sr(II). However, its small portion (~12%) was adsorbed and was not eluted out by water. This is probably due to the hydrolysis of Ru(III) inside the resin, and the elution method for the adsorbed Ru(III) must be further investigated. On the other hand, all the Ln(III) strongly adsorbed onto the resin and the adsorbed Ln(III) were eluted off efficiently by using only water. The elution effect of Ln(III) is considered to result from the decomposition of the Ln(III) complex, as shown in Eq. (2) with the decrease of NO_3^-

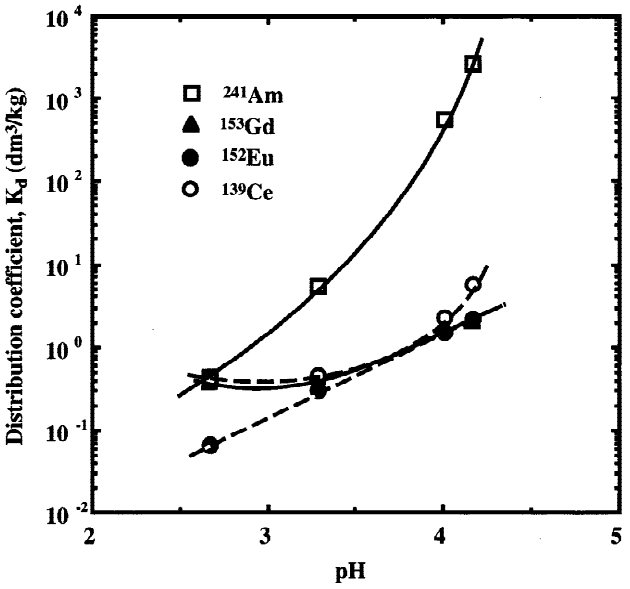


Fig. 6. Effects of pH on the adsorption of Am(III) and Ln(III) onto Cyanex 301–impregnated resin [0.46 g Cyanex 301/SiO_2-P, 298 K, 1.0×10^{-3} mol/dm^3 Eu(III)].

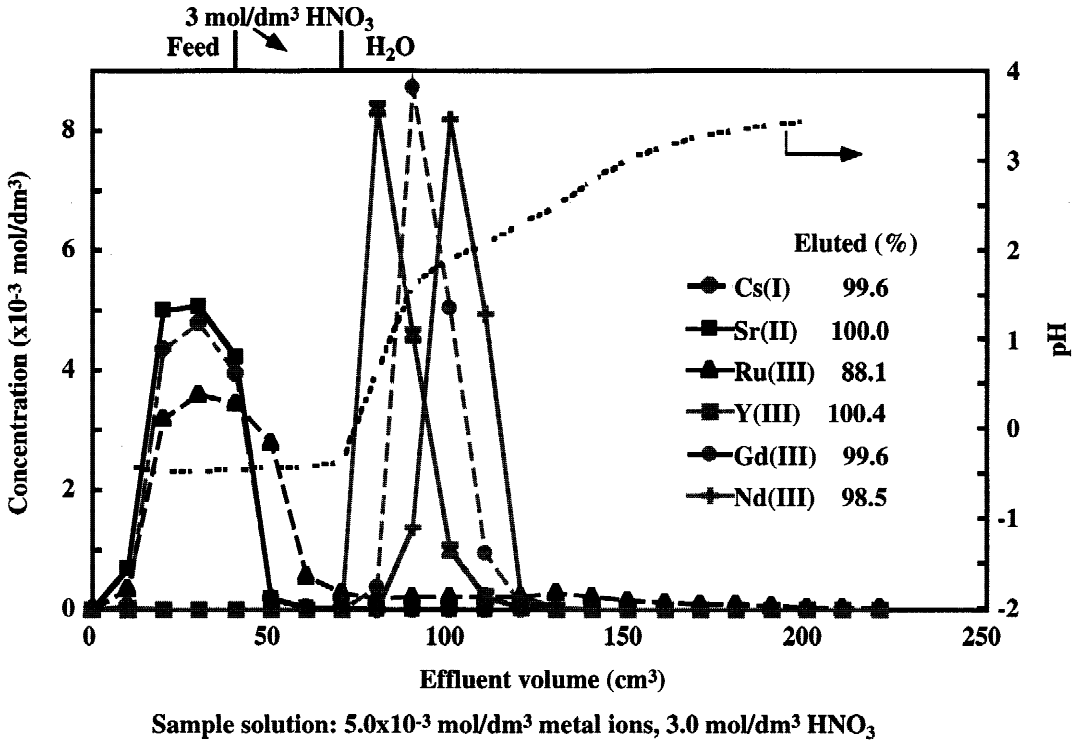


Fig. 7. Results of separation experiment for a simulated HLW solution using CMPO-impregnated resin (0.57 g CMPO/SiO_2-P; 323 K; flow rate, 0.76 m/h).

