R&D activities on actinide separation in China

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Abstract

A brief status of the development of actinide separation in China is presented. The activities on actinide separation include:
1) Neptunium chemistry and its separation in Purex Process;
2) actinide separation from HLLW;
3) separation of actinides from rare earth; and
4) preliminary studies on uranium cathode deposit by pyrochemical process.

Keywords: Actinide separation, Neptunium chemistry, Reprocessing, HLLW

1. Introduction

The active and efficient development of nuclear power is a significant strategic option for China in order to meet huge demand of energy and to realize controlling greenhouse gas emission. The sustainable development of nuclear energy must take into account the durability of the uranium resource, the economic competitiveness and the ecological benefits. The development of the closed fuel cycle technologies is really important for the sustainable development of nuclear energy in China, both for the full utilization of uranium resources and the minimization of nuclear waste.

To reach these goals, China follows the route from PWRs to FRs option. Based on the nuclear energy development policy, actinide separation R&D has been conducting in China.

The main aim of this work is to present a brief status of the development of actinide separation in China.
2. Neptunium chemistry and its separation in Purex Process

2.1. Purpose and complexity of Neptunium chemistry and its separation

In the advanced Purex process, the separation of Neptunium will be taken into consideration. It is of significance to study the recovery of neptunium for the following purposes: 1) to reduce the long term radioactive toxicity of high level waste, because of its long half-life \( (2 \times 10^6 \text{ a}) \); 2) to recycle the usable material (fertile) for fast reactor/ADS systems.

However, Np recovery is challenging because of the difficulty to control its pathway in Purex process due to the Np complicated chemical behavior:

- \( \text{Np}^{4+} \), \( \text{NpO}_2^{4+} \), \( \text{NpO}_2^{2+} \) can co-exist in acid solutions, proportion for the three species varying with temperature, acidity, nitrous/nitric acid ratio, concentration of reductant, etc.
- Extraction behaviors are different for Np(IV), Np(V) and Np(VI), the order of their distribution coefficients being \( \text{Np}(\text{VI}) > \text{Np}(\text{IV}) >> \text{Np}(\text{V}) \), influenced by acidity, uranium concentration, etc.
- Technological measurements for Np recovery must be handled precisely to meet U and Pu recovery rate, production specification, and possible influence on solvent degradation.

Based on this fact, the investigation of neptunium chemistry was focused on Np extraction with U and Pu in co-decontamination step, Np stripping in U/Pu separation step and the control of Np pathway during Pu purification cycle.

2.2. Neptunium chemistry in dissolution and co-decontamination step

Main reactions of Np in dissolving and co-decontamination step are as follows:

\[
2\text{NpO}_2^+ + 4\text{H}^+ \Leftrightarrow \text{Np}^{4+} + \text{NpO}_2^{2+} + 2\text{H}_2\text{O}
\]

\[
2\text{NpO}_2^+ + 3\text{H}^+ + \text{NO}_3^- \Leftrightarrow 2\text{NpO}_2^{2+} + \text{HNO}_2 + \text{H}_2\text{O}
\]

\[
\text{NpO}_2^+ + \text{H}^+ + \text{HNO}_2 \Leftrightarrow \text{NpO}_2^{2+} + \text{NO} + \text{H}_2\text{O}
\]

\[
2\text{NpO}_2^{2+} + \text{H}_2\text{O} + \text{HNO}_2 \Leftrightarrow 2\text{NpO}_2^+ + \text{HNO}_3 + 2\text{H}^+
\]

In this step, nitrous acid plays a important role. When the concentration of HNO\(_2\) is in the range \( 10^{-5} \text{~t} 10^{-3} \text{ mol/L} \), it plays as a catalyst in the oxidation of Np(V) to Np(VI) by HNO\(_3\); When the concentration of HNO\(_2\) is above \( 10^{-3} \text{ mol/L} \), it behaves as a reductant which reduces Np(VI) to Np(V). It is a reversible reaction, and the equilibrium of the reaction is shifted towards Np(VI) which is continuously extracted into the organic phase.

