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Radiochemical Separation and Purification of ^{144}Ce from Purex High-Level Waste

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ABSTRACT

A solvent extraction technique has been developed for the radiochemical separation and purification of ^{144}Ce from Purex high-level waste (HLW). The feed solution initially was in contact with granulated ammonium molybdophosphate for the selective removal of cesium to reduce the gamma dose during the subsequent process. In the next step, uranium and plutonium were removed quantitatively by using 20% 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (KSM-17) in dodecane. The trivalent cerium present in the cesium-, uranium-, and plutonium-depleted raffinate was oxidized to its tetravalent state by using $K_2Cr_2O_7$ and was extracted into KSM-17. The loaded cerium from the organic phase was stripped with 0.5 M nitric acid. Final decontamination from

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trace impurities such as ^{106}Ru and ^{125}Sb could be achieved by an additional cerium-extraction step with KSM-17 at pH 2, followed by its stripping with 0.5 M HNO_3. About 10 mCi of cerium was separated from Purex HLW by using this technique. This method is amenable for automation and scale up.

Key Words: Radiochemical separation; ^{144}Ce; Purex HLW; KSM-17.

INTRODUCTION

High-level waste (HLW) generated during the reprocessing of spent fuel by the Purex process contains many useful radionuclides. Among these, ^{144}Ce ($T_{1/2} = 285\,d$) finds applications in nuclear research. Its gamma energy ($E_\gamma = 133.5\,keV$) is ideal for the excitation of K_α x-rays of heavy elements such as thorium, uranium, plutonium, etc., and is a useful source for gamma-induced x-ray analysis. Among other applications, it is used as a standard for calibration of detectors, as a monitor for the determination of burn up of nuclear fuel and for the assay of leached hull. Numerous methods are reported in the literature for the separation of cerium from other fission products using solvent extraction,[1–5] ion exchange,[6] extraction chromatography,[7,8] and membrane-based techniques.[9] These methods involve the extraction of cerium from a corrosive medium such as sulfuric or hydrochloric acid. Though Saha et al.[5] have reported the extraction of cerium from nitric acid medium, the extraction was carried out from a dilute solution obtained by dissolving the spent fuel.

This study focuses on the development of a solvent extraction process that can be used for the separation of multicurie amounts of ^{144}Ce from Purex HLW without any feed conditioning. Depending on the irradiation and subsequent cooling of the fuel, the ^{144}Ce content will vary; ^{137}Cs, ^{90}Sr, ^{106}Ru, ^{106}Rh, ^{125}Sb, etc., are the other major radionuclides present in the feed. Among these ^{137}Cs is a gamma emitter and will contribute a maximum to the man-rem exposure. In addition to these fission products, the feed will also contain residual Pu and U, along with small amounts of minor actinides such as Am and Cm. Hence, the procedure developed should be able to separate and to purify ^{144}Ce from all these impurities and should be amenable for automation and scale up.

The present paper describes the steps involved in the separation of ^{144}Ce from actual Purex HLW having an acidity 2–3 M HNO_3 by using a multistage solvent extraction process with 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (KSM-17) as extractant.

EXPERIMENTAL

Reagents and Chemicals

The HLW solution generated during the reprocessing of spent fuel from a research reactor was used as feed for the separation of cerium. The nitric acid content of the feed was about 2 M. Granulated ammonium molybdophosphate (AMP) used for Cs depletion was prepared as described in the literature.[10] Solvent extraction grade (>95%) KSM-17 synthesized by the Solvent Development Section, Material Group of Bhabha Atomic Research Centre, Mumbai was used as received. Diluent dodecane (~93% C-12) was procured from M/s. Transware Chemia Handelsgeselschaft, Hamburg, Germany. Tracer ^{144}Ce used in this study was separated from Purex streams by using the method reported else where.[1] All other chemicals used were of analytical reagent grade.

Batch Extraction Studies

Optimization of extraction parameters was carried out through a set of batch extractions using a cerium tracer and 20% KSM-17 in dodecane from nitric acid medium. In these experiments, equal volumes of aqueous and organic phases (generally 2.0 mL) were contacted for about 10 min, which was found to be sufficient for attaining equilibrium. After attaining equilibrium, the phases were centrifuged and separated. The extraction conditions were optimized by using these experiments, varying the parameters one at a time. The parameters studied are the dichromate concentration in the feed, the iron content in the feed, and the effect of concentration of strippant (nitric acid). Iron exits as a corrosion product in the waste stream, hence, its effect on the extraction was studied.

Radiometry

The gamma-emitting radionuclides were assayed by using a high-purity germanium detector coupled to a 4k multichannel analyzer. Alpha spectrometry was used to assay the alpha-emitting radionuclides.

