

PARTITIONING OF MINOR ACTINIDES FROM RARE EARTHS BY SOLVENT EXTRACTION WITH DI(2-ETHYL HEXYL) PHOSPHORIC ACID

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ABSTRACT

A flowsheet of the solvent extraction process to separate minor actinides(MA) from rare earths(RE) was devised and experimentally tested. The process is based on the high extractabilities of minor actinides and rare earths by di(2-ethyl hexyl) phosphoric acid at low nitric acid concentrations. The extraction process, composed of one extraction and three selective strippings in series, was installed with four miniature mixer-settler banks of a total of 44 stages in a glove box. The operation was performed by using a simulated waste solution containing 15 inactive compounds as the stands-in for rare earths and other fission products, and ^{241}Am and ^{237}Np as radioactive tracers for the minor actinides. For each element fed to the extraction bank, more than 99% of Am, Np, and rare earths were extracted by 1M HDEHP/n-dodecane. Then each of the Am, Np, and RE was selectively back extracted into the aqueous phase by 0.05M DTPA, 6M HNO_3 , and 0.5M $\text{H}_2\text{C}_2\text{O}_4$, respectively, in consecutive stripping processes. In these steps, 99.8% of Am, 97~99% of rare earths elements and 99.4% of Np were separated from one another. The Am and Np products, however, may require further purifications because of other impurities accompanied these elements into their respective product streams.

BACKGROUND ON PARTITIONING & TRANSMUTATION STUDIES IN KOREA

In Korea, 11 nuclear reactors (10 PWRs and 1 CANDU) are currently in operation with total generating capacity of 9.6 GWe. In addition, 7 reactor units are under construction which will be completed in the years from 1997~2002. Accordingly, the total nuclear generating capacity will reach 15.7 GWe in the year 2002. The amount of spent nuclear fuels annually arising from the current operating reactors accounts for 280 MTHM and the cumulative amount reaches about 2800 MTHM (PWR 1600, CANDU 1200 MTHM). The spent fuels are now in storage at each reactor site. However, they are to be stored at a central interim storage facility for the time being before they are reprocessed or disposed of. This program addresses the national policy of just "wait & see" because the procedure for a back-end fuel cycle has not been established yet.

Reactor wastes, namely, low-level wastes are also in storage at each reactor site. They will be disposed of in a final repository in the future. For the last 10 years, lots of effort has been devoted to find a candidate repository site in the midst of strong anti-nuclear movement throughout the country. As a result, a tiny island in the west sea was determined as the candidate site in 1995. However, it was immediately canceled because an active fault was discovered near the island in the survey of geological characteristics. Consequently, the national program on radwaste disposal has changed in that the project should be transferred to the Korea Electric Power Corporation from the Korea Atomic Energy Research Institute (KAERI).

At present, we have no high-level wastes in Korea because we do not have any fuel recycling activities. However, it might be necessary in the future to complete the nuclear fuel cycle in view of the Korean situation, that is, it depends not only on import for almost all of its energy resources, but also on nuclear energy for the major part of its electricity generation. In addition, the amount of spent fuels accumulated will increase year by year. Moreover, it might become more and more difficult to get public acceptance for the direct disposal of the spent fuels in the Korean peninsula. An alternative prospective solution for this might be the transmutation of long-lived radionuclides.

Though several countries are planning to dispose of vitrified high-level wastes at a deep underground repository, there are no countries yet in the world which have put it into action. In fact, even the environmental impact of high-level wastes disposal has not been fully elucidated yet. Actually, there is lots of concern as to whether they can be sustained without the release of radioactive material to the biosphere for hundreds of thousands of years when buried in the geologic repository. In this

respect, it would be attractive to convert the long-lived radionuclides into short-lived or stable nuclides. Residual waste management after transmutation could result in the reduction in the final disposal cost at hand, as well as in the possible contamination of the environment in the future.

