RECENT PROGRESSES ON PARTITIONING STUDY IN TSINGHUA UNIVERSITY

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Abstract

Recent progresses on partitioning studies in Tsinghua University are reviewed. Declassification of the commercial HLLW to a waste that is suitable to shallow land disposal is possible. An enhanced TRPO process with optimal process parameters can meet the required DF of TRU elements. A Total Partitioning process for commercial HLLW was developed by modification of the TP process for Chinese HLLW. The Total Partitioning process for commercial HLLW consists of an enhanced TRPO process to remove TRU elements and ^{99}Tc, a CESE process to separate strontium, a KTiFC ion exchange process to segregate cesium and an An/Ln separation process with HBTMPDTP. The flow sheet of the total partitioning process for commercial HLLW was given.

1. Introduction

The final disposal of radioactive waste is one of the key problems that effect the development of nuclear energy industry. Partitioning and Transmutation (P&T) concept [1] involves chemical separation of transuranium (TRU) elements as well as long-lived nuclides (for example, ^{99}Tc, ^{129}I, etc.) from HLLW, and transmutation of them to either stable or short-lived nuclides. The P&T constitutes an advanced nuclear fuel cycle. The implementation of the P&T could significantly reduce long-term risk of the radioactive waste.

The partitioning of HLLW can also be used as a pre-treatment method of HLLW to reduce α-waste and HAW volume. In recent years a clean use of nuclear energy (CURE) concept was proposed for the back-end of nuclear fuel cycle [2]. In the CURE concept the partitioning requires not only to remove the TRU, ^{99}Tc and ^{129}I, but also to segregate ^{90}Sr and ^{137}Cs from HLLW. After partitioning the original HLLW would be de-classified to a non-α, low and intermediate lever radioactive waste that could be suitable for shallow-land disposal. So for the CURE concept the required decontamination factors (DF) for TRU elements will be much higher than that for the P&T concept. The required DF of TRU, ^{99}Tc, ^{137}Cs and ^{90}Sr are given in Table 1 for a typical commercial HLLW. The spend nuclear fuel had a burn-up of 33 000 MWd/tU, a cooling time of 10 years and 99.75% of U and Pu had been removed in reprocessing [3]. In Table 1 the α- waste standard of 4×10^5 Bq/kg is chosen and 0.40 m^3 concrete/tU waste is supposed to be produced after solidification of the declassified liquid waste. In order to get a higher waste volume reduction, the separation of lanthanides (Ln) and actinides are necessary for commercial HLLW. The required DF for TRU elements in Ln fraction should be higher than 2.4×10^5 [4].

Table 1. **The required DF for treatment of typical commercial HLLW to a waste suitable to shallow land disposal**

Nuclides	**Activity in HLLW Bq/tU**	**Chinese standard GB-9132-88 Bq/kg**	**Required DF (Solidify by cementation, 0.4 m^3/tU)**
TRU	1.26×10^{14}	4×10^5	4.0×10^5
^{99}Tc	4.78×10^{11}	–	–
^{90}Sr	2.07×10^{15}	4×10^{10}	71
^{137}Cs	3.01×10^{15}	4×10^{10}	104

In recent years, the study on the partitioning process was carried out in Tsinghua University in order to meet the DF requirement for typical commercial HLLW. The aim is to declassify the HLLW to a waste suitable to shallow land disposal. In this paper the recent progresses on partitioning studies in Tsinghua University will be reviewed. The flow sheet of total partitioning process for commercial HLLW was given.

2. The enhancement of TRPO process for commercial HLLW

A TRPO process was developed in Tsinghua University for removing TRU elements from HLLW [5,6] in 1980s. Hot tests of the TRPO process were carried out with HLLW of WAK in Institute for Transuranium Elements (ITU) at Karlsruhe, Germany in 1993 [7]. The hot test was completed with 24 stages of miniature centrifugal contactor in hot cell. The DF value of TRU elements obtained in the

hot tests (See Table2) was enough for the P&T requirement. However, it is not sufficient to meet the required DF for CURE project because the TRPO process was designed for P&T project in the period. In recent year, the TRPO process was improved in order to increase the DF values of TRU elements.

