

**WASTE MINIMISATION IN ACTINIDES (III)/LANTHANIDES (III) SEPARATION
PROCESS FROM HIGH-LEVEL LIQUID WASTE**

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Abstract

Minimisation of the secondary waste from the SETFICS processing for the PUREX process raffinate was studied. Organic solvent waste can be minimised by using a mixture of high TBP concentration, replacing TBP and n-paraffinic hydrocarbon into fluoride compound, and replacing the liquid solvent with silica based adsorbent that CMPO is impregnated. Application of hydroxylamine nitrate as a “salt free” salting out reagent will contribute for reducing aqueous waste solution as well as employing HEDTA instead of DTPA for selective complexation with actinides(III).

Introduction

As a part of the feasibility study for Advanced Fast Reactor Fuel cycle, Japan Nuclear Cycle Development Institute (JNC) started research and development of its Phase II programme in 2001. [1] For aqueous process development, the reference flowsheet as shown in Figure 1 has been studied as well as some alternative separation methods; such as supercritical fluid extraction. The reference flowsheet is based on the crystallisation of uranium nitrate hexahydrate for dissolver solution, the PUREX process without selective reduction of Pu, and recovery of Am and Cm by the SETFICS process using CMPO. [2] An organophosphorus extractant OØD[iB]CMPO is well known for extraction of trivalent actinides, An(III), from highly acidic solution, and as a main extractant of the TRUEX process. [3] The SETFICS process was developed for recovery of Am and Cm from the PUREX raffinate and separation from lanthanides, and is a variation of the TRUEX process. It was confirmed by a counter-current experiment using highly active solution that about 90% of lanthanides could be rejected from the Am-Cm product solution. [4] The major objective for further development is reducing secondary waste generated through processing solutions in order to establish a recovery process for actinides(III).

The SETFICS process is based on the TRUEX solvent that is a mixture of CMPO, TBP and normal paraffinic hydrocarbon diluent, and employs a concentrated nitrate solution in order to extract lanthanides from the solution of pH 2 while Am and Cm are complexed with DTPA in the aqueous phase. The amount of the solvent and aqueous solution should be minimised even though those will be extensively recycled before final treatment and disposal. JNC pursues several ways to reduce those solutions as summarised in Table 1. Some of the candidates cannot be simultaneously applied for improvement of the SETFICS process; for example, introduction of fluorinated diluent and extraction chromatography are incompatible. This paper summarises our recent results on the SETFICS process development for reducing secondary waste.

Table 1. Ways for reducing secondary wastes generated in the SETFICS processing

Way for reducing waste solutions	Expected results
High loading with 1.4 M TBP solvent	The maximum metal concentration is increased and the amount of solvent and aqueous solution used will be decreased.
Use of hydroxylamine nitrate as a “salt-free” reagent	Solid waste will be decreased by eliminating sodium.
Alternative complexant instead of DTPA	Replacing DTPA with a chelating reagent that has less stability constants will result in reducing nitrate concentration.
Chromatography application	Eliminating diluent and modifier TBP will reduce waste of organic materials. Chromatographic separation is suitable for dilute solution and effective to reduce aqueous waste.
Changing diluent into fluoride compound	Fluoride diluent provides possibility to increase the limited concentration of third phase formation, and will strongly contribute to reduce organic and aqueous waste solution.

Salt-free and high loading flowsheet

Third phase formation limits the maximum metal concentration in the TRUEX solvent. [3,5] In order to avoid third phase, increasing TBP concentration is effective. Typical TBP concentration of the TRUEX solvent is 1.2-1.4, and a 1.4 M solvent provides the greatest metal loading. Increase of TBP concentration in the solvent results in enhancing extraction of nitric acid with TBP. This affects on the stability of pH and complexation of DTPA with trivalent cations in the selective An(III) stripping step of counter-current operation. Consequently high loading should affect on An(III) recovery and rejection of lanthanides.

As sodium nitrate is easy to use, JNC mainly employed it for batch and counter-current experiments. From the viewpoint of generating salt waste, it is favourable to choose “salt-free” nitrate compounds; such as hydroxylamine nitrate (HAN). Although hydroxylamine as a counter cation of nitrate fortunately does not have effect on separation with CMPO and DTPA complexation, it was needed to examine separating performance in the counter-current procedure.

