Journal of Hazardous Materials 278 (2014) 566–571

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Application of annular centrifugal contactors in the hot test of the improved total partitioning process for high level liquid waste

Wuhua Duan*, Jing Chen, Jianchen Wang, Shuwei Wang, Xiaogui Feng, Xinghai Wang, Shaowei Li, Chao Xu

Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- An improved total partitioning process for high level liquid waste was developed.
- Genuine high level liquid waste was used in the hot test.
- 72-Stage 10-mm-dia annular centrifugal contactors were used in the hot test.
- The decontamination factors of actinides, Sr and Cs were very high.
- The stripping efficiencies of actinides, Sr and Cs were very high.

ARTICLE INFO

Article history:
Received 21 April 2014
Received in revised form 20 June 2014
Accepted 23 June 2014
Available online 30 June 2014

Keywords:
Total partitioning process
High level liquid waste
Annular centrifugal contactor
Hot test
Solvent extraction

ABSTRACT

High level liquid waste (HLLW) produced from the reprocessing of the spent nuclear fuel still contains moderate amounts of uranium, transuranium (TRU) actinides, ^{90}Sr, ^{137}Cs, etc., and thus constitutes a permanent hazard to the environment. The partitioning and transmutation (P&T) strategy has increasingly attracted interest for the safe treatment and disposal of HLLW, in which the partitioning of HLLW is one of the critical technical issues. An improved total partitioning process, including a TRPO (tri-alkylphosphine oxide) process for the removal of actinides, a CESE (crown ether strontium extraction) process for the removal of Sr, and a CECE (calixcrown ether cesium extraction) process for the removal of Cs, has been developed to treat Chinese HLLW. A 160-hour hot test of the improved total partitioning process was carried out using 72-stage 10-mm-dia annular centrifugal contactors (ACCs) and genuine HLLW. The hot test results showed that the average DFs of total α activity, Sr and Cs were 3.57×10^3, 2.25×10^4 and 1.68×10^4 after the hot test reached equilibrium, respectively. During the hot test, 72-stage 10-mm-dia ACCs worked stable, continuously with no stage failing or interruption of the operation.

1. Introduction

High level liquid waste (HLLW) produced from the plutonium uranium extraction (PUREX) process for the reprocessing of spent nuclear fuel (SNF) still containing moderate amounts of uranium, transuranium (TRU) actinides, ^{90}Sr, ^{137}Cs, etc., and thus constitutes a permanent hazard to the environment [1–3]. The partitioning and transmutation (P&T) strategy for converting long-life nuclides into short-life radioactive or stable species constitutes an advanced nuclear fuel cycle, and has increasingly attracted interest for the safe treatment and disposal of HLLW [4,5]. The partitioning of HLLW is one of the critical technical issues of the P&T strategy. Various advanced processes based on solvent extraction have been developed for the partitioning of HLLW [6–13].

An old total partitioning process, including the TRPO (tri-alkylphosphine oxide) process for the removal of actinides, the CESE (crown ether strontium extraction) process for the removal of Sr, and the ion exchange process for the removal of Cs using potassium titanium hexacyanoferrate (II) (KTiFC), was developed to treat Chinese highly saline HLLW at the Institute of Nuclear and New Energy Technology (INET), Tsinghua University, China in the 1990s [14]. This total partitioning process was verified by a hot laboratory-scale test in which 50 stages of 10-mm-dia annular centrifugal contactors (ACCs) were used in both the TRPO process and the CESE process in 1996 [15]. In this hot test, the decontamination factors (DFs) for total α activity, ^{99}Tc, ^{90}Sr, and ^{137}Cs were 588, 125, >2500, and >200, respectively. And then, this total partitioning process was verified by a cold pilot-scale test in which pulsed columns

* Corresponding author. Tel.: +86 1080194038; fax: +86 1062771740.
E-mail address: dwh203@mail.tsinghua.edu.cn (W. Duan).

http://dx.doi.org/10.1016/j.jhazmat.2014.06.049
0304-3894/

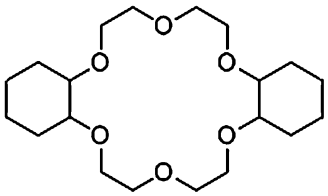

Fig. 1. DCH18C6.

were used in the extraction and scrub section of the TRPO process and the CESE process, while 24-stage 70-mm-dia ACCs were used in the stripping section of the TRPO process, and a set of moving bed ion-exchange column was used for the removal of Cs in 2005 [16]. In this cold test, the DFs were >3000, >500, >1000, ~150, and 94 for U, Nd, Zr, Sr, and Cs, respectively. In the cold test, Nd and Zr were used to simulate Am and Pu, respectively.

The TRPO process for the removal of actinides has been studying in China since 1980s [17]. 30% TRPO-kerosene is a good extractant for tetra- and hexa-valent TRU ions in the nitric acid solution [18]. It is also effective for the extraction of tri-valent Pu, Am and Cm at low and moderate HNO_3 concentration (<2 mol/L). However, the extraction of penta-valent Np by 30% TRPO-kerosene is found to be very poor. Among fission product elements, Zr(IV) is highly extracted by 30% TRPO-kerosene at a wide range of acidity, while Tc(VII) and Mo are extracted at low and medium nitric acid concentration. The stripping of products from the organic phase can be easily realized step by step using different solutions. In the old total partitioning process, Np and Pu were stripped by 0.6 mol/L $H_2C_2O_4$. But in the cold pilot-scale test in 2005, there were oxalate crystals found in the aqueous phases of the Np/Pu stripping section due to low solubility of the oxalate compounds, resulting in blocking up of the under flow of the rotor. Therefore, the Np/Pu stripping section needs to be further improved.