Procedure for Separation of Cerium from HLW

About 10 mL of HLW was kept in contact with ~300 mg of granulated AMP overnight, with intermittent agitation. The supernatant was separated by filtration. More than 99% of the Cs was selectively removed from the waste solution. From this supernatant, uranium and plutonium were separated by solvent extraction by using 20% KSM-17 in dodecane. Three successive contacts (10 min each) at a phase ratio 2 : 1 organic to aqueous volume ratio (O/A) were given to deplete uranium and plutonium to near total. Weighed amount of solid $K_2Cr_2O_7$, so as to get the required concentration of 0.05 M, was added to the aqueous raffinate for oxidizing trivalent cerium to its extractable tetravalent state. Three batch extractions with 20% KSM-17 in dodecane (~10 min each) were carried out at a phase ratio of 2 : 1 (O/A). Loaded organic phases from all the contacts were mixed to get a mixed organic phase. Cerium from this mixed phase was stripped in three successive contacts of 0.5 M nitric acid. The cerium product obtained during this step was found to contain trace quantities of ^{125}Sb and ^{106}Ru. To purify the cerium, the stripped product was conditioned to pH 2 by the addition of 2 M NaOH and was subjected to a final solvent extraction purification step by using the same extractant, followed by stripping with 0.5 M HNO_3.

RESULTS AND DISCUSSION

Cerium exists in trivalent state in nitric acid medium. $K_2Cr_2O_7$ was used as oxidizing agent for cerium in these studies. To find out the optimum concentration of dichromate required for quantitative extraction of cerium batch extraction data when using a tracer has been obtained from 2 M nitric acid medium. Table 1 shows the results of these studies, which clearly indicate that above 0.05 M concentration, cerium is quantitatively extracted by KSM-17.

Iron will be present in the HLW as a corrosion product. Because KSM-17 coextracts iron, the effect of iron on the extraction of cerium up to ~16 g/L

Table 1. Extraction of cerium from 2 M HNO_3 medium by using 20% KSM-17 in *n*-dodecane in the presence of varying concentrations of dichromate.

$[K_2Cr_2O_7]$ (M)	Extraction (%)
0.001	<1.00
0.01	62.52
0.05	~100
0.10	~100
0.20	~100

Note: Experimental conditions: phase ratio, 1 : 1; contact time, 10 min; volume, 2.0 mL; ^{144}Ce in feed, 320.2 CPS/mL.

was studied. The results are presented in Table 2. An iron concentration of 0.5 g/L shows no interference in the extraction of cerium. The extraction of cerium decreases as iron concentration increases above 0.5 g/L. This level of tolerance is sufficient to take care of iron present as a corrosion product.

The presence of excess dichromate in the feed and strippant nitric acid concentration play an important role in the stripping of cerium from the loaded organic phase. The extraction of cerium from 2 M nitric acid medium with 0.10 M dichromate generated a loaded organic phase that was stripped by using varying concentrations of nitric acid. The results of cerium stripping are presented in Table 3. Less than 5% stripping was observed in all the cases, which shows that the coextraction of dichromate into the organic phase leads to poor stripping. Similar studies were carried out with cerium extracted from 0.05 M dichromate containing feed that showed more than 90% stripping from the organic phase in a single contact. More than 98% stripping was obtained when the concentration was 0.5 M HNO_3. Poor stripping was observed with water (Table 3).

Figure 1 shows the gamma spectra of a diluted HLW sample. The gamma-emitting radionuclides present in the sample were ^{137}Cs, ^{106}Ru, ^{144}Ce, ^{125}Sb, and ^{134}Cs, in addition to the pure beta emitters ^{147}Pm and ^{90}Sr. ^{137}Cs is the most intense peak in HLW spectra due to its high fission yield and long half-life. Its removal in the initial stage by AMP[1] will reduce the exposure, as well as give good decontamination from it. Gamma spectra taken before and after AMP contact showed that more than 99% cesium removal was achieved during this step. The KSM-17 has a high distribution ratio for both

Table 2. Extraction of cerium in the presence of varying concentrations of iron in the feed.

Concentration of iron in the feed (g/L)	Extraction of Ce in the organic phase (%)
Nil	~100
0.14	~100
0.50	99.8
1.00	97.5
2.00	95.3
4.20	91.00
8.40	73.83
16.80	63.41

Note: Experimental conditions: phase ratio, 1 : 1; [$K_2Cr_2O_7$], 0.05 M; ^{144}Ce in feed, 320.2 CPS/mL; volume, 2.0 mL; contact time, 10 min.

Table 3. Stripping of cerium from loaded organic phase (extracted from 2 M nitric acid medium in presence of $K_2Cr_2O_7$).

