Advanced Flow-Sheet for Partitioning of Trivalent Actinides From Fast Reactor High Active Waste

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Abstract

Partitioning of radiotoxic elements present in the high-level liquid waste (HLLW) followed by transmutation of them (P&T strategy) into stable or short-lived products in accelerated driven systems or fast-reactors is a viable option for the safe management and minimizing the radiotoxicity of HLLW. In this context, a typical high-active waste (HAW) arising from reprocessing of spent carbide fuel, $(U_{0.3}Pu_{0.7})C$ irradiated to a burn-up of 155 GWd/Te in the Fast Breeder Test Reactor (FBTR) was characterized by various analytical techniques. The composition of this fast reactor high-active waste (FR-HAW) differed significantly from the HAW, arising from thermal reactor fuel reprocessing in terms of radioactivity and elemental composition of various metal ions, which are likely to pose several challenges in the handling, treatment, management and disposal of FR-HAW. A method has been developed for partitioning of minor actinides from the FR-HAW using a solvent system composed of 0.2 M n-octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) – 1.2 M tri-n-butylphosphate (TBP) in n-dodecane (n-DD), and subsequently demonstrated with the actual (FR-HAW) (155 GWd/Te) using a 16-stage ejector mixer settler in hot cells. The results established the recovery of >99% of trivalents (Am(III) + Ln(III)) using citric acid-nitric acid formulation, developed for back extraction. About 5 - 10% of 106Ru was found in the product and nearly 20% of radioruthenium was carried to the lean organic phase after the first cycle requiring cleanup of the solvent.

However, the demonstrated method and the other the existing methods available in various countries for partitioning of trivalent actinides from high level liquid waste (HLLW) use organic phase modifiers in significant concentrations to maneuver the undesirable third phase formation encountered during trivalent actinide partitioning, even though the solvent system without any phase modifier was desirable. To avoid these complications novel unsymmetrical diglycolamides (UDGAs) and diglycolamic acids were developed in our laboratory and systematically studied for the group separation of Ln(III)-An(III) as well as for Ln-An separation from fast reactor simulated high-level liquid waste (SHLLW). In this paper, it is proposed to provide the summary of our research and development activities carried out at IGCAR towards the development of advanced flow-sheet for trivalent actinide group separation, lanthanide-actinide separation and demonstrations with real high-active waste.

Keywords: Minor actinide partitioning, TRUEX solvent, Unsymmetrical diglycolamide, Lanthanide-actinide separation.

1.   Introduction

PUREX process is being adopted for reprocessing of $(U_{0.3}Pu_{0.7})C$ fast reactor fuel, irradiated to a burn-up of 155 GWd/Te in a fast breeder test reactor at Indira Gandhi Centre for Atomic Research, Kalpakkam. The method involves the dissolution of the spent nuclear carbide fuel in nitric acid medium followed by the liquid-liquid extraction of uranium and plutonium by a solution of 1.1 M tri-n-butyl phosphate (TBP) in n-dodecane (n-DD) [1]. The raffinate rejected after the extraction of uranium (VI) and plutonium (IV) from the fast reactor dissolver solution is known as high active waste (HAW), which is usually concentrated to obtain high level liquid waste (HLLW). The high active waste is a complex mixture of several elements such as the radioactive actinides, short and long-lived fission products and stable fission products present in nitric acid (3 –4 M) medium. Since the transplutonium elements exist in trivalent oxidation state in dissolver solution, they are inextractable by TBP/n-DD and rejected to HAW. There are several factors that affect the composition of the HAW. They are burn-up and type of the fuel, cooling time, materials for

storage, aging, efficiency of PUREX process, additives, if any, employed during reprocessing etc.

It is well recognized that estimation of radioactivity and characterization of various elements present in nuclear waste is essential and mandatory for the treatment and safe disposal of HAW. However, the estimation procedure is one of the most challenging tasks, since it involves determining the various elements and isotopic composition in multi-elemental matrix of HAW. Moreover, the radioactivity of strong gamma emitting fission products and the acidity of HAW pose several complications during estimation. It requires advanced methods and hyphenated techniques for the separation of target element from the host of other elements followed by estimation of the target by a suitable analytical procedure.