Table 2. **Material balance of major elements obtained in inactive counter-current experiment**

Stream	Balance (%)										
	Sr	Y	Zr	Mo	Ru	La	Ce	Pr	Nd	Sm	Eu
Feed	100	100	100	100	100	100	100	100	100	100	100
Raffinate	108	89	102	52	99	14	0.9	1.0	0.4	0.7	1.1
Acid waste	0.02	16	0.01	1.7	0.03	0.03	0.02	0.1	0.04	0.2	0.04
An(III) product	0.03	1.1	7.7	26	0.4	0.5	0.2	4.3	25	92	95
Ln waste	0.1	0.1	0.1	0.5	0.2	79	68	66	55	1.0	1.5
Used solvent						0.09	0.7	1.1	0.4		
Total	108	106	110	80	100	93	69	71	80	94	97

Table 3. **Decontamination factor obtained in inactive counter-current experiment**

Sr	Y	Zr	Mo	Ru	La	Ce	Pr	Nd	Sm
2800	83	12	3.7	230	210	540	22	3.8	1.0

An inactive counter-current experiment was conducted using mixer-settler type contactors. The experimental flowsheet is shown in Figure 2. The solvent used was a solution of 0.2 M CMPO–1.4 M TBP in n-dodecane. Hydroxylamine nitrate was added to the strips for acid and An(III). Europium can be a stand-in of An(III), since it has two-fold distribution ratio of Am. The material balance for major elements is summarised in Table 2. Yttrium and La were rejected at the extraction–scrubbing step and the acid stripping step due to their small distribution ratio from nitric acid solution. Nitric acid was successfully removed from the loaded solvent from the first step by using a solution of 0.5 M HAN (pH 2.0). Lanthanum, Ce and Pr were retained on the organic phase at the An(III) stripping step and separated from Eu. HAN can be used as a salting-out reagent instead of NaNO₃. However, decontamination of Nd and Sm were worse compared with the former experiment. [4] From the data of material balance and decontamination factor of Nd, Sm and Eu shown in Table 3, it is concluded that this experimental flowsheet is not ideal for An(III) recovery, and further flowsheet optimisation is essential.

Reducing nitrate concentration

Besides eliminating sodium cation in the strip, the nitrate concentration should be lowered as far as possible. Weaker complexation of An(III) with chelating reagent helps to retain lanthanides at lower nitrate concentration. As an alternative N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) was selected from its selectivity for lanthanides, small acid dissociation constant and solubility into an acidic solution, and examined its separation property of Ln(III) and Y.

The distribution ratio D of Ce, Nd, Eu and Y as a function of pH and HEDTA concentration are plotted in Figure 3 as typical data. The D values decrease with pH and [HEDTA]. Increasing nitrate concentration results in increasing distribution ratio of lanthanides. This behaviour is similar to that of DTPA system. From the batchwise distribution data, nitrate concentration that provides same distribution ratio of Nd will be decreased to one half of that for the DTPA system.

The mutual separation behaviour of lanthanides is shown in Figure 4. The separation factor was defined as the ratio of the distribution ratio of metal to that of yttrium. The extractability decreases with atomic number. Consequently the separation mechanism for HEDTA solution is the same in DTPA system. The separation between light lanthanides is worse than that in DTPA system, while for heavy lanthanides provides better. The separation of La/Lu (this may represent total performance for DTPA and HEDTA system) is also worse in the use of HEDTA. It is worth to examine the separation performance of An(III)/Ln(III) in batchwise and counter-current procedure.

Chromatography application

Extraction chromatography does not need diluent, therefore, its application provides some effects on reducing organic waste. And, in general, chromatographic separation is suitable for recovery from a dilute solution; the raffinate from the PUREX process. An adsorbent based on macroporous silica particle coated with styrene-divinylbenzene polymer, SiO₂-P, provides variety of extraction capability, because SiO₂-P can hold many kinds of extractant molecule. [6] The SiO₂-P is also good for reducing degradation products from organic material. JNC studied its application for CMPO, mainly on safety and waste treatment.

The DT/TG analysis was conducted to confirm thermal stability of CMPO/SiO₂-P that CMPO retained on the SiO₂-P. Figure 5 shows the results of DTA/TG analysis. At 40°C, endothermic peak in the DTA curve is observed and this is attributed to the melting of CMPO molecule on the surface of the SiO₂-P. CMPO is decomposed beyond 200°C, and the reaction is terminated at 290°C. The polymer coated decomposes from 300 to 600°C. The TGA curve decreases with temperature and shows that phosphorus compound is remained on the SiO₂ particle after reacting at 10³°C. Similar curves were obtained with CMPO/SiO₂-P contacted with 3 M HNO₃ solution. This suggests that particular reaction of CMPO and nitric acid remained on the silica particle does not react to generate extensive heat.