	Stripping (%)	
$[HNO_3]$ (M)	Extracted from 0.10 M $K_2Cr_2O_7$[a]	Extracted from 0.05 M $K_2Cr_2O_7$
H_2O	1.39	0.94
0.10	4.01	92.84
0.30	4.39	98.91
0.50	3.24	98.83
1.00	0.85	97.34

Note: Experimental conditions: phase ratio, 1 : 1; volume, 2.0 mL; contact time, 10 min.

[a] Organic phase was highly colored because of the dichromate extracted in it.

uranium and plutonium and has practically no uptake for trivalent actinides and lanthanides above 1 M HNO_3.[11] Thus, uranium and plutonium could be removed quantitatively in 3 successive contacts by using 20% KSM-17 in dodecane. The raffinate from this step contained all the trivalent actinides, such as americium; lanthanides, such as cerium; and other inextractable fission products. Ce(III) was oxidized to Ce(IV) by using dichromate and was

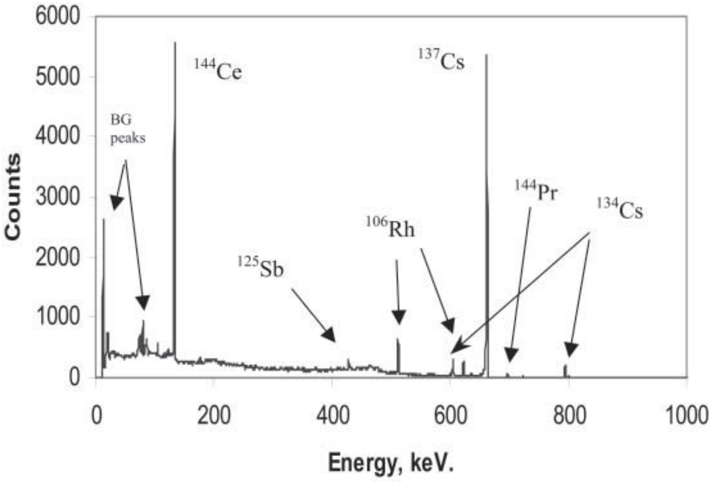

Figure 1. Gamma spectrum of HLW.

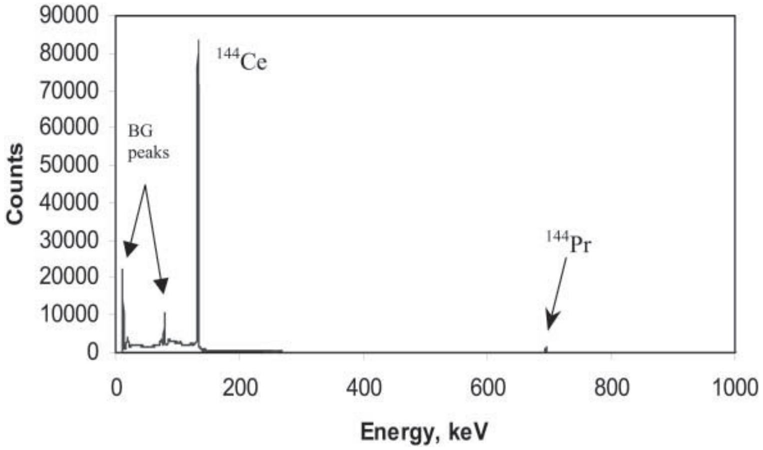

Figure 2. Gamma spectrum of ^{144}Ce product.

extracted into KSM-17. Extracted cerium was stripped by using 0.5 M HNO_3. Gamma spectrum of the stripped product taken at this stage was found to contain traces of impurities, such as Ru, Sb, and Cs. The decontamination factor obtained is $>10^5$ for Am, Pu, Cs, and Eu, whereas, it is $\sim 10^3$ for ^{125}Sb and ^{106}Ru. This necessitated an additional cerium purification step by using a solvent extraction of Ce(III) at pH 2 with 20% KSM-17 followed by its stripping with 0.5 M HNO_3. At pH 2, cerium alone gets extracted in KSM-17, leaving the impurities viz ^{106}Ru and ^{125}Sb in the aqueous phase.[12] About 10 mCi of cerium was separated by using the technique. Figure 2 shows that gamma spectrum of the product was cerium free of other gamma emitters. Alpha spectrometric analysis of the product confirms the effectiveness of the removal of plutonium and other alpha-emitting nuclides. This indicates good radiochemical purity of the product, with a decontamination factor $>10^5$ for all the nuclides present. Uptake of nonradioactive impurities by KSM-17 was found to be insignificant from our earlier studies.[11] The recovery of ^{144}Ce was found to be $\sim$70% and can be further improved by increasing the extraction stages. The procedure used can be scaled up to separate larger amounts of ^{144}Ce, and it also is amenable for automation.

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