2.   Characterization of fast reactor HAW

In this context, the chemical characterization of the high active waste (HAW) arising from reprocessing of nuclear fuel $(U_{0.3}Pu_{0.7})C$ irradiated to the burn-up of 155 GWd/Te in a fast breeder test reactor was taken up at IGCAR and the radionuclides and elements present in the HAW were estimated by various analytical techniques. The procedure adopted for the pre-concentration/separation step prior to the analysis is described in detail elsewhere [2]. The results are summarized in Table I. Our findings on the analysis of high active waste arising from reprocessing of fast reactor fuel -$(U_{0.3}Pu_{0.7})C$ indicate that the composition is significantly different from other high active wastes in terms of radioacitivties and elemental concentrations. The composition of HAW would have several implications and bearings on handing and treatment, and the management and disposal of HLLW. The results showed that the presence of excessive β- and γ- activity of HAW could induce the radiation damage to the solvents/resins, to structure materials. Since, bulk of the radioactivity is carried by ^{137}Cs, ^{90}Sr, ^{106}Ru, it is desirable to remove these radionuclides selectively, prior to any treatment and disposal. It can be seen from Table I that the total amount of lanthanides and trivalent actinides in HAW is < 0.5 mg/mL. However, the presence of other metal ions such as iron (4.3 mg/mL), chromium (0.63 mg/mL), nickel (0.7 mg/mL) and uranium (0.2 mg/mL) are likely to interfere during minor actinide partitioning albeit low distribution ratios exhibited by these metal ions and pose problems during immobilization. The composition also indicates that there is a need to develop the matrices for holding large amount of fission and corrosion products of widely varying composition, and necessary studies to be taken up for assessing the long-term durability of those matrices, in case of immobilization.

As indicated above, the high-active waste contains significant quantities of lanthanides and transplutonium elements produced as fission products and activation products. Since the stable oxidation state of lanthanides and transplutonium elements (e.g. Am and Cm) in HAW is +3, they are inextractable in PUREX process and rejected to HAW. The radiotoxicity of high-active waste is therefore essentially due to these alpha emitting actinides. Since the half-life of these alpha emitting radionuclide (e.g. ^{241}Am, $t_{1/2}$ = 433 y) are quite long, it is necessary to ensure the long-term safety and protection of these waste forms. In this context, partitioning of trivalent actinides from high active waste and transmutation of them into stable or short half-life radionuclides in advanced fast reactors play a very important role in reducing the long term concerns of HAW to a significant extent [3]. This method is an attractive and viable option for the safe management of HAW.

TABLE I: ISOTOPIC AND ELEMENTAL COMPOSITION OF HAW ARISING FROM REPROCESSING OF $(U_{0.3}PU_{0.7})C$ FUEL IRRADIATED TO A BURN-UP OF 155 GWD/Te.

Elements	µg/mL	Radioisotope	µCi/mL
Plutonium	3.6	^{60}Co	16.3
Uranium	222	^{106}Ru	698
Neptunium	< 2	^{125}Sb	43
Lanthanum	56	^{134}Cs	121
Neodymium	162	^{137}Cs	4190
Cerium	87	^{144}Ce	325
Praseodymium	38	^{154}Eu	37.5
Samarium	38	Nitric acid	4.6 M
Europium	3		
Trivalent actinides (Am+Cm)	77		
Molybdenum	202		
Chromium	884		
Dysprosium	< 5		
Iron	3602		
Gadolinium	6		
Manganese	368		
Nickel	787		
Palladium	8.7		
Silver	<5		
Strontium	32		
Ruthenium	82		
Zirconium	3		
Calcium	316		
Magnesium	20		
Sodium	16800		

3. Partitioning of trivalent actinides

Partitioning procedure involves a challenging task of separating trivalent actinides from high-active waste containing chemically similar trivalent lanthanides. These lanthanides are formed as fission products in significant quantities as compared to trivalent actinides. In addition, the high concentration of nitric acid (3-4 M) prevailing in HLLW also complicates the selective separation of trivalent actinides. Therefore, the existing method for partitioning of minor actinides is a two-cycle approach, namely, i) the group separation i.e., the separation of trivalent actinides together with lanthanides, in the first step, which is followed by the ii) lanthanide –actinide separation in the second-step [4]. The mutual separation of actinides and lanthanides is necessary prior to transmutation, since the lanthanides act as neutron poisons during transmutation. Several reagents such as the organophosphorous compounds, amides, and diglycolamides have been proposed as potential candidates for actinide partitioning from HLLW. Horwitz *et al.* [5] introduced the TRUEX process, in which Ln(III) and An(III) are selectively extracted in to a solution of 0.2 M n-octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO)-1.2 M tri-n-butylphosphate (TBP) in n-dodecane (n-DD). A number of studies have been reported on the

recovery of minor actinides from waste solutions using the TRUEX extractant [5-7]. Therefore, the TRUEX solvent has been chosen for partitioning of trivalent actinides from FR-HAW, in the present study.