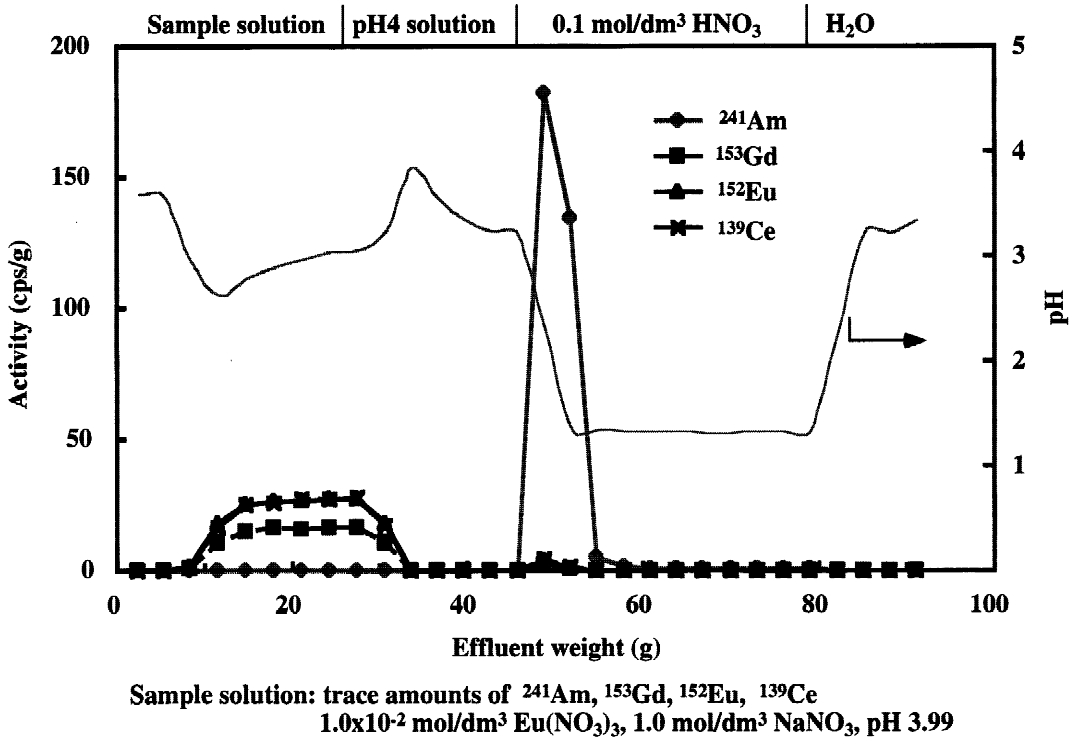


Fig. 8. Results of separation experiment for a sample solution containing Am(III) and Ln(III) using a new Cyanex 301–impregnated resin (0.46 g Cyanex 301/SiO_2-P; 298 K; flow rate, 0.76 m/h).

concentration in the resin bed by supplying water to the column. The elution bands observed are quite narrow and showed very slight tailing, which indicates that the silica-based extraction resin has a rapid kinetics. Moreover, no pressure loss inside the column was observed during solution supply. However, because of the low selectivity of CMPO for MA(III)/Ln(III) (Refs. 1, 2, 3, and 15), distinct separation between MA(III) and Ln(III) cannot be expected by using CMPO/SiO_2-P resin.

Figure 8 shows the results of a separation experiment for the sample solution (pH 3.99) containing trace amounts of ^{241}Am(III), ^{153}Gd(III), ^{152}Eu(III), ^{139}Ce(III), 10^{-2} *M* Eu(III), and 1 *M* $NaNO_3$ using the column packed with Cyanex 301–impregnated resin. In this experiment, a newly purified (within 10 h of preparation) Cyanex 301/SiO_2-P resin was employed. Twenty cubic centimetres of the sample solution, 20 cm^3 of HNO_3 acidic solution with pH 4.0, and 30 cm^3 of 0.1 *M* HNO_3 were successively applied to the column. It was found that the Am(III) was completely adsorbed by the resin, while only a very small portion (~1 to 2%) of Ln(III) was adsorbed. The adsorbed Am(III) was efficiently eluted off by 0.1 *M* HNO_3 solution, corresponding to the decrease of the pH value. The results exhibited good agreement with the adsorption behavior shown in Fig. 6.

