



# An Overview of R&D Activities on High Level Liquid Waste Partitioning at Tsinghua University, China

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**Abstract.** Safe management of radioactive waste is of great importance to ensure the sustainability of nuclear energy. The reprocessing of spent nuclear fuel generates huge quantities of High-Level Liquid Waste (HLLW) that need to be further treated to minimize its long term hazards prior to the final geological disposal. Partitioning of HLLW into different groups not only would reduce the waste burden, but also could benefit the implementation of transmutation technologies and the utilization of the abundant nuclide resources in HLLW. China has a long history working on the partitioning of HLLW. An overview of recent R&D activities on this subject at Tsinghua University in China are presented in this paper.

**Keywords:** Nuclear waste · HLLW · Partitioning · Actinide · Extraction

## 1 Introduction

High level liquid waste (HLLW) is produced from the plutonium uranium extraction (PUREX) process for the reprocessing of spent nuclear fuel (SNF). Although a majority of U and Pu has been recovered, HLLW still contains a moderate amount of U/Pu, and transuranium (TRU) actinides such as Np, Am, as well as other highly radioactive nuclides such as  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ . Due to the high radiotoxicity and long-term hazard, HLLW imposes a potential hazard to the environment and human health. A so-called partitioning and transmutation (P&T) strategy has been proposed for the treatment of HLLW by first partitioning the waste into different groups and then converting the long-lived nuclides into short-lived or stable nuclides [1]. Obviously, partitioning of HLLW is one of the critical steps for the implementation of the P&T strategy. A variety of processes based on solvent extraction have been developed for the partitioning of HLLW worldwide [2].

China is one of the fast-growing countries in nuclear energy production and has adopted a closed fuel cycle policy [3]. A huge amount of spent fuels has been and will be continuously discharged from nuclear power plant in China. There will be a great pressure for the safe management of HLLW if these spent fuels are processed through PUREX process. Therefore, there is an urgent demand to develop efficient techniques for the treatment of HLLW. To solve this problem, research groups in China has conducted R&D work on the partitioning of HLLW for more than 30 years. This paper will give an overview of the recent progresses on this issue at Tsinghua University, China.

## 2 Technology and Key Progresses

HLLW partitioning at Tsinghua University, China is mainly based on solvent extraction technology by using a variety of functional extractants to selectively extract targeted components from HLLW. This is also the preferred technology for HLLW partitioning worldwide considering the maturity of this technology in nuclear industry and its easy coupling with the PUREX process. The longtime R&D work on HLLW partitioning in China focuses on the recovery of minor actinides, strontium and cesium from HLLW and the subsequent trivalent actinide and lanthanide separation.

### 2.1 Chemical Fundamentals

Recovery of minor actinides is a primary task in HLLW partitioning. A TRPO process was developed at Tsinghua University in 1980s [4]. The functional extractant TRPO is trialkyl phosphine oxides with the alkyl group contains 6–8 carbons. TRPO is commercially available and is well soluble in the preferred solvent such as kerosene in nuclear industry. TRPO has very strong affinity to actinides in III, IV and VI oxidation states, thus could be used for the recovery of actinides such as Am(III), Pu(IV) and U(VI) from HLLW. The best performances are usually achieved with a nitric acid concentration of around 1 M in the feed solution. It should be noted that the fission product lanthanides are coextracted with the trivalent actinides by TRPO, and therefore subsequent lanthanide/actinide separation is required to obtain the desired actinide product for future transmutation.