In order to reuse the extractant, it should be removed after a certain times of extraction and elution cycles. The extractant can be removed by contacting with solvent; such as acetone and dichloromethane. Recovery of CMPO was confirmed by batchwise and column experiment. A scheme of treatment of used CMPO/SiO₂-P for reuse of CMPO and SiO₂-P, and for final disposal of adsorbent was deduced and shown in Figure 6. The used adsorbent CMPO/SiO₂-P is first contacted with acetone or other lipophilic solvent to remove CMPO. The eluent containing degraded CMPO will be treated by, for example, distillation and provided for CMPO purification for recycling. The obtained SiO₂-P could be used after holding CMPO again, otherwise thermally decomposed to have SiO₂ particle that can be easily disposed as a stable form.

Figure 1. The reference process for aqueous reprocessing of advanced fast reactor fuel cycle

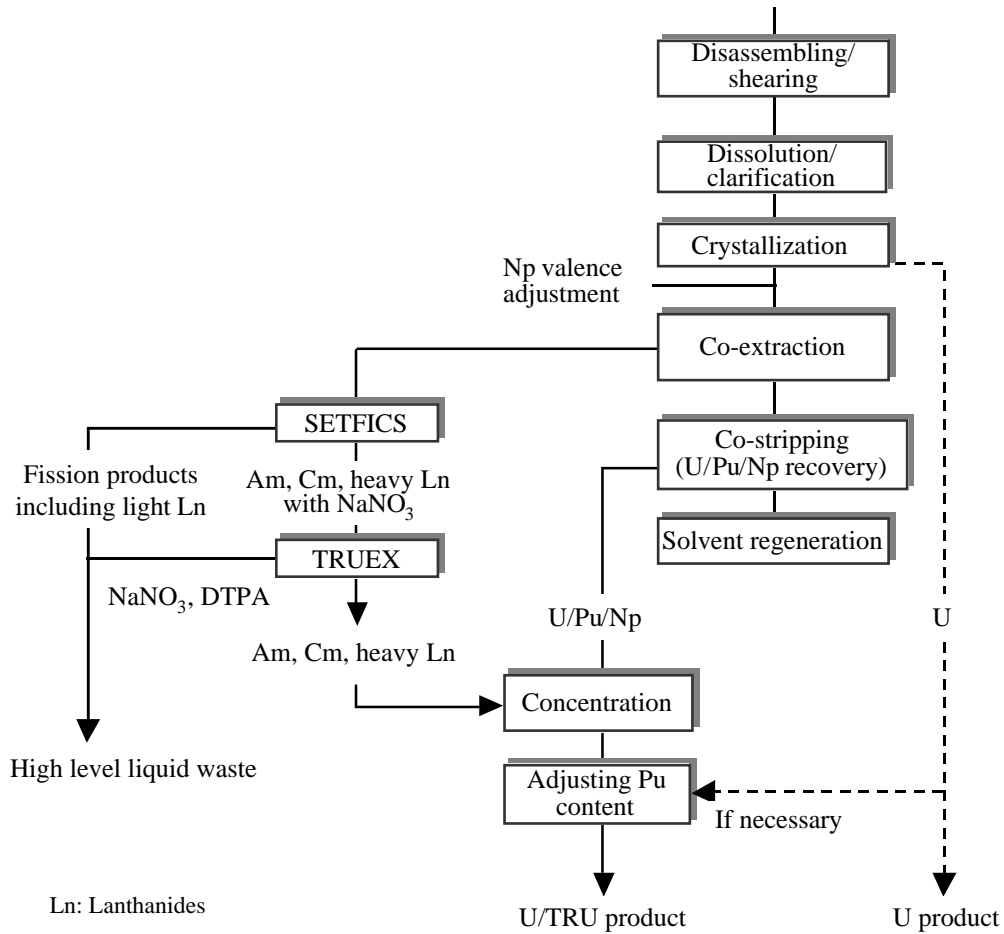


Figure 2. Experimental flowsheet of the SETFICS process using mixer-settlers for high loading and application of hydroxylamine nitrate