At the dissolution step, the Np disproportion is the main reaction, whereas at the complementary dissolution step with oxide atmosphere, Np(IV) will be oxidized to Np(VI). In the co-decontamination step, Np recovery increased with increasing acidity of the feed and scrub solutions. Besides, the flow rate of the scrub solution also influences the recovery of Np.

2.3. Reduction of Np in the U/Pu separation step

In the U/Pu separation step, a great effort was made to control the Np in the Pu purification cycle. The key issue is the application of the reductant. The kinetics of the Np(VI) to Np (V) reduction reaction was studied with various reductants at 24-25 °C, and the results are shown in table 1.

As contrast, the equation rate of reactions between DMHAN/ MMH and Np(V) were obtained, and kinetics parameters were shown in table 2.
Table 1 Reaction kinetics between Np(VI) and various reductants in 24-25 °C

| Reductant                      | Result                                                                 |
|--------------------------------|------------------------------------------------------------------------|
| 2-hydroxyethyl-hydrazine       | $k_2 = 391 \text{min}^{-1}$,                                           |
|                                | $E = 56.6 \text{kJmol}^{-1}$.                                           |
| Methyl-hydrazine (MHN)         | $k_2 = 61.3 \text{min}^{-1}$,                                           |
|                                | $E = (59.62 \pm 1.12) \text{kJmol}^{-1}$.                               |
| 1,1-dimethyl-hydrazine         | $E_a = 47.2 \text{kJmol}$,                                              |
|                                | $-dC(\text{Np(VI)})/dt = k C(\text{Np(VI)}) C(CH_3)2 NNH_2) C(\text{HNO_3})$. |
| Tert-butyl-hydrazine           | $-dC(\text{Np(VI)})/dt = k C(\text{Np(VI)}) C(0.9(\text{TBH})) C(0.75 (H^+))$, |
|                                | $K = 5.44 \text{molL}^{-1} \cdot 0.15 \text{min}^{-1}$,               |
|                                | $E = 61.2 \text{kJmol}$.                                               |
| N,N-diethyl-hydroxyamine       | $-dC(\text{Np(VI)})/dt = k C(\text{Np(VI)}) C(\text{DEHAN}) C(1(H^+))$, |
|                                | $K = (23.0 \pm 1.8) \text{min}^{-1}$,                                 |
| N,N-dimethyl-hydroxyamine (DMHAN) | $-dC(\text{Np(VI)})/dt = k C(\text{Np(VI)}) C(\text{DMHAN}) C(0.6(H^+))$, |
|                                | $K = 289.8 \text{molL}^{-0.4} \cdot \text{min}^{-1}$.                 |

Table 2 Reaction kinetics between Np(V) and reductants in 35°C

| Reductant                      | Result                                                                 |
|--------------------------------|------------------------------------------------------------------------|
| N,N-dimethyl hydroxylamine (DMHAN) | $-dC(\text{Np(V)})/dt = k C(\text{Np(V)}) C(\text{DEHAN}) C(H^+)$,  |
|                                | $K = 0.0444 \pm 0.0020 \text{molL}^{-2} \cdot \text{min}^{-1}$.        |
| Methyl-hydrazine (MHN)         | $-dC(\text{Np(V)})/dt = k C(\text{Np(V)}) C(0.36(\text{DMHAN}) C(H^+)$, |
|                                | $k = (0.00479 \pm 0.00075) \text{molL}^{-1.36} \cdot \text{min}^{-1}$.  |

The reductive back-extraction behavior of Np(VI) from 30%TBP/kerosene-HNO₃ with DMHAN and MMH has been investigated. It was found that the reduction of Np(VI) to Np(V) by DMHAN or MMH is fast, while the reduction of Np(V) to Np(IV) is very slow, thus Np(VI) could be rapidly stripped into aqueous phase. It only takes 5 minutes to reach the equilibrium. Stripping efficiency of Np is improved with a higher concentration of reductant, a lower acidity and a higher temperature.