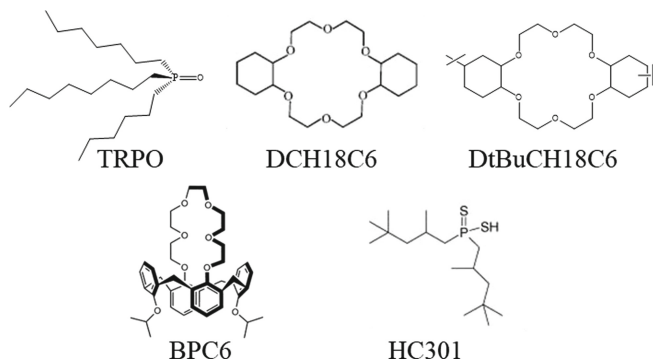
$^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , with half-lives of 28.9 y and 30.1 y, respectively, contribute a large part of the heat load and radioactivity in HLLW. Removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from HLLW can greatly reduce the waste volume and thereby save the repository capacity by eliminating most of the heat load and radioactivity. Removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  can also facilitate the handling and transportation of HLLW, either for subsequent treatment or for disposal. Moreover, the recovered  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  are useful isotopes that can be used as radiation-source for radiation therapy or radioisotope power generator.

For the removal of  $^{90}\text{Sr}$ , crown ethers (DCH18C6 or DtBuCH18C6) are used as the functional ligands at Tsinghua University, China [5]. For the removal of  $^{137}\text{Cs}$ , the KTiFC (potassium titanium ferrocyanide) ion exchanger was first used to selectively adsorb  $\text{Cs}^+$ . But this method was abandoned soon due to safety issues and the large amount of secondary waste produced. Currently, solvent extraction by a calix crown ether (bis(2-propyloxy)calix [4] crown-6, abbreviated as BPC6) is adopted as the preferred technique to fulfill this purpose. Both the deliberately selected crown ethers and calix crown ethers show high selectivity to  $\text{Sr}^{2+}$  and  $\text{Cs}^+$ , respectively, through accurate supramolecular recognition.

As mentioned earlier, subsequent trivalent actinide/lanthanide (An(III)/Ln(III)) separation is required after minor actinide recovery by TRPO process. Such a separation task is very challenging due to the chemical similarity between the two groups of f-elements. Soft donor ligands containing N or S atoms are suggested to show selectivity to An(III) over Ln(III). The research group in Tsinghua University first demonstrated the effectiveness of dithiophosphinic acids in An(III)/Ln(III) separation in 1990s [6]. The purified Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic Acid, abbreviated

as HC301 hereafter) could achieve an extremely An(III)/Ln(III) high separation factor ( $> 5000$ ) in one single solvent extraction contact.

The molecule structures of the functional ligands (TRPO, DCH18C6, DtBuCH18C6, BPC6, HC301) currently used for HLLW partitioning at Tsinghua University, China are shown in Fig. 1.



**Fig. 1.** Structures of functional ligands for HLLW partitioning at Tsinghua University, China

## 2.2 Key Progresses

TRPO process was first proposed in 1980s. Since then, a large amount of work has been conducted to test and demonstrate this process [4]. A hot test of the TRPO process was first carried out with HLLW of WAK in the Institute for Transuranium Elements (ITU) at Karlsruhe, Germany in 1993. The hot test was conducted on 24 stages of miniature centrifugal contactors in a hot cell. The decontamination factors (DF) for actinides such as  $^{239}\text{Pu}$ ,  $^{237}\text{Np}$  and  $^{241}\text{Am}$  were generally above  $10^3$ , but the value for  $^{241}\text{Am}$  was not very satisfied. The process was then optimized and a multistage counter current cascade experiment with simulated HLLW spiked with  $^{241}\text{Am}$  was carried out in a glove box. A DF of  $^{241}\text{Am}$  as high as  $10^6$  was obtained [7]. Very recently, TRPO process were further demonstrated in Tsinghua University on 30 stages of miniature centrifugal contactors using simulated HLLW spiked with  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{241}\text{Am}$ . The total DF for alpha elements was above  $10^5$ , meeting the requirements to produce non-alpha raffinate. Further hot tests to demonstrate the TRPO process for the treatment of genuine Chinese HLLW have been planned in the next few years.

