Study on the properties of saline HLLW in China*

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Abstract The properties and the component of HLLW (High Level Liquid Waste) were studied. The genuine saline HLLW is a blue-green liquid without any deposition. Its density and acidity are 1.399 g/ml(23±1°C) and 2.1 mol/L HNO_3, respectively. The activities of ^{137}Cs, ^{90}Sr, ^{99}Tc, ^{237}Np, ^{239}Pu, ^{241}Am, total α, total β, total γ are determined. The extractabilities of actinides in the genuine HLLW were examined with a five-stage cross extraction experiment. More than 98% of Pu is in Pu^{4+} species, and more than 70% of Np is in Np^{4+} species. More than 99.97% α-nuclides could be extracted by 30%TRPO-Kerosene in 1 mol/L HNO_3 from the HLLW.

Keywords HLLW, Extraction, Actinides, Analysis

1 Introduction

The reprocessing of spent nuclear fuels are valuable to recover the fissile materials, but it produces a lot of HLLW. After separating the fissile materials, the HLLW is conditioned in a glass form for future disposal into an underground repository. Considering the hazards of the vitrified waste, after about six centuries, the main potential hazards for the repository are the alpha-emitting minor actinide nuclides: ^{237}Np, $^{241-243}Am$, $^{242-244}Cm$ as well as ^{99}Tc. In recent years a P-T concept has been developed, which involves the partitioning of the long-lived nuclides and the transmutation of them to short-lived nuclides.

TRPO process is developed for separation of the long-lived nuclides from HLLW in China.[1] In the TRPO process, a trialkyl (C_6-C_8) phosphine oxide is used to extract the actinide elements and ^{99}Tc from HLLW.

The research on applying the TRPO process to treat highly saline HLLW is being carried out in China. The genuine HLLW has a salt concentration about 380 g/L. The main compositions are nitrate of Na, Al, Fe and corrosion products. According to the activity of actinide elements, the decontamination factor required for converting the HLLW to a non α waste is only 100 for the total α activity. This paper presents the hot test results of TRPO process for the removal of TRU elements from a genuine HLLW by cross extraction in China.

2 Experimental

2.1 Analysis of the density and the acidity of the HLLW

The samples of the HLLW were sampled quantitatively with electronic pipettor(1-ch, 0.020-0.500 ml, Biohit Finland), and balanced at 23±1°C. The density is an average value of six samples.

The quantitative samples were added to 30 ml 8% potassium oxalate solution (adjusting pH= 7.0 with 1% oxalic acid and 0.1 mol/L KOH). The solution was titrated with standard basic solution to pH 7.0. The acidity of the HLLW was calculated from the consumption of the standard basic solution.

2.2 Determining the radionuclides in the HLLW

2.2.1 Uranium

Uranium was extracted by 30%TRPO-Kerosene (TRPO, trialkyl phosphine oxide, Jinan Phosphorous Fertiliser Factory, China; Kerosene, 240#, Jinzhou Refinery Factory, China) in 1.0 mol/L HNO_3 from the HLLW twice, and was stripped with 5% Na_2CO_3 from the organic phase. The stripping solution was quantitatively diluted and adjusted to pH 7.0, the concentration of uranium was determined with Laser fluorimetric analyzer (LMA-1, Beijing Institute of Nuclear Industry, China).

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2.2.2 α-nuclides

The activity of total α-nuclides was determined with Au-Si surface barrier detector (FH445, ϕ20 mm, Beijing Nuclear Instrument Factory, China). The activities of ^{237}Np, ^{239}Pu, ^{241}Am were determined after Np, Pu, Am were separated from the HLLW with HDEHP process.[2]

2.2.3 The activity of the total β-nuclides

The activities of the total β-nuclides in the HLLW were detected with liquid scintillation analyzer (TRI-CARB 2200-CA, Parkard, USA).

2.2.4 The activities of the γ-nuclides

The activities of the nuclides in the HLLW were determined with Ge-Li detector (EG& G, USA). The multichannel analyzer was scaled with the standard solutions of the γ-nuclides.

2.2.5 Technetium

^{99}Tc is extracted by cyclohexenone from 1 mol/L H_2SO_4 and is detected with liquid scintillation counting method and activity is obtained by efficiency tracing DPM method.

2.2.6 Stronium-90

Activity of ^{90}Sr comes from that of ^{90}Y that is the daughter of ^{90}Sr. After the RE and TRU are removed by 30% TRPO-Kerosene two times in 0.5 mol/L HNO_3, the HLLW is laid for 30 days when ^{90}Y grows to equilibrium with ^{90}Sr, then ^{90}Y is extracted using 30% TRPO-Kerosene again and detected by LSC, its activity is corrected by tsie method.