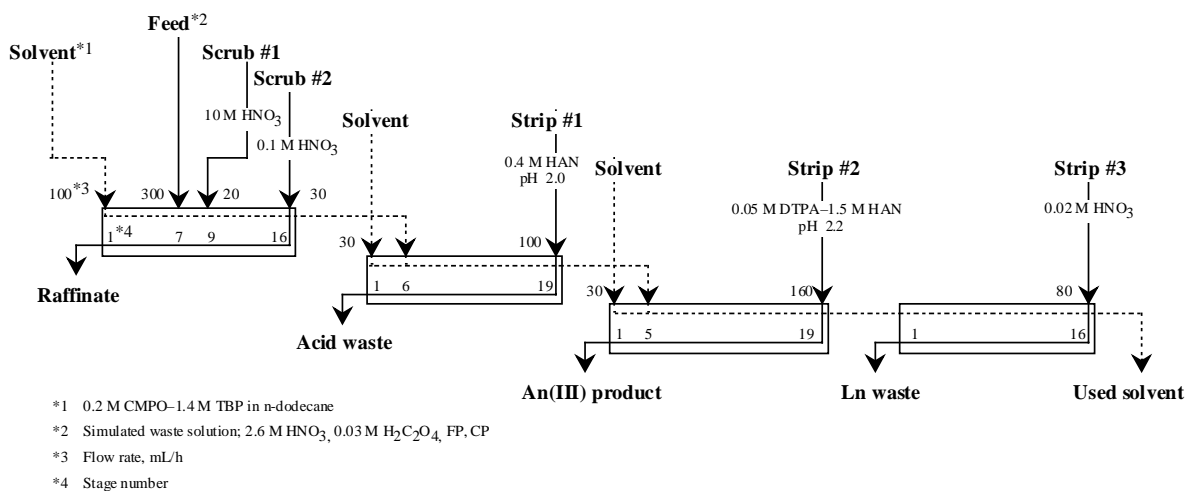


Figure 3. The distribution ratio of rare earth elements in the TRUEX solvent and HEDTA–NaNO₃ solution system. Solvent: 0.2 M CMPO–1.4 M TBP in n-dodecane, aqueous solution: 0.2 M HEDTA–1 M NaNO₃ for left figure, HEDTA–1 M NaNO₃ (pH 2.0) for right figure

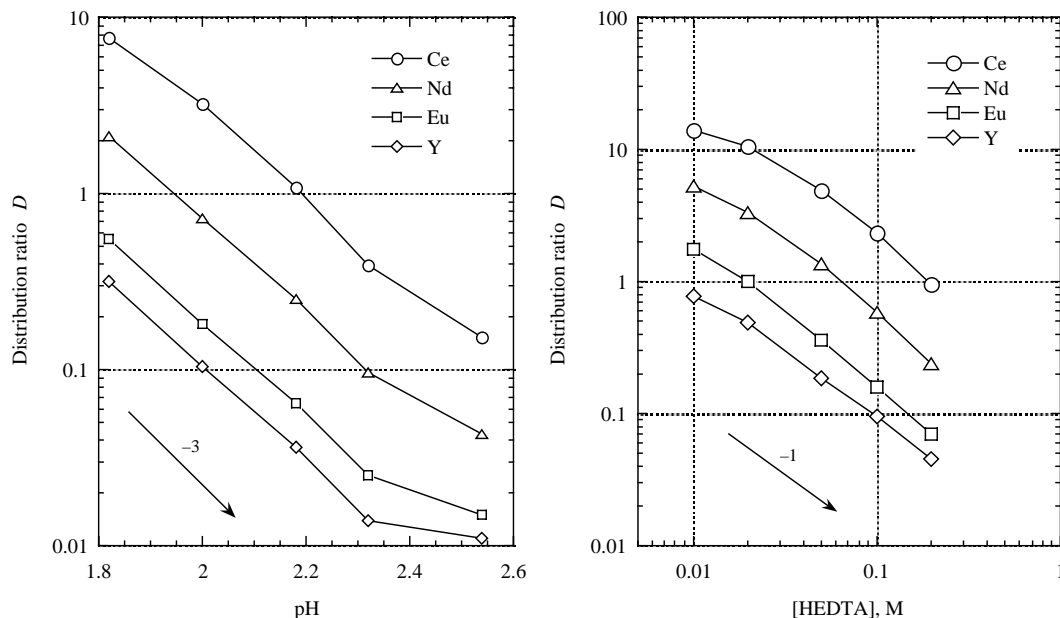


Figure 4. The Separation of lanthanides in the TRUEX solvent and HEDTA–NaNO₃ solution system. HEDTA system: 0.2 M CMPO–1.4 M TBP in n-dodecane and 0.05 M HEDTA–1 M NaNO₃ (pH 2.0), DTPA system: 0.2 M CMPO–1.0 M TBP in n-dodecane and 0.05 M DTPA–3 M NaNO₃ (pH 2.0)