Table 2. **The DF of TRU elements, ^{99}Tc and Nd in the TRPO hot tests**

	HNO_3 in feed	**Extraction stages**	**Decontamination factors**						
			^{237}Np	^{238}U	^{239}Pu	Am/^{241}Pu	^{243}Am	^{99}Tc	^{144}Nd
Run 1	0.75	6	12.4	>5 400	>760	>2 800	>900	>1 400	>22 000
Run 2	1.36	10	>4 100	>7 000	>950	>3 200	>760	>1 700	>33 000

Tetra- and hexa-valent TRU elements are highly extracted by 30% TRPO-kerosene. The controlling elements for the removal of TRU elements are trivalent americium and curium. The extraction behavior for Am and Cm is very similar. So improving Am extraction is a key issue. A simplified optimised objective function [8] was introduced into the TRPO mathematical model for americium extraction [9]. The objective function was designed as that the second waste from the TRPO process should have a minimal volume to improve the safety, cost and to decrease the environmental impact. In addition, in the calculation, the Am decontamination factor should be above 4.0×10^5 and for a conservative consideration, the DF of 4.0×10^6 for Am was fixed. The acidity of feed and scrub solution was chosen to improve neptunium extraction, and was 1.35 M and 0.5 M respectively. The optimal parameters of the TRPO process for Am extraction were obtained [8] and are listed in Table 3.

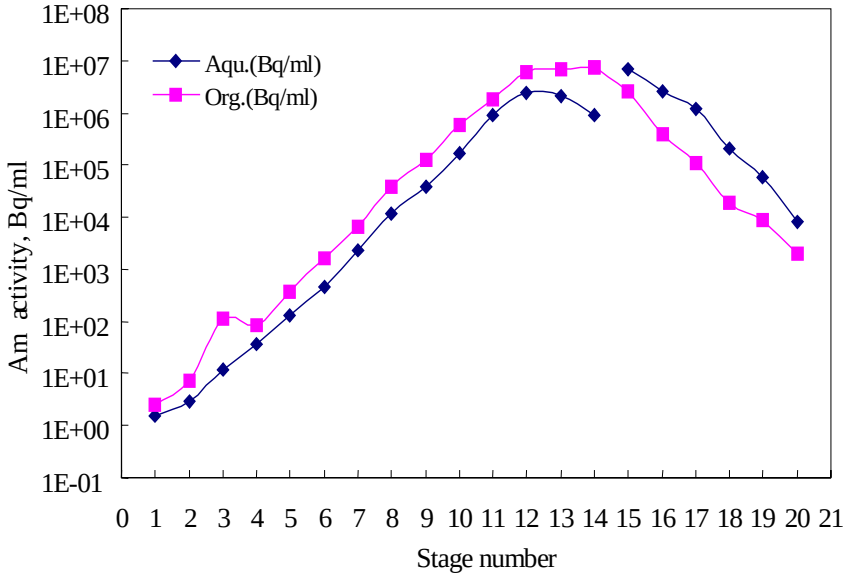
A multistage counter current cascade experiment with simulated HLLW skipped with ^{241}Am was carried out to verify the calculated results [10]. A set of 20 stages miniature centrifugal extractor was installed in a glove box. Optimal parameters were used in the process experiment (see Table 3). The cascade included 12 stages for extraction, 2 stages for scrubbing and 6 stages for Am stripping. The simulated feed solution had a specific volume of 1 850 L/tU and skipped americium with a specific activity of 7.83×10^6 Bq/ml. The flow ratio of feed/organic/scrub/stripping was 1/1.21/0.265/1.21.

Very good results were obtained in the cascade experiments [10]. The obtained DF_{Am} was 1.25×10^6 and the material balance for Am was 92.6% in the experiments. The americium profiles in each stage are given in the Figure 1. The experiments show that the calculated results fit with the experimental ones very well. The required DF for treating typical commercial HLLW to a waste, that is suitable for sallow land disposal, can be reached with the TRPO process.

Table 3. **Calculated and experimental parameter of the TRPO process (For a typical HLLW of a burn-up of 33 000 MWd/tU, Calculated $DF_{Am} = 4.0 \times 10^6$)**

Parameter	Calculated value[8]	Experimental value [10]
Specific volume of Feed (*F*)	1 750 L/tU	1 875 L/tU
Volume of 30%TRPO-kerosene	1.18 *F*	1.21 *F*
Volume of scrubbing solution	0.267 *F*	0.265 *F*
Volume of stripping solution	1.18 *F*	1.21 *F*
Number of extraction stages	10	10
Number of scrubbing stages	2	2
Number of stripping stages	–	6
HNO_3 concentration in feed solution	1.35 mol/L	1.35 mol/L
HNO_3 concentration in scrubbing solution	0.5 mol/L	0.5 mol/L
HNO_3 concentration in stripping solution	–	5.0 mol/L

Figure 1. **Americium activity profiles in TRPO process**



3. The separation of lanthanide and actinides

The separation of trivalent lanthanide (Ln) and actinides is a difficult subject in the separation chemistry. However the separation of Ln and Actinides is necessary no matter how for the P&T concept or for the CURE concept. The study on the separation chemistry of lanthanide and actinides is one of research subjects in Tsinghua University.