With this background in Korea, both partitioning and transmutation studies are being carried out in preparation for future application. In parallel with this, the development of high-level wastes disposal technology is also being performed in KAERI. The future objective facilities for transmutation in Korea include a liquid metal reactor, and an accelerator-driven subcritical reactor (the same as a few other countries). A research project on the former is being carried out with the target of proto-type reactor completion by 2011. As to the latter, a new research program is under planning in order to establish a concept of the reactor.

A study on partitioning is also being conducted with simulated waste solutions in KAERI focused on the development of MA, Cs, Sr and Pt-group metals separation methods. It is also considered to include such research area in the near future as thorium fuel cycle with pyroprocessing which is known as an alternative fuel cycle favorably applicable to the subcritical reactor.

INTRODUCTION

Most of minor actinides contained in the typical high-level liquid waste (HLLW) from reprocessing of spent nuclear fuels are composed of long-lived radionuclides. These radionuclides, if they are intended to be transmuted, must be separated from HLLW and then made into the form of target for transmutation.

One of the prospective methods to recover MA from HLLW is the extraction of them at low nitric acid concentrations using di(2-ethyl hexyl) phosphoric acid (HDEHP) as an extractant [1~6]. In this process, however, most of RE and MA have similar properties in their extractability and thus RE elements are accompanied with MA in the organic phase. Another process for the mutual separation of MA and RE is, therefore, necessary to recover the MA alone. A representative process to separate Am and Cm from RE is the reverse-TALSPEAK process [1,6] where Am and Cm can be selectively stripped from the organic phase of HDEHP by di-ethylenetriamine pentaacetic acid (DTPA). As for Np, it exists in the state of Np(IV), Np(V), and Np(VI) in nitric acid solution by the disproportionation. The extractability of Np(IV) or Np(VI) with HDEHP is high without regard to the nitric acid concentration, whereas that of Np(V) is much lower. These properties lead to the possibility of separation of Np from either Am or RE. However, Np tends to have

TABLE 1. CHEMICAL COMPOSITION OF THE SIMULATED WASTE SOLUTION

Component		Concentration
TRU	²⁴¹ Am	5.90×10^4 Bq/ℓ
	²³⁷ Np	1.66×10^4 Bq/ℓ
RE	Eu	1.05×10^{-3} M
	La	2.96×10^{-2} M
	Ce	3.47×10^{-2} M
	Nd	5.07×10^{-2} M
	Y	7.90×10^{-3} M
FP	Cs	3.48×10^{-2} M
	Ba	2.37×10^{-2} M
	Rb	7.72×10^{-3} M
	Pd	6.58×10^{-3} M
	Fe	2.02×10^{-2} M
	Ni	4.09×10^{-3} M
	Mo	1.36×10^{-2} M
	Sr	2.08×10^{-2} M
	Zr	4.82×10^{-5} M
	Rh	4.66×10^{-3} M
Media	HNO ₃	0.1 M
	H ₂ O ₂	1.0 M

Apparatus for Extraction and Stripping

Four banks of miniature mixer-settler made of acrylic plastic were used for extraction and selective strips. The volume of each mixer, same with that of settler, was 13 ml. Like conventional mixer-settlers, this apparatus was also fabricated so that the aqueous and organic phase move in counter-current flow. Air pulsation produced by a membrane type pulse generator and distributed to each mixer through a pulse header was used to mix aqueous and organic phases. All the four banks of mixer-settler, as shown in Fig. 1, were installed inside an α -tight glove box in order to shield the α activities of ²³⁷Np and ²⁴¹Am. Whenever they are started to run, blank-operation was carried out for over 4 hours by feeding 0.1 M HNO₃ instead of the simulated solution and by adjusting the interface level in the settlers so that they can reach an optimal hydraulic condition in advance. Then the regular operation was started by switching the feed to the simulated solution.