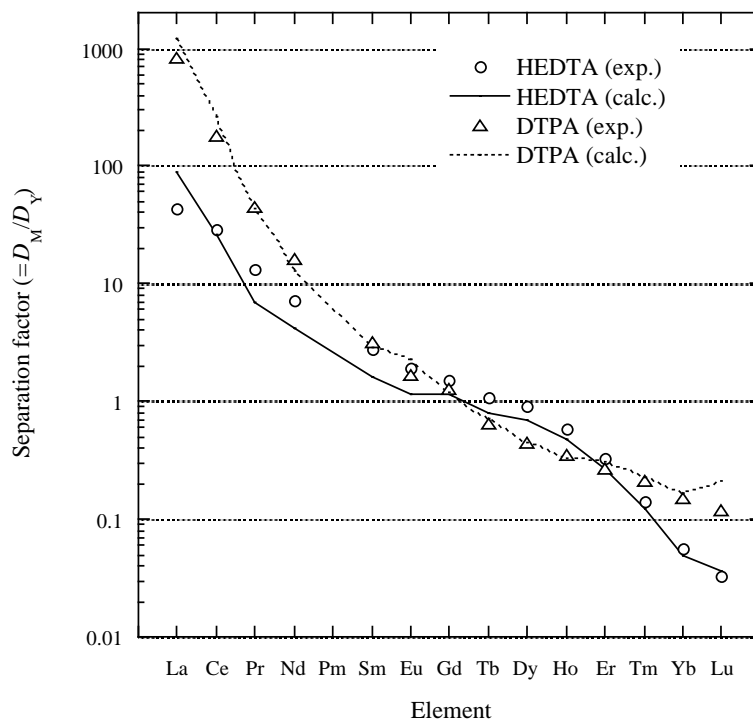


Figure 5. TGA and DTA curves for CMPO/SiO₂-P

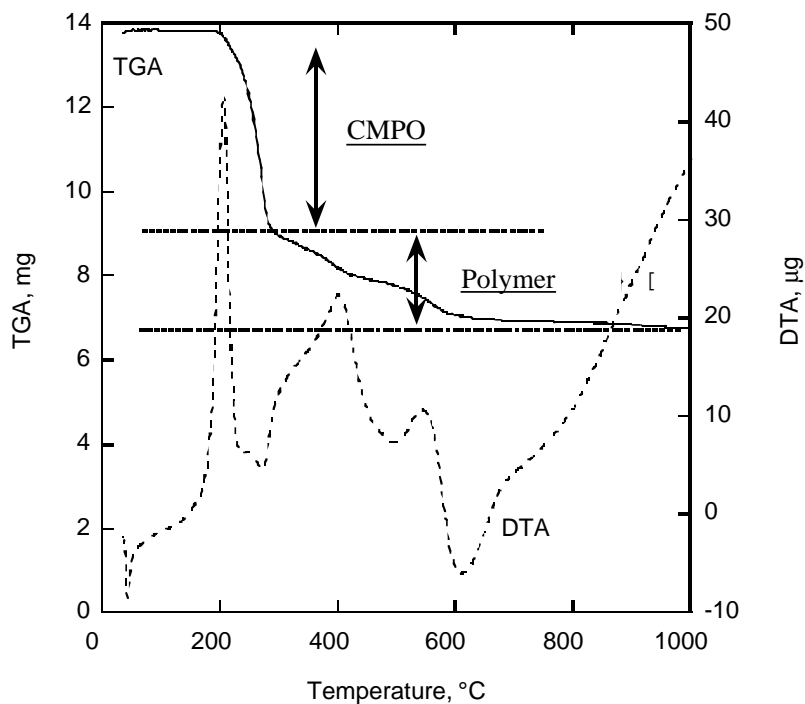
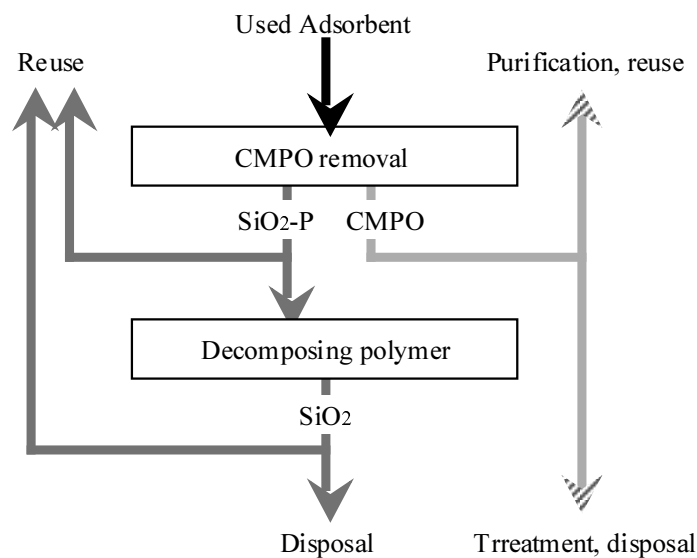


