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Reprocessing Th-based spent fuels with di-1-methyl heptyl methyl phosphonate using centrifugal extractors

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ABSTRACT

In this paper, a reprocessing Th-based spent fuels process using di-1-methyl heptyl methyl phosphonate (DMHMP) as extractant was proposed and tested by multistage countercurrent extraction using batch simulation and centrifugal extractors. The analysis results of process samples show that the recovery of Th and U in 1A (co-extraction of Th and U), 1B (separation of Th from U) and 1C (stripping of U from organic to aqueous phase) section was more than 99.8% and 99.9%, respectively. The separation factor of Th from U and U from Th in 1B section was 5.9×10^3 and 7.1×10^3, respectively. Compared with Thorex process using TBP as extractant, the process could be operated under lower acidity and flow ratio of O:A due to the strong extraction ability of DMHMP. Thus, DMHMP would be a promising alternative extractant for Th-based spent fuels process.

1. Introduction

The rise in population coupled with a better standard of living results in an increasing demand of power, which is particularly relevant in developing countries. In this context, nuclear power has played an important role to meet the world's energy demand with the constant consumption of fossil fuels. There are now over 430 commercial nuclear power reactors operated in 31 countries, with 372,000 MW of total capacity, and providing about 13.5% of the world's electricity as continuous, reliable base-load power (Neelam Kumari et al., 2012). Thorium, as a potential nuclear resource, is about three times more abundant than uranium in the crust (Chandra et al., 2007), and the irradiation of ^{232}Th (a fertile material) in a reactor can lead to the formation of the fissile isotope ^{233}U. Furthermore, the probability of the formation of transuranium elements during the irradiation of thorium fuel is much less than that in U–Pu fuel cycle. It can reduce the long-term problems of management of high-level nuclear waste. So, the use of thorium in nuclear energy has been paid more and more attention for energy demands and environment concerns in recent years, especially in China and India (Huang et al., 2014; Abbasizadeh et al., 2013; Rao et al., 2014; Pathak et al., 1999; Tan et al., 2015). Reprocessing of irradiated thorium-based fuel and separation of converted ^{233}U are necessary steps of the thorium fuel cycle, and it has significant influence on the economy and environment of using thorium in nuclear reactors (Nagy et al., 2012; Furukawa et al., 1990). Conventionally, the Thorex process employing 30% tri-n-butyl phosphate (TBP) as the extractant can be used for the reprocessing of irradiated thorium-based fuel. However, during the development of Thorex process, it is found that there would be some disadvantages when TBP is used for reprocessing Th-based spent fuels (Suresh et al., 1995), such as 1) salting out acid is needed to ensure the recovery of thorium due to the low distribution coefficient of thorium in TBP, leading to a complicated process and higher acidity of aqueous waste (HLLW) (Zijjer and Ganguly, 1987; Rainey et al., 1962); 2) a higher organic flow ratio is adopted because third phase formation in the extraction of Th is a serious issue with TBP (Borkowski et al., 2002; Chiarizia et al., 2003; Vasudeva Rao and Kolarik, 1996); 3) the deleterious nature of degradation products (mono and dibutyl phosphoric acids) leading to decreased decontamination of U from fission products (FPs) and production of a relatively large amount of secondary radioactive waste (Pathak et al., 2004). Our previous studies have shown that Di-1-methyl heptyl methyl phosphonate (DMHMP) possesses better physical properties, such as low solubility in aqueous phase and density (Li et al., 2017). It can achieve less extractant residue in aqueous phase and has the favor to split organic phase from aqueous phase in extraction process. Furthermore, the extraction capacity of DMHMP for Th and U is much stronger than that of

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TBP, which is in favor the recovery of Th and U. The most important advantage is that no third phase is formed for the extraction of Th using DMHMP even above the loadings (Pathak et al., 1999; Li et al., 2017). In addition, the methylphosphonates have better irradiation stability than trialkylphosphates due to the replacing of P—O—C with P—C (Sheng et al., 1965), so, the irradiation stability of DMHMP should be better, and the generation of radiolytic products would be less than TBP. Therefore, DMHMP would be a promising alternative extractant of TBP for the reprocessing of irradiated thorium fuel. In this paper, the process for reprocessing Th-based spent fuels using DMHMP was proposed and tested by multistage countercurrent extraction using batch simulation and centrifugal extractors. The treatment efficiency of the process was analyzed to estimate the use of DMHMP in reprocessing Th-based spent fuels.

2. Experimental

2.1. Materials

DMHMP was purchased from Hengyang chemical factory (Changzhou, China) and further purified by vacuum distillation and silica gel chromatography. Characterization datas of DMHMP such as IR, NMR, MS and its structure are shown as Fig. S1, Fig. S2, Fig. S3 and Fig. S4 in Supplementary material. Before using, some acidic impurities of DMHMP were removed by washing with 0.47 mol/L Na_2CO_3, 0.10 mol/L HNO_3 and distilled water sequentially and then mixed with diluent n-dodecane as required. Thorium and uranyl nitrate hydrate were provided by the warehouse of Shanghai Institute of Applied Physics. All other chemicals were analytical reagent (AR) grade.