more stable form of Np(V) in larger proportion at lower concentration of nitric acid and thus it is necessary to reduce it to the state of Np(IV) or to oxidize to Np(VI) in order to extract it into the organic phase. These characteristics make it possible to combine a few unit processes to a probable process for the partitioning of Am, Cm group, RE group and Np one another. On the basis of the above concept, a partitioning process constituted of one extraction and three selective stripping was drawn out and its validity was experimentally tested in this study. The experiments were conducted with a simulated waste solution containing 17 metal elements. The simulated solution was prepared with 15 inactive compounds as the stands-in for RE and other fission products, and with tracers of ^{241}Am and ^{237}Np as the stands-in for Am and Np, respectively. Four banks of miniature mixer-settler with a total of 44 stages were used for extraction as well as selective stripping apparatus. The stripping agents, DTPA, HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$ were respectively employed for back extraction of Am, RE and Np.

EXPERIMENTAL

Preparation of a Simulated Waste Solution

A simulated waste solution was prepared to contain major metal components of the typical high-level liquid waste from the reprocessing of spent fuels. Inactive compounds of rare earths, Fe, Ni, Mo, Sr, Zr, Cs, Ba, Rb, Pd and Rh were dissolved in the medium, 0.1 M HNO_3 , in order that they have similar concentrations to those of the high-level liquid waste. Trace amounts of ^{241}Am and ^{237}Np were also added to the solution as stands-in for minor actinides, to track the behaviors of Np, Am and Cm in the partitioning process. Hydrogen peroxide [7, 8] was added to the stock solution to control the oxidation valence of Np as Np(IV) because it has higher extractability with HDEHP. Chemical composition of the simulated waste stock solution is illustrated in Table 1.

Extraction of TRU and RE

A 14-stage bank (A1) as shown in Fig. 1 was used for extraction. The simulated solution (aqueous feed), 0.1 M HNO₃ (scrub) and 1M HDEHP/ n-dodecane (extractant) were respectively injected into the 10th, 14th and 1st stage. The operation conditions of the banks are listed in Table 2.

TABLE 2. FEEDING MATERIALS AND THEIR FLOW RATES IN EACH BANK

Bank No.	Feed	Feeding stage	Flow rate(ml/hr)
A1	① : simulated waste	10	80
	③ : 0.1 M HNO ₃	4	15
	② : 1M HDEHP	1	80
A2	④ : loaded HDEHP	5	80
	② : 1M HDEHP	1	15
	⑦ : 0.05M DTPA in 1.5M Lactic acid	14	95
A3	⑥ : loaded HDEHP	1	95
	⑪ : 6M HNO ₃	8	30
A4	⑧ : loaded HDEHP	1	95
	⑮ : 0.5M H ₂ C ₂ O ₄	8	95

Stripping of Am

A 14-stage bank(A2) was used to strip Am from the organic phase. 0.05M DTPA and 1.5M lactic acid mixture (pH : 3.1) [9] was fed to the 14th stage as a stripping agent while the organic feed containing MA and RE was supplied to the 5th stage. 1M HDEHP/n-dodecane, injected to the 1st stage, served as the scrubber of aqueous stream by extracting Np and RE again to the organic phase.

Stripping of RE

RE elements were stripped from the organic phase by 6 M HNO₃ in the 8-stage bank A3. In this bank, only RE were selectively washed out to the aqueous phase leaving Np still in the organic phase.

Stripping of Np

Finally Np was stripped from the organic phase by 0.5 M H₂C₂O₄ [10] through the 8 stages of the bank A4. The Np-loaded solvent was injected into the 1st stage while oxalic acid was fed into the 8th stage.

Chemical Analyses

Radioactivities of ²³⁷Np and ²⁴¹Am were measured using a multichannel analyzer (Afora Model LP-4900B) with Ge(Li) detector. Since the elements Ba, Sr, Eu, La, Zr, Ce, Nd and Y are inactive, their concentrations were obtained by an Inductive Coupled Plasma Spectrophotometer. The concentrations of Cs, Rb, Fe, Ni, Pd, Mo and Rh were measured with an Atomic Absorption Spectrophotometer (Hitachi Model 180.80).