Figure 6. A schematic diagram of treatment for used CMPO/SiO₂-P adsorbent



Introducing fluoride diluent

Changing hydrocarbon diluent that commonly used also provides possibility to increase the maximum concentration of metallic cation in an organic phase. A fluoride compound fluoropol-732 supplied by Rhodia is a candidate. The mixture of CMPO and fluoropol-732 shows similar tendency

of extraction compared with typical TRUEX solvent system. When extracting lanthanides, there is no limited metal concentration for third phase formation, that is, trivalent metals can be extracted without organic phase splitting so far as free extractant is available. It should be checked that separation in counter-current separation procedure and degraded fluoride removal or treatment procedure.

Future plan

The Chemical Processing Facility (CPF) had been served to examine the PUREX and the TRUEX/SETFICS process for 10 years. In March 2002, improving work for a hot cell and glove boxes in order to study various separation methods was completed. From late 2002, JNC is going to conduct experimental study to obtain fundamental data that will be provided to evaluate aqueous and pyroprocesses for feasibility study of Advanced Fast Reactor Fuel cycle.

It is planned to conduct experiments to confirm the methods described in this paper using fast reactor irradiated MOX fuel. Also some alternative methods and Am/Cm separation techniques from the SETFICS product solution will be examined.

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REFERENCES

- [1] S. Nomura, A. Aoshima, T. Koyama and M. Myochin (2001), *Development of Challengeable Reprocessing and Fuel Fabrication Technologies for Advanced Fast Reactor Fuel Cycle*, Global 2001, September 9-13, Paris, France.
- [2] Y. Koma, M. Watanabe, S. Nemoto and Y. Tanaka (1998), *Trivalent f-Element Intra-group Separation by Solvent Extraction with CMPO-complexant System*, J. Nucl. Sci. Technol., 35(2), 130-136.
- [3] E.P. Horwitz, D.G. Kalina, H. Diamond, G.F. Vandegrif and W.W. Schulz (1985), *The TRUEX Process – A Process for the Extraction of the Transuranic Elements from Nitric Acid Wastes Utilizing Modified PUREX Solvent*, Solv. Extr. Ion Exch., 3(1&2), 75-109.
- [4] Y. Koma, M. Watanabe, S. Nemoto and Y. Tanaka (1998), *A Counter Current Experiment for the Separation of Trivalent Actinides and Lanthanides by the SETFICS Process*, Solvent Extr. Ion Exch., 16(6), 1357-1367.
- [5] E.P. Horwitz, K.A. Martin, H. Diamond and L. Kaplan (1986), *Extraction of Am from Nitric Acid by Carbamoyl-Phosphoryl Extractants: The Influence of Substituents on the Selectivity of Am over Fe and Selected Fission Products*, Solvent Extr. Ion Exch., 4(3), 449-494.
- [6] Y-Z. Wei, M. Kumagai, Y. Takashima, G. Modolo and R. Odoj (2000), *Studies on the Separation of Minor Actinides from High-level Wastes by Extraction Chromatography Using Novel Silica-based Extraction Resins*, Nuclear Technology, 32(3), 413-423.