Since it has been reported that purified Cyanex 301 shows low stability due to oxidation and decomposition,[18,25,26] we have conducted a separation experiment using an "aged" Cyanex 301/SiO_2-P to examine the effect of this on the separation performance. Figure 9 illustrates the experimental results for the same sample solution as utilized in the experiment of Fig. 8 using the Cyanex 301/SiO_2-P resin, which had been prepared 4 weeks earlier. Note that both Am(III) and Ln(III) showed two occurrence peaks. Most of the Am(III) (~90%) was adsorbed and eluted off by 0.1 *M* HNO_3 solution. However, a portion (20 to 40%) of each Ln(III) was also adsorbed and eluted out together with Am(III). This effect is considered to be caused by impurities such as R_2PSOH and R_2POOH, which were produced by the oxidation of R_2PSSH. It is known that these oxygen-containing organophosphoric compounds show high adsorbability for Ln(III).[18,25,26]

These separation experiments demonstrated that Am(III) can be effectively separated from a macro amount of Ln(III) in simulated HLW solution with pH 4 by using a newly purified Cyanex 301/SiO_2-P resin. However, the separation performance is very sensitive to the purity of Cyanex 301, and the improvement of its stability is an important task for practical utilization.

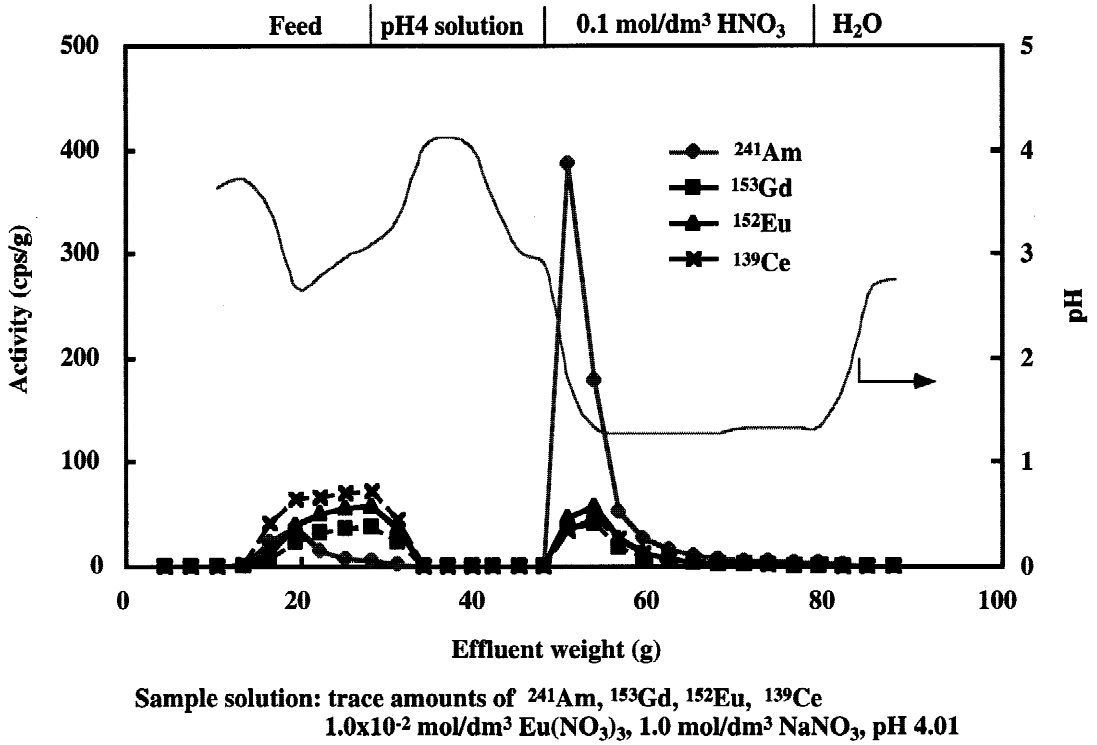


Fig. 9. Results of separation experiment for a sample solution containing Am(III) and Ln(III) using an old Cyanex 301–impregnated resin (0.46 g Cyanex 301/SiO_2-P; 298 K; flow rate, 0.76 m/h).