2.4. Adjustment of Np valence in Pu purification to control its amount in Pu product or in extraction raffinate

The valence adjustment before Pu purification is very important. Electrolytic method was selected as a salt-free process. Platinum was used as anode, while titanium was used as cathode. The results show that monomethyl-hydrazine was completely electro-oxidized, while N,N-Dimethylhydroxylamine was indirectly oxidized. One of the reduction reaction products on the cathode is nitrous acid which can quickly oxidize Pu(III) to Pu(IV). After electro-oxidation of the solution, the Pu(IV) proportion exceeds 99.7%, and the Pu(VI) one is less than 0.3%. Np(IV) proportion is approximately 92%.

Galvano-static electrolysis was used to adjust the valence of Pu and Np ions
In the future, more work should be done:
1. improve Np extraction in 1A step, etc.;
2. carry out a hot test using spent fuel;
3. improve the process of reprocessing pilot plant to recover Np firstly from 2AW+2DW, et al.

3. Partitioning of HLLW for minor actinides

3.1. Goals and technical choices

To reduce the long term radiotoxicity of high level liquid waste (HLLW) and decrease greatly the volume of the waste, partitioning of HLLW is an important research goal.

Establishment of partitioning process should aim at the following goals: 1) Connection with PUREX directly, without concentration or dilution; 2) Recovery of all of the actinide elements (U, Pu, Np, Am, Cm); 3) Removal of the heat emitters (Sr, Cs).

The technical choices for the partitioning of HLLW are Group separation (U, Pu, Np + Am, Cm and rare earth, leaving Cs, Sr in the residual HLLW); Separation of Am, Cm from RE; and removal of the heat emitters from residual HLLW.

3.2. Group separation

Fig. 1 shows the schematic diagram of group separation of HLLW. Some possible process options for group separation include:
1. extraction process using TRPO as an extractant, which has been demonstrated with genuine nuclear fuel solutions;
2. extraction process using N,N,N',N'-tetraoctyldiglycolamide (TODGA) as an extractant, for which lab-scale basic studies have been finished and
3. chromatographic process using silica-based extraction resins, for which basic studies have just started.

\[
\begin{align*}
\text{Pu}^{3+} & \xrightarrow{0.982V} \text{Pu}^{4+} \xrightarrow{1.17V} \text{PuO}_{2}^{3+} \xrightarrow{0.916V} \text{PuO}_{2}^{2+} \\
\text{Np}^{4+} & \xrightarrow{0.739V} \text{NpO}_{2}^{2+} \xrightarrow{1.137V} \text{NpO}_{2}^{2+}
\end{align*}
\]

Fig. 1 Schematic diagram of group separation of HLLW
For the partitioning, the engineering feasibility of the TRPO process will be tested whereas process studies of MAs partitioning with TODGA process will be performed.

### 3.2.1. TRPO process

TRPO with good physico-chemical properties and irradiation stability has excellent extraction selectivity to tri-, tetra- and hexa-valent actinides. TRPO process for actinides removal from HLLW has been invented in China. Several hot tests and the pilot test demonstrated that the HLLW could be conditioned into non-α waste after treatment by TRPO process.

### 3.2.2. TODGA process

Fig. 2 shows one of the new flow-sheets developed in CIAE for MAs partitioning from HLLW using TODGA with tridentate ligand and DHOA with monoamide (TODGA process). Investigations on MAs partitioning from HLLW have been conducted in CIAE, and the main results showed that: (1) By adding DHOA, the third phase diminished while the distribution ratio of Sr decreased, thus separation of Sr should be realized using TODGA alone; (2) U, Np and Pu could be back extracted together using AHA as complexant; (3) More than 95% of Am were back extracted with RE.

![Schematic diagram of TODGA process](image)

With regard to actinide/lanthanide separation, a conceptual process (TODGA process) was proposed, and has been examined with synthetic HLLW in multiple-stage centrifugal extractors. From the experiments, promising results were obtained.