Solvent Regeneration

The used solvent, containing Fe and mono-ethylhexyl phosphoric acid (H₂MEHP) as the major degradation components, was washed with the mixture of 5% (NH₄)₂CO₃ and 2M manitol.

Definition of Relative Concentration

In order to evaluate the state of extraction or stripping of a metal component, the relative concentration (C*) of the metal component concerned was defined as follows :

$$C^* = \frac{M_i \cdot F_i}{M_f \cdot F_f} \quad (1)$$

M : concentration of the metal component (Bq/ℓ or mole/ℓ)

F : flow rate (ml/hr)

where the subscripts f and i denote feed stream to the bank A1 and internal stream in the corresponding bank, respectively.

RESULTS AND DISCUSSION

Extraction of TRU and RE

Over 99% of Am and Np were found to be extracted by 1M HDEHP/n-dodecane in the bank A1. The contents of Np and Am released to the raffinate were less than 50 Bq/l which were the measurable limits of radioactivity. Fig. 2 shows the steady state concentration profiles of Am, Np, and Eu for the relative concentrations as defined in Equation (1). The high extractability of Np was due to the valency control of Np ($\text{Np(V)} \rightarrow \text{Np(IV)}$) by means of H_2O_2 .

Among the impurities contained in the stream of Np and Am, the major ones were found to be RE, Zr, Mo and Fe because 99% of RE, Zr and Fe and 97.8% of Mo were extracted into the organic phase together with Np and Am. Though Ba, Ni, Sr, Cs, Rh, Pd and Rb were also accompanied into the organic phase, their contents lay within the range of only 1 ~ 4% out of the quantities in the feed. Since these impurities tend to cause the forming of the third phase, it would be quite desirable to remove them prior to the solvent extraction.

Selective Stripping of Am

Experimental results show that 99% of Am was selectively stripped from the organic phase in the bank A2. Fig. 3 shows the steady state aqueous concentration profiles of Am, Np, and Eu in the aqueous phase of the bank A2. Np content in the aqueous outlet stream was measured as less than 50 Bq/l assuring that Am and Np can be mutually separated by this selective strip. However, 2.3% of RE, 7% of Fe, 85% of Mo and 0.01 ~ 2% of Ba, Ni, Sr, Cs, Rh, Pd and Rb were accompanied with Am into the aqueous outlet stream. Among the RE elements, Eu showed the largest portion of stripping by displaying 2% of the original amount in the feed was liberated to the aqueous phase, which is over 100 times higher than those of other RE elements. These experimental results show that additional purification procedures must be introduced if pure Am product is required.

Selective Stripping of RE

Since the distributions of all RE elements by 1M HDEHP/n-dodecane are very low at high nitric acid concentrations, the loaded RE could be stripped with 6M HNO_3 . Experimental results show that over 98% of RE were stripped whereas other elements, Np, Ba, Ni, Sr, Cs, Rh, Pd and Rb, were washed out by only 0.01 ~ 2%. Fig. 4 shows the steady state aqueous concentration profiles of La, Nd, Y, and Np in the bank A3. When the aqueous concentration profiles of La, Nd and Y are compared

one another, as shown in Fig. 4, they represent almost same pattern of profiles meaning that RE elements have very similar behaviors in the extraction and the strippings.

Stripping of Np

The Np loaded in the organic phase was finally stripped with 0.5 M $\text{H}_2\text{C}_2\text{O}_4$. More than 99.4% of Np was stripped back into the aqueous phase accompanying 6.6% of Fe whereas other elements were back extracted from the organic phase by less than 0.1%. The steady state aqueous concentration profile of Np in the bank A4 was illustrated in Fig. 5.

Composition in the Aqueous Outlet Stream of Each Bank

The aqueous outlet streams of the bank A1 and A3 correspond to raffinates while those of A2 and A4 correspond to products. The compositions of these outlet streams, expressed as relative concentrations of the unit of percentage ($C^* \times 100$), are given in Table 3. The Am product stream of the bank A2 shows that 99.8% of Am was recovered from the original simulated waste. However, it contains appreciable amounts of impurities such as 86.4% of Mo and 7.3% of Fe. The Np product stream of the bank A4 also shows that 99.4% of Np was recovered, however, containing 6.6% of Fe as the only considerable amount of impurity.