4.   Mixer-settler studies with HAW

The extraction of trivalents from HAW was performed by passing the feed (HAW) and organic phase (0.2 M CMPO-1.2 M TBP/n-DD) in a counter current mode in a 16-stage mixer settler. Mixing of the organic and aqueous phases was achieved by air pulsing in the column by applying vacuum and pressure alternatively with the help of a solenoid valve operated by a cyclic timer. The aqueous and organic solutions were fed into the mixer settler at a constant flow rate of 4.5 ml per minute. Steady state was attained in four hours. The details of the experimental procedure are described elsewhere [7]. Samples were taken from organic and aqueous phases, in all stages, as well as they were collected at the outlet. The organic phase obtained after extraction was known as loaded organic and the aqueous phase was known as raffinate in this case. The lanthanides and actinides were recovered from the loaded organic in a counter current extraction process using the same mixer settler in a separate run. The stripping formulation was composed of 0.1 M citric acid (CA) and 0.1 M HNO_3. The aqueous and organic samples were taken from various stages for constructing the radioactivity profile. The organic phase obtained after back extraction was known as lean organic and the aqueous phase was known as aqueous product.

TABLE II: THE PERCENTAGE OF EXTRACTION AND STRIPPING OF SOME RADIOISOTOPES DURING MINOR ACTINIDE PARTITIONING

Radioisotopes	Percentage of extraction from HAW	Percentage of stripping from loaded CMPO phase
Americium-241	> 99.9	> 99.9
Europium-154	> 99.9	> 99.9
Cerium-144	> 99.9	> 99.9
Cesium-137	negligible	-
Ruthenium-106	30	10

The separation and recovery of trivalent actinides during this run was monitored by the γ-emitting radionuclides present HAW. The gamma spectrum of the raffinate obtained after the extraction of trivalents showed that the emissions characteristic to [241]Am, [155]Eu, [154]Eu, and [144]Ce, were insignificant. Table II shows the quantity of different radionuclides extracted in CMPO phase. It is observed that extraction of trivalents (Am(III) and Eu(III)) from the feed is more than 99%. Stage sample analysis obtained from the mixer settler run also confirmed that the extraction was complete in 6 stages. The trivalents present in the extracted organic phase was recovered by using a solution of 0.1 M citric acid in 0.1 M nitric acid, in a counter-current stripping run. It was noted from the gamma spectrum that the isotopes characteristic to [241]Am, [155]Eu, [154]Eu, and [144]Ce in the lean organic were negligible. The gamma spectrum of the aqueous product indicated the presence of all the peaks corresponding to [241]Am, [155]Eu, [154]Eu, and [144]Ce isotopes. Quantitative analysis of the data showed that the recovery of lanthanides is ~99% (Table II). The stage sample analysis of the mixer settler stripping run confirmed that back extraction was complete in 10 stages. The estimation of [241]Am in the sample was also determined by alpha counting of raffinate, loaded and lean organic, and product stream. The analysis indicated that loading of [241]Am in 0.2 M

CMPO-1.2 M TBP/n-DD was near quantitative and the [241]Am in the raffinate is negligible (<100 nCi/mL). Analysis of [241]Am(III) in the product showed that the recovery was > 95 %. Lower value in this case could be due to the interference of citric acid salt deposit in the product during analysis. However, the demonstration run showed the contamination of [106]Ru in the lean organic phase to the extent of 20-25% and calls for the clean-up of the lean organic phase.

5.   Decontamination of radioruthenium

Ruthenium forms a wide variety of nitrosyl complexes during the dissolution of spent nuclear fuel and they are stable even in strongly acidic or alkaline conditions. In the PUREX stream, ruthenium exits in the form of cationic, neutral and anionic complexes with the ligands such as nitrite, nitrate and water present in aqueous phase [8]. It can be seen from Table II that significant amount of ruthenium-106 was extracted by the CMPO-TBP solution. The analysis of the feed and lean organic organic after the run indicates that nearly ~20 % of [106]Ru is retained in the lean organic phase. Therefore, decontamination of radioactive ruthenium from lean organic phase was studied using several aqueous based reagents, ion exchange resins and inorganic sorbents to identify the best suitable formulation. The details of decontamination studies are described elsewhere [9].   Among the various reagents examined, sodium hydroxide, sodium carbonate were found promising candidates for the removal of radioactive ruthenium from the organic phase. Nearly, 95 % could be removed in 10 contacts using these reagents. Further treatment with adsorbents such as alumina and Dowex 1X4 (OH- form) quantitatively decontaminated the radioactive ruthenium from the lean organic phase.