An S-coordinated extractant bis (2,4,4 trimethylpentyl) dithiophospninic acid (HBTMPDTP) had been proven to be an effective extractant for the separation of trivalent Am from Ln [11]. The HBTMPDTP is prefers to extract Am rather than Ln and the separation factor reaches to 5 000 for

trace amount of Am and Eu. The HBTMPDTP (>99% purity) was obtained by purification of a commercial extractant Cyanex 301 [12]. The extraction chemistry of Am and Ln was studied with HBTMPDTP. An empirical model of distribution ratio for Am and Ln was derived and a computer program for counter current separation of Am/Ln by HBTMPDTP extraction was compiled [13]. The An/Ln separation process parameters were calculated and were verified by batch multistage counter current extraction experiments.

A conceptual Am/Ln separation flow sheet by HBTMPDTP extraction was proposed for the Am/Ln fraction from partition process of HLLW [14]. The feasibility of the separation flow sheet was verified with a hot test of crossing flow extraction [15]. Am specific activity of was 2×10^5 Bq/ml and the lanthanide concentration was 0.021M in the feed solution. After denitration to 0.3 M HNO_3, the feed solution was first extracted by Cyanex 301 to remove impurities. It was adjusted to pH 3.5 and was then fed into extraction unit. More than 99.999% of Am was extracted into the organic phase with 4 stages of cross extraction. The Am concentration in the raffinate was 1 Bq/ml. Only ~3% Ln was extracted by HBTMPDTP. The average separation factor between Am and Ln was 3 500 for first three stages. The hot test results proved that the separation process was effective.

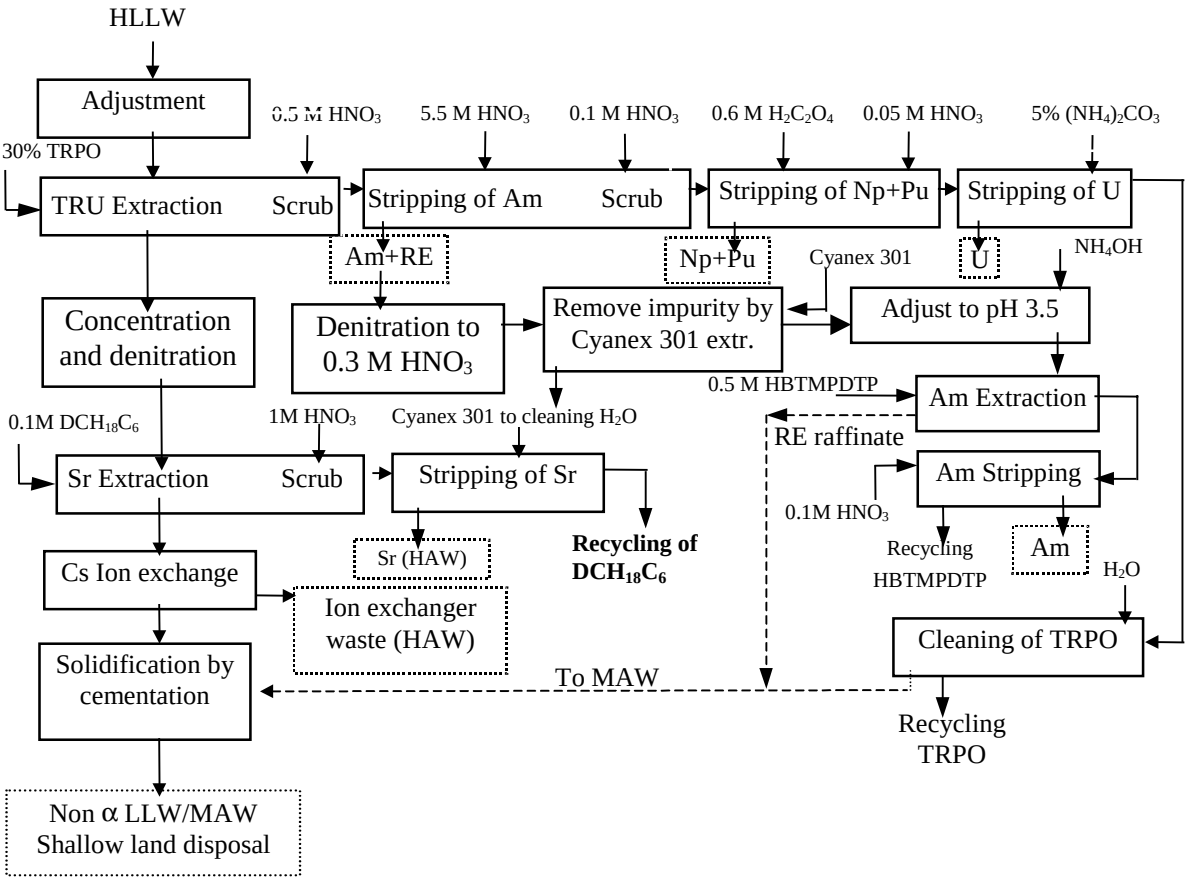
The synergic extraction and separation of Am and Ln by HBTMPDTP/TBP-Kerosene was also studied. At pH about 2.8, quite high separation factor for Am/Ln could be obtained. A multistage counter current cascade experiment was performed. It included 7 stages for extraction, 3 stages for scrubbing and 2 stages for stripping. Americium was effectively separated from Ln. The separation factor of Am from Ln was 5×10^4 and the separation factor of Ln from Am was 2500 [16].