Solvent Regeneration

The Fe still left in the organic phase was favorably removed by treating with the washing agent mentioned earlier. However, the H_2MEHP , one of the degradation products of HDEHP, was removed only in part from the used solvent.

TABLE 3. THE RELATIVE CONTENTS OF THE VARIOUS ELEMENTS IN THE AQUEOUS OUTLET STREAM OF EACH BANK (Unit : %)

Element	A1 (Raffinate)	A2 (Am product)	A3 (RE stream)	A4 (Np product)
Am	0.03	99.83	0.04	0.02
Np	<0.31	<0.31	0.34	99.37
La	0.01	trace	98.1	trace
Ce	trace	0.08	99.7	"
Nd	"	0.03	99.7	"
Y	0.02	0.03	99.4	0.01
Eu	0.08	2.32	97.5	0.09
Cs	98.75	1.05	0.06	trace
Rb	98.18	0.32	0.11	"
Ba	98.65	0.05	0.03	"
Sr	98.24	0.16	0.2	"
Pd	99.43	0.43	0.86	"
Rh	97.5	0.48	0.77	"
Fe	0.51	7.26	0.08	6.58
Ni	96.2	1.73	1.11	trace
Mo	2.2	84.61	0.77	0.01

trace : < 0.01

CONCLUSIONS

It was shown that the Am and Np, can be effectively recovered from the simulated waste solution by extraction with HDEHP followed by selective strippings. In addition, Am, Np, and RE could be independently separated from each other. As a result, the recovery ratios of Am and Np were found to be 99.8 % and 99.4 %, respectively. However, the Am and Np products were carrying some amounts of impurities, that is, 7.3 % Fe and 84.6 % Mo in the former, and 6.6 % Fe in the latter, with respect to the original quantities contained in the feed. 97.5 ~ 99.7 % of rare earth elements were removed into the RE outlet stream of the bank A3.