### 3.2.3. Chromatographic process

To develop an advanced Am and Cm partitioning process by extraction chromatography using a minimal volume of organic solvent and compact equipment, 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 (SiO₂-P). The extractants include octyl(phenyl)-N, N-diisobutylcarbamoyl methylphosphine 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 fast kinetics and significant 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 HLLW 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 HLLW solution at pH4 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.

3.3. Separation of minor actinides from RE

The effective separation of trivalent actinides from lanthanides is one of the key steps to realize the advanced nuclear fuel cycle based on the “partitioning-transmutation” strategy. However, their effective separation is always difficult in the separation field because of the very similar physical and chemical properties between trivalent actinides and lanthanides. In the separation by solvent extraction, ligands containing soft donor, e.g. S and N, show good performance to separate trivalent actinides from lanthanides.

Fig. 3 shows the schematic diagram of the minor actinides separation from RE. Some possible processes for MA-RE separation are: 1) extraction process using Cyanex301 as extractant; 2) extraction process using BTPs as extractant; 3) chromatographic process using silicon particles as supporting material.

![Fig. 3 Schematic diagram of the minor actinides separation from RE](image)

3.3.1. Cyanex301 process

In 1995, Cyanex301 was found to be able to separate trivalent actinides from macro amount of lanthanides. Then the purified product bis(2,4,4-trimethylpentyl) dithiophosphinic acid was proven to have remarkable ability to separate actinides from both micro and macro amount of lanthanides. The separation process was studied and demonstrated by hot test. The dominant complex in extraction is of cubic structure with a coordination number of 8.

The process has been tested for its high efficiency using actual lanthanide-actinide mixtures, and is promising for trivalent actinide/lanthanide separation because of the outstanding separation performance.

3.3.2. BTPs process

Recently, studies on An/Ln separation with BTP (a kind of neutral N bearing extractants) as extractant has been done in our laboratory. The results showed that separation factor (SF$_{Am/Eu}$) is always over 100 at various acidity, and recovery of Am is 98.42% containing 0.9% Eu with counter-current cascade extraction; also the stripping efficiency of Am and Eu is 99.9%. The total separation factor was over 104.

The advantages of the BTP as an extractant are: 1) high separation efficiency of An/Ln; 2) efficient stripping, which will bring an easy reuse of the solvent. However, since instability of the n-propyl-BTP, methods for overcoming the problem will be further studied.
3.4. Removal of the heat emitters

Removal of Cs could be accomplished with Zirconium pyrophosphate adsorption process. Compared with Cs, several methods could be selected to separate Sr: 1) extraction process using crown ether; 2) chromatographic process with crown ether on silicon particle; 3) new super-molecular selective ligands.

4. Development of pyrochemical reprocessing in China

Based on the ambitious program to develop FR nuclear power, R&D on pyrochemical process has been restarted in CIAE.

Our recent work on pyrochemical studies mainly focuses on the measurement of basic parameters, including: 1) electrochemical studies of uranium and rare earths both in molten chloride salts (LiCl-KCl) and molten fluoride salts (LiF-CaF2 or Lithium type cryolite); 2) dissolution of simulated fuel in molten salts; 3) purification and recycle of molten salts; 4) some physical and chemical properties of the molten salts. Besides, development of equipment and technique for process monitoring and control, precise measuring and control of temperature in molten salts also received much attention.

5. Conclusions

In conclusion, a brief status of the development of actinide separation in China was presented.

The Np control pathway in Purex process was studied with DMHAN and MMH as reductants in the U, Pu co-decontamination/separation cycle and Pu purification cycle.

In the separation of actinide form HLLW and subsequent An/Ln separation, several processes with promising applications were proposed, such as TRPO process, TODGA process and Cyanex301 process.

For the sake of FR spent fuel reprocessing, the preliminary investigations of pyrochemical process based on molten salts were initiated, and the directions for process improvement were suggested.