4. The Total Partition process for commercial HLLW

A Total Partition (TP) process was developed in Tsinghua University during 1990s for Chinese high saline (defence) waste [17,18]. The TP process consists of the TRPO process to remove TRU elements, a Crown extraction process (CESE) to separate strontium and a potassium titanium ferrocyanide (KTiFC) ion exchanger to segregate caesium. After the treatment by the TP process, the high saline HLLW was declassified to a non-α low and intermediate waste, that could be cementation and sallow land disposal. The hot test proved that the TP process worked very well for the waste.

In commercial HLLW, the salt content is much lower than that in the high saline HLLW. Low salt content benefits the TRU extraction by TRPO extractant. However, it is detrimental to the strontium extraction by crown ether $DCH_{18}C_6$. This problem can be solved by addition a concentration and denitration unit between the TRPO and the CESE process. The unit was used for increasing the salt content by evaporation and then to adjust the acidity of the solution. The crown ether extraction and the KTiFC ion exchanger can meet the required DFs of strontium and cesium for commercial HLLW. The hot test of the TP process for Chinese HLLW had proved the fact. So the TP process for high saline HLLW can also be used for commercial HLLW after modification. The general flow sheet of the TP process for commercial HLLW is given in Figure 2. In the flow sheet, the An/Ln separation process is also included.

Figure 2. **General flow-sheet of Total Partition process for commercial HLLW**



The auxiliary processes of the TP process are now being studied. They include the denitration and calcination for Am (RE) stripping solution, Np/Pu separation in $H_2C_2O_4$-HNO_3 solution, the conversion process for uranium stripping solution and immobilization process for Cs-loaded KTiFC ion exchanger. The advanced extraction equipment such as pulsed column and centrifugal contactor for the TP process are also being studied.

5. The radiation stability of TRPO extractant

The radiation stability of TRPO extractant was studied in recent year. The physical properties of 30% TRPO do not have obvious change between a dose of 1×10^4 to 5×10^5 Gy [19]. Main gaseous radiolytic products and acidic radiolytic products of 30% TRPO-kerosene extractant were analysed. Their radiation yield (G value) was determined [20]. At a dose of 1×10^4 to 1×10^6 Gy, radiolytic products do not have obvious effect on the extraction. When the radiation dose was above 2×10^6, some retention of heave elements were observed [21]. Research indicates that the polymeric products with high molecular weight cause the retention. The studies show that the TRPO extractant is much more stable than TBP.

6. Conclusion

Declassification of the commercial HLLW to a waste that is suitable to shallow land disposal is possible. An enhanced TRPO process can meet the required DF for TRU elements with optimal process parameter. A Total Partition process for commercial HLLW was developed by modification of the TP process for Chinese HLLW. It consists of an enhanced TRPO process to remove TRU elements and ^{99}Tc, a CESE process to separate strontium, a KTiFC ion exchange process to segregate caesium and an An/Ln separation process with HBTMPDTP.

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