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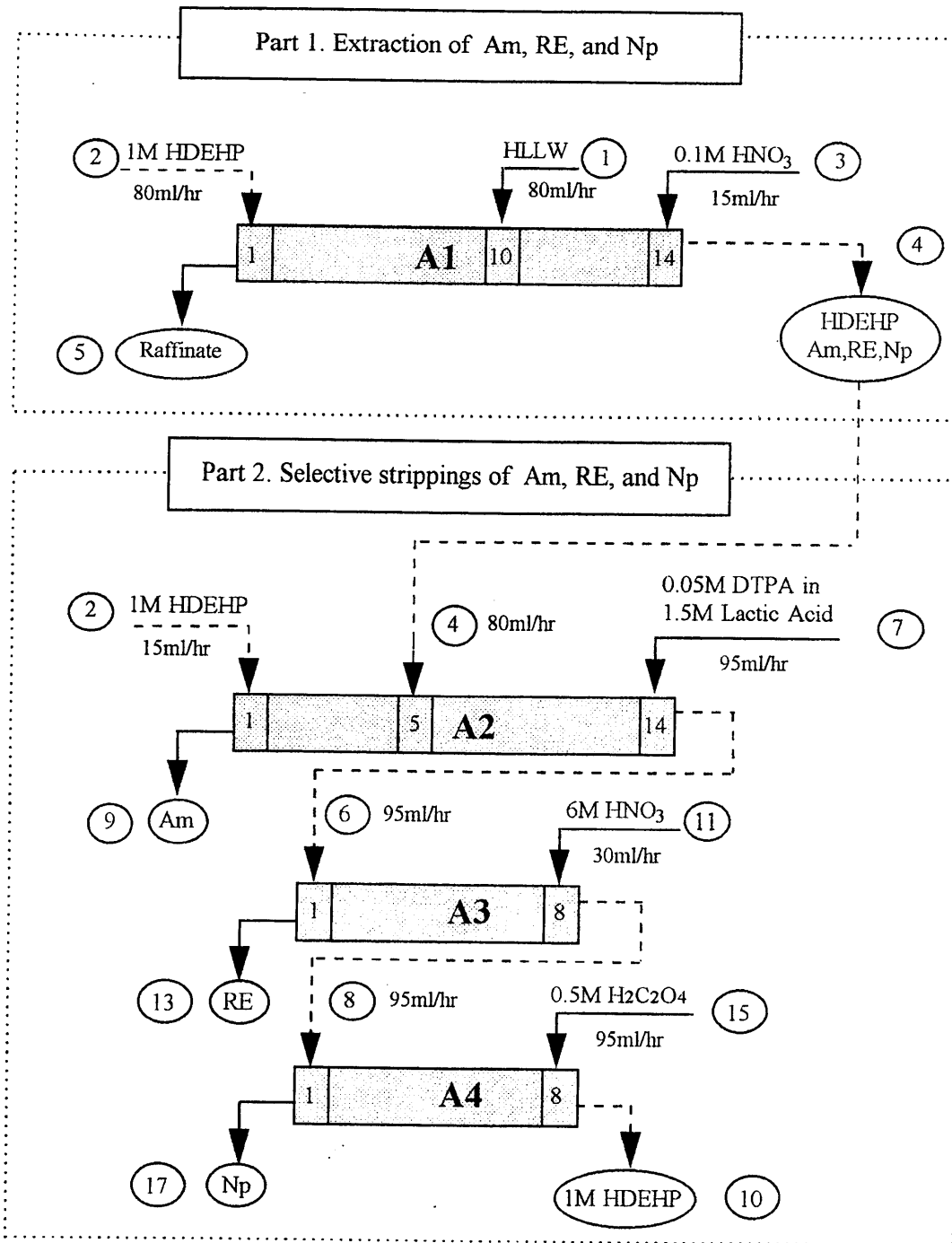


Figure 1. Flowsheet for respective partitioning of Am, RE and Np by extraction with HDEHP and selective strippings