An Advanced Separation Process

Based on the preceding experimental results, a separation process, as shown in Fig. 10, has been proposed for the isolation of Am and Cm from the nitrate acidic HLW solution by extraction chromatography using the novel silica-based extraction resins. In the first step, the HLW solution is applied to the column packed with CMPO/SiO_2-P resin, and the adsorptive Am(III), Cm(III), and Ln(III) are adsorbed by the resin. In the second step, most FPs (non- or weakly adsorptive FPs) such as Cs(I), Sr(II), and Ru(III) are washed off by concentrated HNO_3, while leaving the adsorptive elements in the column. In the third step, the adsorbed Am(III), Cm(III), and Ln(III) are eluted off the column by dilute HNO_3 or water, and the pH value in the eluate is ~2.0 to 2.5. In the fourth step, the pH in the eluate is adjusted to 3.5 to 4.0 by the addition of an alkali such as sodium hydroxide. Subsequently, the resulting solution is introduced into the column packed with Cyanex 301/SiO_2-P resin, which adsorbs Am(III) and Cm(III) selectively (step 5). In the sixth step, a nitrate acidic solution with pH 3.5 to 4.0 is supplied to the column to wash out the nonadsorptive Ln(III). In the final step, the adsorbed Am(III) and Cm(III) are then eluted out by using a dilute HNO_3 solution. The conceptual design and evaluation for this process is under way.

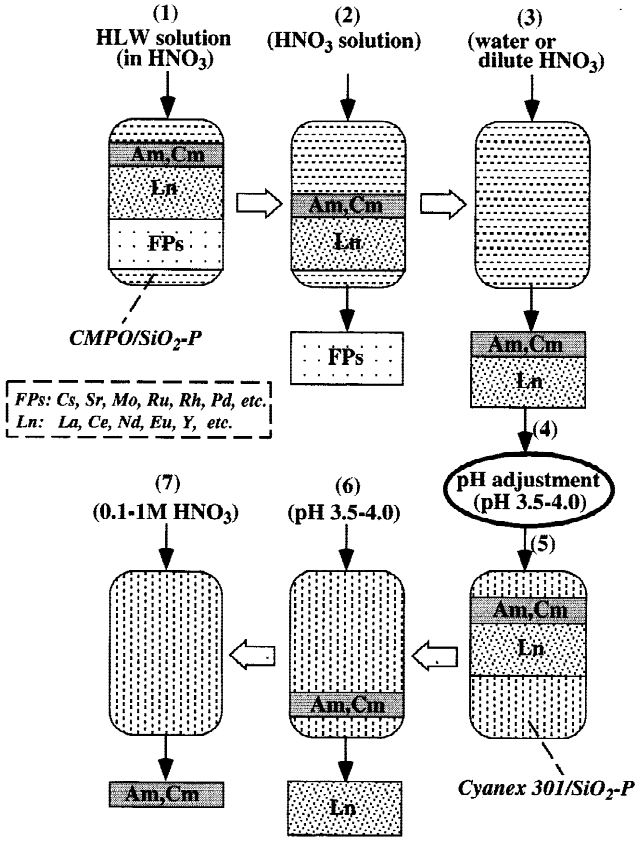


Fig. 10. A proposed process for the separation of minor actinides from HLW solution by extraction chromatography.

CONCLUSIONS

The novel silica-based extraction resins were prepared by impregnating CMPO, HDEHP, or purified Cyanex 301 into the styrene-divinylbenzene copolymer, which is immobilized in porous silica particles. The adsorption characteristics of Am(III) and Ln(III) from nitrate acidic solutions onto the extraction resins were investigated, and their separation behavior from simulated HLW solutions was demonstrated by extraction chromatography.

In the separation experiment for a simulated HLW solution containing typical Ln(III), FPs, and 3 *M* HNO_3 using a CMPO/SiO_2-P resin-packed column, the adsorbed Ln(III) ions were effectively eluted off by water and separated from other FPs such as Cs(I), Sr(II), and Ru(III).

Am(III) showed almost the same adsorbability as Ce(III) onto HDEHP/SiO_2-P resin in 0.1 to 1.0 *M* HNO_3 solutions. The separation between Am(III) and the light Ln(III), such as La(III), Ce(III), and Nd(III), is very difficult using HDEHP/SiO_2-P resin.

Am(III) exhibited significantly strong adsorption onto purified Cyanex 301/SiO_2-P resin at a pH higher than 3.5, while Ln(III) showed only slight adsorption, and the separation factor for Am(III)/Ln(III) is up to nearly 1000. Satisfactory separation between Am(III) and a macro amount of Ln(III) from simulated HLW solution with pH 4 was achieved by using a newly purified Cyanex 301/SiO_2-P resin. However, the separation performance is very sensitive to the purity of Cyanex 301, and the improvement of its stability is an important task for practical utilization.

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