2.3 Cross current extracting TRU elements from HLLW by 30% TRPO-Kerosene

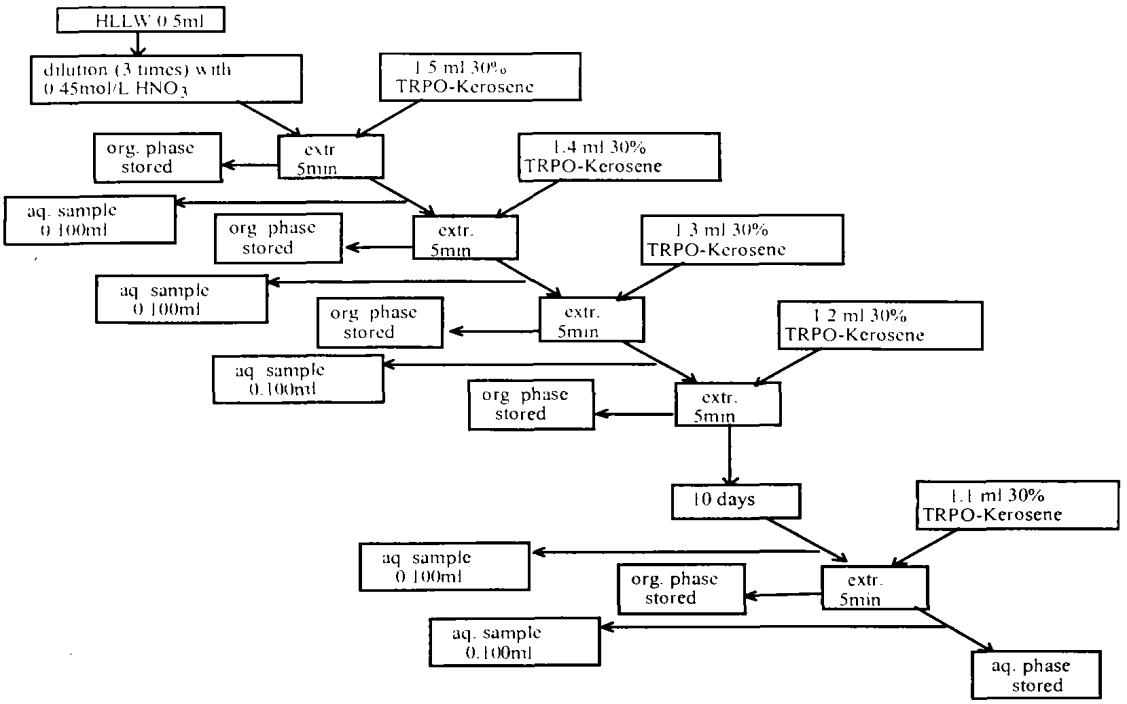

Fig.1 Flowsheet of the cross current extraction

30% TRPO-Kerosene was washed stepwise with 5% Na_2CO_3, 1 mol/L HNO_3 and deionized water. The genuine HLLW was diluted 3 times and regulated to 1 mol/L HNO_3 and the 30% TRPO-Kerosene solution was pre-equilibrated with 1 mol/L HNO_3 before use. The flowsheet of the experiments is shown in Fig.1. The extraction experiments were performed by mixing

equal volumes of aqueous and organic solution in a stoppered tube for 5 min at 23±1°C. Two phases were separated after centrifuge. The organic phase was collected. However, the aqueous phase was contacted with equal volume of a fresh organic phase and the cross extraction repeated several times. The activities of the actinide elements in the aqueous samples were analyzed by α spectrometry.

3 Results and discussion

3.1 The density and the acidity of the HLLW

The density is 1.39 g/ml, which is consistent with the result in Ref.[3]. The acidity is 2.1mol/L HNO_3, which is lower than 2.6 mol/L HNO_3 in Ref.[3], because some HNO_3 in the HLLW was decomposed for the irradiation during the ten years storage.

3.2 The radionuclides in the HLLW

The determined results of the radionuclides in the HLLW are given in Table 1. After adjusted by the half-life of the nuclides, the values of the activities of the radionuclides in the HLLW were consistent with those in Refs.[4~6]. The results show that the analytical methods are suitable for the HLLW.

Table 1 The activities of the radionuclides in the HLLW

Nuclides	U /g·L^{-1}	Tc /g·L^{-1}	^{90}Sr /Bq·ml^{-1}	^{137}Cs /Bq·ml^{-1}	^{237}Np /Bq·ml^{-1}
Activity or concentration	5.54	0.26	7.71×10^{8}	1.13×10^{9}	7.74×10^{2}
Nuclides	$^{238-240}$Pu /Bq·ml^{-1}	^{241}Am /Bq·ml^{-1}	$\sum\alpha$ /Bq·ml^{-1}	$\sum\beta$ /Bq·ml^{-1}	$\sum\gamma$ /Bq·ml^{-1}
Activity or concentration	–	2.90×10^{5}	3.74×10^{5}	2.71×10^{9}	1.14×10^{9}

3.3 The extractability of the α-nuclides in the HLLW

In the test condition, the distribution ratios of americium varied at different cross extraction stages (see Table 2). In the first three stages of cross extractions, the distribution ratios in americium increased with the increasing of the stages due to the decrease in the extractable element concentration, such as RE and Fe^{3+}. After four stages of the cross extraction the concentration of Am in aqueous solution was very low. At the 5 th stage the americium activity was near to the detection limit and very high decontamination factor was obtained.