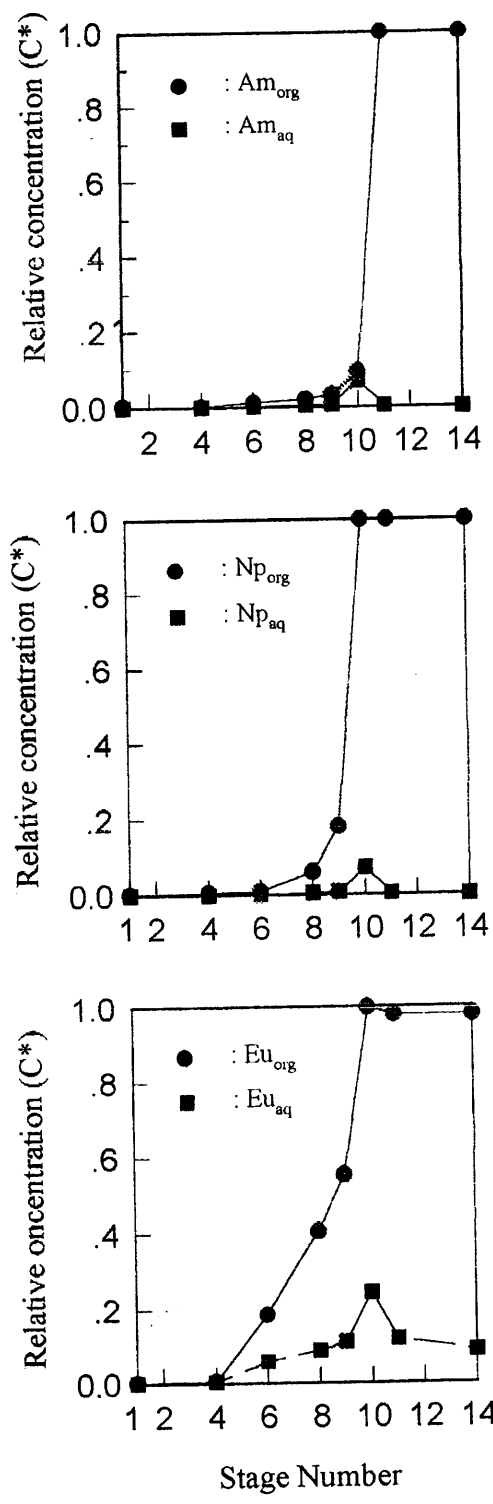


Figure 2. Concentration profiles of Am, Np, and Eu in the organic and aqueous phases of the bank A1

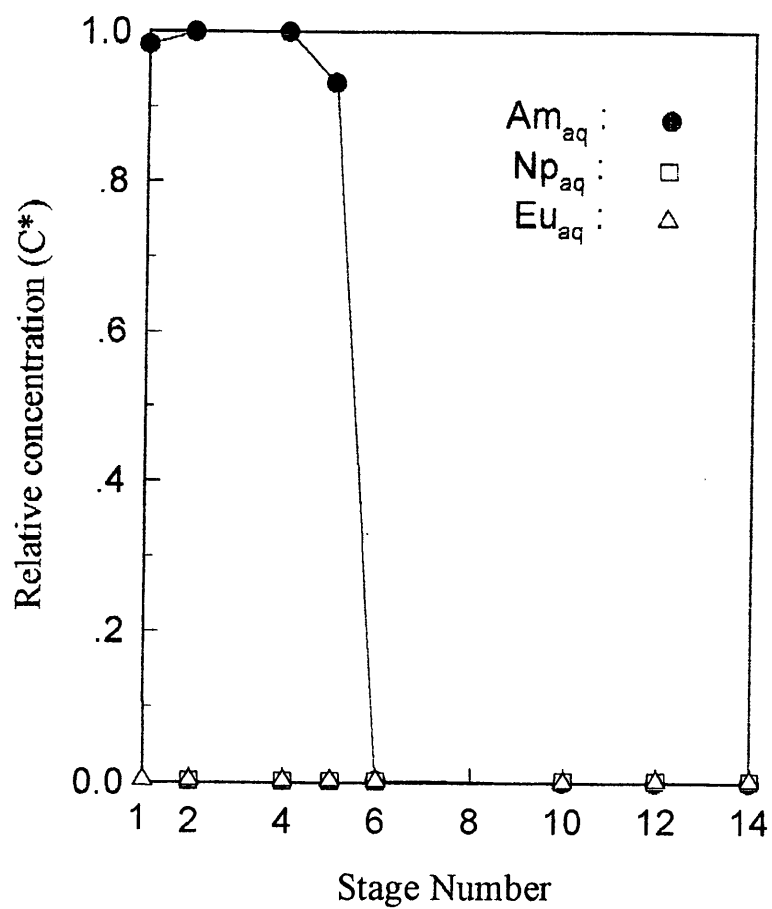


Figure 3. Concentration profiles of Am, Np, and RE in the aqueous phase of the bank A2