In the old total partitioning process, dicyclohexano-18-cown-6 (DCH18C6 as shown Fig. 1) as extractant and *n*-octanol as the diluents have been used in the CESE process for the removal of Sr [19]. DCH18C6 showed good ability and selectivity for the extraction of Sr. No improvement was made in the improved total partitioning process.

In the old total partitioning process, although KTiFC ion exchanger can meet requirement for removing Cs from HLLW, the operation of the ion exchange equipment is complicated. Moreover, both drying and curing of the used KTiFC were found to be uneasy to control. It is necessary to develop new methods for the removal of Cs from HLLW. The calixcrown ether has good extracting ability and selectivity to Cs, and therefore has been selected as extractant for removing Cs from HLLW in several partitioning processes [20,21]. Recently, 25,27-bis(2-propyloxy)calix[4]-26,28-crown-6 (iPr-C[4]C-6) as shown in Fig. 2 has been synthesized in our laboratory. The extraction performance of iPr-C[4]C-6 for Cs with *n*-octanol as the diluents has been investigated [22,23]. The results showed that iPr-C[4]C-6/*n*-octanol had a good extraction ability and selectivity to Cs, and the extracted Cs could be easily stripped with diluted nitric acid solution (pH = 2–10).

With all considerations mentioned above, an improved total partitioning process, including the TRPO process for the removal of actinides, the CESE process using DCH18C6 as extractant and *n*-octanol as diluent for the removal of Sr, and the CECE (calixcrown ether cesium extraction) process using iPr-C[4]C-6 as extractant and *n*-octanol as diluent for the removal of Cs, has been developed to treat Chinese HLLW at the INET recently. In comparison to the old total partitioning process, 0.6 mol/L $H_2C_2O_4$ solution was replaced with 0.6 mol/L $H_2C_2O_4$ + 0.2 mol/L HNO_3 solution for the stripping of Np/Pu in the TRPO process, and the ion exchange process is replaced with the CECE process for the removal of Cs. In this

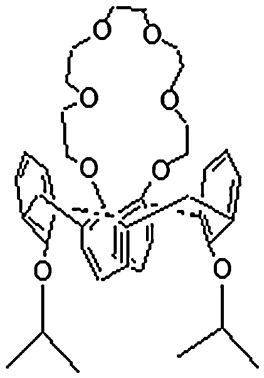

Fig. 2. iPr-C[4]C-6.

paper, a 160-hour hot test was carried out with genuine HLLW and 72-stage 10-mm-dia ACCs to verify the improved total partitioning process, and the hot test results were reported.

2. Experimental

2.1. Chemicals

TRPO (commercial name Cyanex 923, CYTEC, USA) comprises a mixture of four trialkylphosphine oxides, with the general formula R_3PO (14%), $R_2R'PO$ (42%), RR'_2PO (31%) and R'_3PO (8%), in which R and R′ denotes n-octyl and n-hexyl group, respectively [24]. Before the hot test, TRPO was diluted with saturated kerosene to 30% TRPO-kerosene (v/v), and firstly purified with anion exchange resin, then scrubbed once with 1.0 mol/L HNO_3, and adjusted to neutral with deionized water, and finally scrubbed with 50 g/L $(NH_4)_2CO_3$ and readjusted to neutral with deionized water. DCH18C6 was synthesized at the INET, and diluted with *n*-octanol to 0.1 mol/L DCH18C6-*n*-octanol, and then pre-equilibrated with nitric acid for the removal of Sr. iPr-C[4]C-6 was also synthesized at the INET [22], and diluted with *n*-octanol to 0.025 mol/L iPr-C[4]C-6-*n*-octanol, and then pre-equilibrated with nitric acid for the removal of Cs.

4.2 L of genuine HLLW was obtained from a reprocessing plant, China. The main composition of the genuine HLLW was given in the previous references [25,26]. The non-radioactive nuclides such as Na, Al, Fe, Ni and Cr contribute 88.2% of total elemental mass. Table 1 gives the main radioactive composition of the genuine HLLW (4.2 L). Before the hot test, 4.2 L of genuine HLLW was diluted 3 times. The volume of diluted genuine HLLW was about 14 L for the hot test, and its acidity was 0.95–1.05 mol/L. Other reagents were all analytical reagents.

2.2. The 10-mm-dia ACC

The 10-mm-dia ACCs were made at the INET. They are made up of two modules [27,28]. Modules are installed together to form a complete ACC by simply inserting one module into the other one, and the modules are fitted without screws and nuts. In this way, it is much easier to manipulate ACCs. Moreover, a multi-stage group housing structure containing multiple stage housings (e.g. 4, 3 or 2 stages) in a set has been adopted in order to further reduce the

Table 1
The main radioactive composition of genuine HLLW (4.2 L).

Type	α	β	γ
Element	^{241}Am, ^{237}Np, $^{238-240}Pu$	$^{90}Sr/^{90}Y$, ^{99}Tc	^{137}Cs
Radioactivity	1.84×10^9 Bq (0.04 Ci)	1.35×10^{13} Bq (293 Ci)	5.7×10^{12} Bq (123 Ci)