Table 2 The distribution ratios for Np, Pu and Am

Stage	^{237}Np		^{239,240}Pu		^{241}Am		Total α
	D	Activity /Bq·ml^{-1}	D	Activity /Bq·ml^{-1}	D	Activity /Bq·ml^{-1}	Activity /Bq·ml^{-1}
feed	–	258	–	1	–	9.59×10^{4}	1.25×10^{5}
1	3.78	54	387	2.6×10^{-3}	4.2	1.85×10^{4}	1.85×10^{4}
2	0.59	34	3.7	5.5×10^{-4}	9.8	1.71×10^{3}	1.76×10^{3}
3	0.55	22	<0.01	7.6×10^{-4}	11.0	1.43×10^{2}	1.87×10^{2}
4	0.57	14	<0.01	4.8×10^{-4}	12.0	11	39
5*	3.7	3	2.9	1.4×10^{-4}	1.8	4	11

*The 5 th stage of cross extraction was carried out after 10 d

Table 2 also shows that TRPO has good extraction ability for plutonium. After first two stages, the plutonium was nearly completely extracted. From the 3rd stage the contents of plutonium in aqueous phases were not changed. The fact means that a few of plutonium (about 0.05%) in HLLW feed solution existed in polymerized or hydrolyzed species, which were not extractable by TRPO. In the experiment, the aqueous phase had been laid aside for 10 d after 4 stages. During this period some polymerized or hydrolyzed plutonium depolymerized and became extractable Pu(IV), thus at the 5th stage some plutonium was further ex-

tracted by TRPO (Table 2).

The extraction behavior of Np was also interesting. Although 30% TRPO has good extraction ability for tri-, tetra- and hexa-valent actinides, its extraction ability for Np(V) was very poor in 1 mol/L HNO_3. $D_{Np(IV)}$, $D_{Np(V)}$ and $D_{Np(VI)}$ between 30% TRPO-Kerosene and 1 mol/L HNO_3 are given in Table 3. In the experiment at first stage D_{Np} is 3.78. It is much lower than that for Np^{4+} and NpO_2^{2+}, but higher than that for NpO_2^+. From the 2nd to the 4th stage the D_{Np} is about 0.5~0.6. It is higher than that for NpO_2^+. These results show that more than 70% of Np is in Np(IV) valence state in the HLLW. However, the others were in Np(V) probably. In the first stage, all Np^{4+} species and a few parts of NpO_2^+ species were extracted into organic phase. From the 2nd to the 4th stage not only NpO_2^+ but also some tetra- and hexa- valent neptuniums were extracted. The fact indicates that some Np(V) was converted to Np^{4+} or NpO_2^{2+} at the experiment condition.

Table 3 The distribution ratio of neptunium between 30% TRPO and 1 mol/L HNO_3

Np valence	Np^{4+}	NpO_2^+	NpO_2^{2+}
D	1000	0.25	100

The valence state of Pu in the genuine HLLW was studied by an extraction method with 0.2 mol/L HDEHP-Kerosene and 0.5 mol/L TTA-Xylene. The results indicated that in the genuine HLLW more than 98% of Pu were in Pu^{4+} species, about 0.86% in Pu^{3+} valence state, but very small in PuO_2^{2+}. It proves that Pu^{3+}, Pu^{4+} and PuO_2^{2+} are in equilibrium in the genuine HLLW based on the disproportionate reaction equation:

$$3Pu^{4+} + 2H_2O \longleftrightarrow 2Pu^{3+} + PuO_2^{2+} + 4H^+$$

4 Conclusions

The density of the HLLW is 1.399 g/ml. The acidity of the HLLW is 2.11 mol/L HNO_3, it becomes lower because the HNO_3 was decomposed by the irradiation. The results of determining the activities of the radionuclides show that the analytical methods are suitable for the HLLW.

The cross extraction of the TRPO process with genuine HLLW proves that the TRPO has good extraction ability for actinide elements. The TRU elements, except ^{237}Np, were completely removed by 30% TRPO-Kerosene with four stages of cross extraction in 1 mol/L HNO_3 solution and the HLLW became a non-α-waste solution. The decontamination factors are as high as 3200, 18, 2100 and 8700 for total α, ^{237}Np, ^{239}Pu and ^{241}Am, respectively. The results prove that the parameters selected for the TRPO process in the cross extraction experiment were quite well. The TRU elements in the HLLW could be removed by the TRPO process.

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