TRPO process was also employed for the treatment of legacy defense HLLW in China. These legacy HLLW contains relatively low level of actinides as compared to HLLW generated from the reprocessing of commercial spent fuel [4]. In 1996, a multistage hot test was conducted with genuine legacy HLLW in the hot cell at Tsinghua University. The hot test lasted for 6 h and a total DF of 588 was achieved for all the actinides. Such a DF value is sufficient to transfer the legacy HLLW into non-alpha waste. In 2009, a much larger scale hot test using multistage miniature centrifugal contactors was further conducted to process genuine legacy HLLW in China. The test lasted for

160 h and more than 300Ci of HLLW was successfully processed. The DFs for actinides such as Np, Pu and Am all exceeded  $10^3$ , well above the required values. Moreover, TRPO process was also tested on semi-industrial scale pulsed column with simulated HLLW. Satisfied results such as good hydraulics and high DFs were obtained. Currently, the construction of a pilot scale facility is under consideration for the treatment of legacy HLLW in China.

For the removal of  $^{90}\text{Sr}$  from legacy HLLW, the crown ether DCH18C6 is employed as the extractant. Octanol is selected as the diluent. The process based on this extraction system was first demonstrated in the hot cell at Tsinghua University in 1996. A  $\text{DF} > 2500$  for  $^{90}\text{Sr}$  was achieved. The process was further demonstrated in a hot test in 2009 and a  $\text{DF} > 10000$  for  $^{90}\text{Sr}$  was achieved. For the removal of  $^{90}\text{Sr}$  from commercial HLLW in China, the crown ether DtBuCH18C6 is employed as the extractant [8]. DtBuCH18C6 shows a higher extractability and selectivity toward  $\text{Sr}^{2+}$ . The DtBuCH18C6 based process has been demonstrated on multistage centrifugal contactors using simulated HLLW and a  $\text{DF} > 1000$  is well achievable. For the removal of  $^{137}\text{Cs}$  from HLLW in China, currently the calix crown ether BPC6 is employed as the extractant and octanol is the diluent. A  $\text{DF} > 10000$  for  $^{137}\text{Cs}$  was achieved in a hot test in 2009.

Most importantly, processes for the removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  have been coupled together with the TRPO process to form a total-partitioning process. The aforementioned hot test for the treatment of legacy HLLW in 2009 is a successful example of this total-partitioning process [9]. The hot test of this combined process was tested on 72 stages of centrifugal contactors (40 stages for TRPO, 16 stages for Sr, and 16 stages for Cs). No operational problems have been encountered during the hot test and high DFs were achieved for all the targeted nuclides.

For the separation An(III) from Ln(III) by purified Cyanex 301 (HC301), two tests have been conducted at Tsinghua University using 14 stages of miniature centrifugal contactors. In the 2011 test, 99.95% Am was separated from lanthanides and only 0.1% lanthanides were extracted together with Am [10]. But problems such as large fluctuations of pH were encountered during this test, which has somewhat lowered the mutual separation of An(III) and Ln(III). The process was thus been improved by introducing a buffer reagent and a new test was conducted recently [11]. In this test, 99.995% Am was separated from lanthanides and less than 1% lanthanides were extracted together with Am.

Moreover, a novel technique for the separation of Am from the lanthanides and Cm based on the oxidation of Am has been developed very recently at Tsinghua University [12, 13]. In this technique, pentavalent Am was prepared and stabilized in a biphasic extraction system by incorporating the oxidative Bi(V) reagents into an organic solvent, leading to ultraefficient separation of Am from the lanthanides and Cm (separation factors  $> 10^4$  through a single biphasic contact).

### 3 Conclusion

Tsinghua University has a long history working on the partitioning of HLLW to minimize its long-term hazard and ensure the sustainability of nuclear energy. Partitioning processes based on functional ligands and solvent extraction technology have been developed to recover nuclides such as minor actinides,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from HLLW in China.

Some of these processes have been successfully demonstrated with genuine HLLW. Further optimization and industrialization of these processes are currently underway at Tsinghua University.

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