2.2. Instruments and equipment

Vortex mixer (Vortex-genie 2, Scientific Industries Company of the united states) and centrifuge (TDZ4-WS, Hunan instrument centrifuge instrument co. LTD of China) were used for the mixing and separation of organic and aqueous phase in batch extraction experiment; Inductively coupled plasma mass spectrometer (ICP-MS) (Perkinelmer NexION 300D of the United States) and inductively coupled plasma atomic emission spectrometer (ICP-AES) (Perkinelmer Optima 8000 of the United States) were used for analyzing the concentration of thorium and uranium; The ϕ10 centrifugal extractor was originally developed by Tsinghua University for multistage countercurrent extraction experiments (Cao et al., 2013; Duan et al., 2007; Duan et al., 2014) and the parameters of centrifugal extractor are listed in Table 1. Fourier infrared spectrometer (IR) (Thermo Nicolet Corporation Avatar 370 of the United States), ^{1}Hydrogen-nuclear magnetic resonance (^{1}H NMR) (Var.ian Inova, Bruker Inc., 400 MHz), Electrospray Ionization Mass Spectrometry (ESI-MS) (Bruker Amazon SL, Bruker Inc.) have been used to analyze the DMHMP after purified.

Table 1
Parameters of the 10 mm diameter annular centrifugal extractor.

Name	Specifications
Size	60 mm (W) × 220 mm (H)
Manufacturing material	stainless steel
Diameter of rotor	10 mm
Diamter of the heavy phase weir	6.6 mm
Rotation speed	4000–5000 r/min
Hold-up volume	4 mL
Nominal total flow rate	20–500 mL/h (O/A = 1)
Nominal flow ratio	O/A = 0.1–1
Operating DC voltage	0–18 V

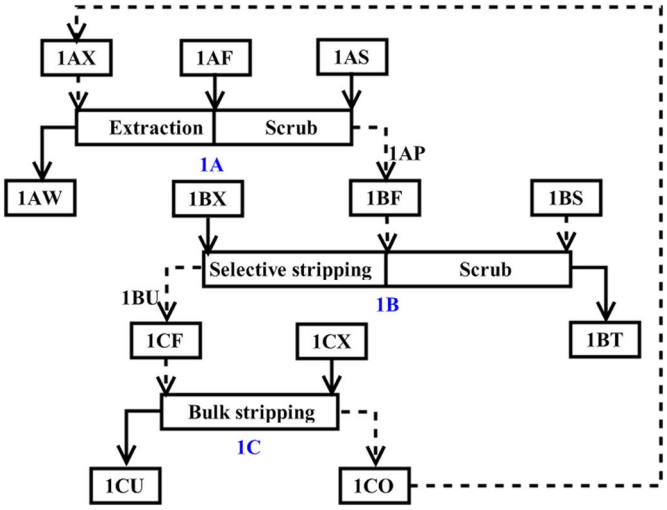

Fig. 1. Process flowsheet for Th-based spent fuel reprocessing using DMHMP. (1AF: feed solution, 1AX: extractant (DMHMP/n-dodecane), 1AS: scrub solution, 1AW: aqueous waste, 1AP/1BF: thorium and uranium loaded DMHMP/n-dodecane; 1BX: stripping solution, 1BS: scrub solution (DMHMP/n-dodecane), 1BT: thorium product, 1BU/1CF: uranium loaded DMHMP/ n-dodecane; 1CX: stripping solution, 1CU: uranium product, 1CO: stripped organic).

2.3. Multistage countercurrent extraction using batch simulation

The process flowsheet for reprocessing Th-based spent fuels using DMHMP is shown in Fig. 1. The feed is contacted with 0.73 mol/L (25.6%, V/V) DMHMP and scrubbed with 0.22 mol/L HNO_3 to co-extract and separate thorium and uranium from FPs in 1A section. The thorium is partitioned from uranium with 0.08 mol/L of HNO_3 in 1B section. The uranium is stripped from the loaded DMHMP/n-dodecane with 0.001 mol/L of HNO_3 in 1C section.

In the batch simulation of multistage countercurrent extraction, the extraction pattern and process parameters of 1A, 1B and 1C section were shown in Supplementary material. The experiment method was the same as the literature (Li et al., 2017) and taking 1A section for example, the feed solution (0.5 mL), extractant (3.5 mL) and scrub solution (0.4 mL) were added into 15 mL of plastic centrifuge tubes repeatedly along the solid and dotted lines in the figure, plus withdrawal of organic and aqueous phases after shake and centrifugation. After a number of extraction equilibrations, the system would achieve a steady state and the liquid in the centrifuge tubes would exist resembling continuous countercurrent extraction. It should be pointed out that the outflow of 1AP and 1BU after equilibrium were collected and used as 1BF and 1CF respectively in batch simulation of multistage countercurrent extraction. The concentrations of U and Th in organic and aqueous outflow in different equilibrations and each stage after equilibrium were determined to estimate the treatment efficiency of the process and calculate the distribution ratio (DM).

The recovery of Th and U in 1A, 1B and 1C section was calculated as Eq. (S1)–(S5) shown in Supplementary material. The distribution ratio (DM) was achieved by the method that suitable aliquots were withdrawn from the phases for analysis, and the D_M of Th(IV) and U(VI) is defined as:

$$D_M = \frac{[M]_{org}}{[M]_{aq}}$$

where $[M]_{org}$ is the concentration of solute in organic phase and $[M]_{aq}$ is the concentration of solute in the aqueous phase. The concentration of uranium was determined using ICP-AES or ICP-MS, while the