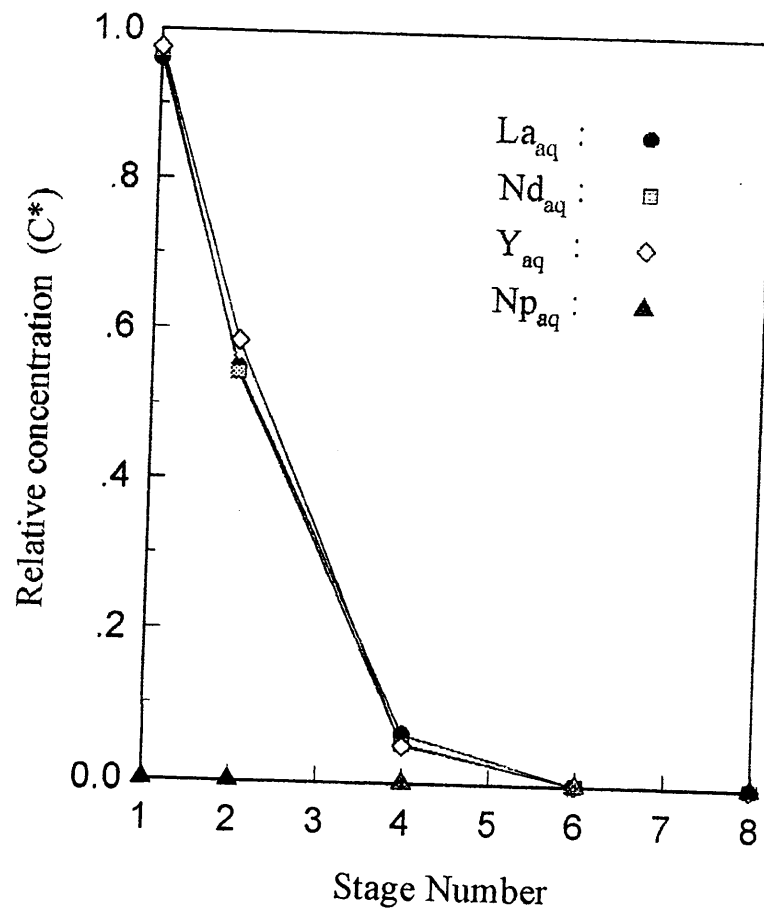


Figure 4. Concentration profiles of RE(La, Nd, Y), and Np in the aqueous phase of the bank A3

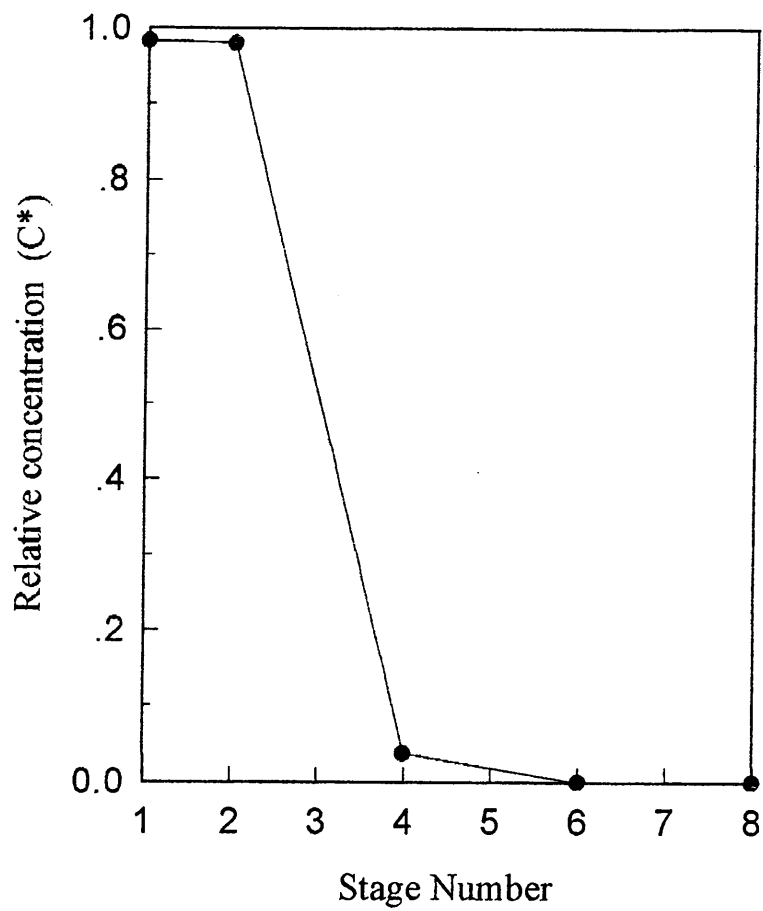


Figure 5. Concentration profile of Np in the aqueous phase of the bank A4