6.   CHON extractants for lanthanide-actinide separation

The aqueous product obtained after minor actinide partitioning was a solution of trivalent actinides and lanthanides in 0. 1 M CA+0.1 HNO_3 medium. Therefore, there was a need to develop a method for the mutual separation of trivalent actinides and lanthanides from 0.1 M citric acid medium. In this context a CHON- based diglyolcamic acid, bis(-2-ethylhexyl)diglolamic acid (HDEHDGA) was developed and studied extensively for the extraction of lanthanides and actinides [10,11].   The conditions required for complete extraction and recovery was optimized by the batch studies.   Based on the optimized conditions, the mixer-settler run was performed [11]. It was found that the extraction of Am(III) and Eu(III) in 0.1 M HDEHDGA/n-DD from the TRUEX product at pH 3 was quantitative in two contacts. Mutual separation of Am(III) from Eu(III) present in the loaded organic phase was performed by using 0.01 M DTPA-0.025 M CA at pH 1.5. The result revealed that more than 96% of Am(III) was recovered from the loaded organic phase after 20-stages of stripping.   The stripping of Eu(III) was only 2%. Therefore, the results, confirmed the feasibility of using HDEHDGA/n-DD for the mutual separation of lanthanides and actinides from citric acid medium. The flow sheet based on the TRUEX solvent and HDEHDGA is shown in *FIG*. 1.
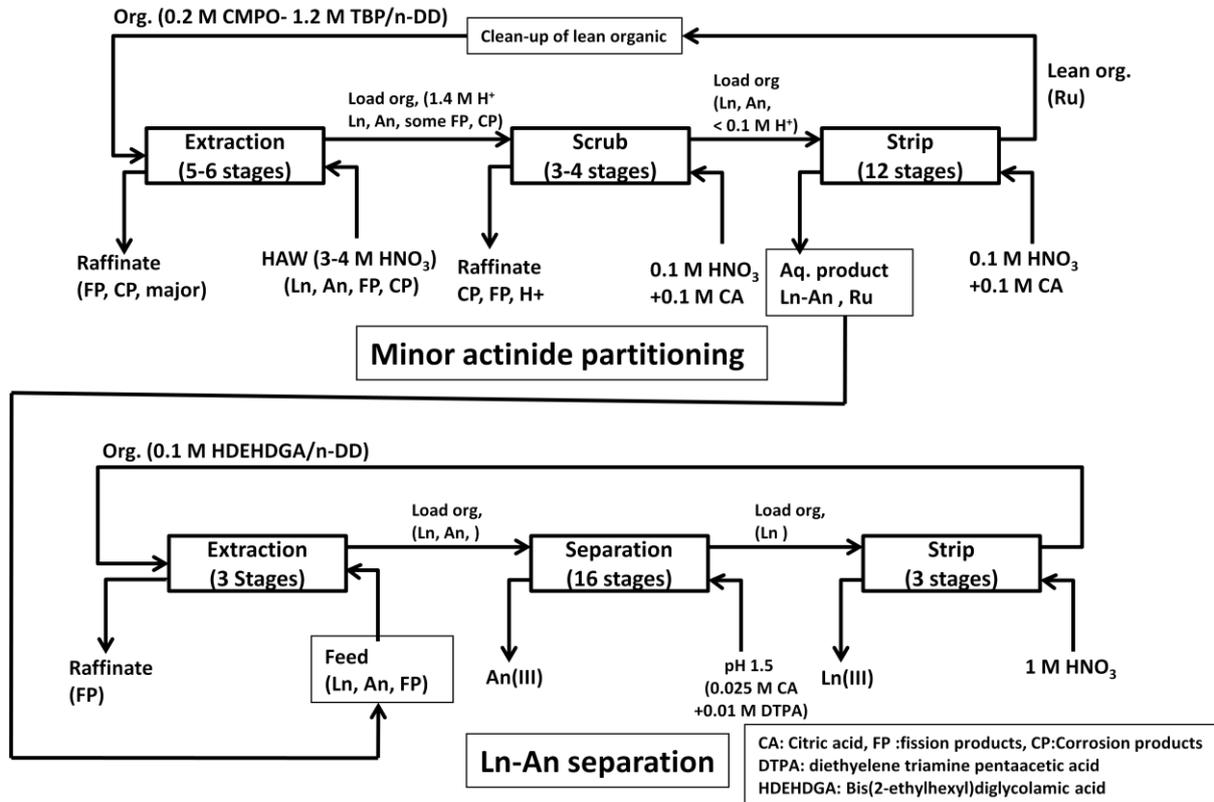
FIG. 1. Proposed flow-sheet for partitioning of trivalent actinides from FR-HLLW using CMPO for group separation and HDEHDGA/n-DD for Ln-An separation. The flow sheet was derived from the demonstration run with real HAW arising from reprocessing of spent carbide fuel, $(U_{0.3}Pu_{0.7})C$ irradiated to a burn-up of 155 GWd/Te in the Fast Breeder Test Reactor.

7. CHON extractants for group separation

As indicated above, the solvent phase demonstrated for trivalent actinide separation is made up of phosphorous based reagents (CMPO and TBP), which are not completely incinerable. It is important to note that CMPO is a reagent for trivalent actinide separation and TBP has been added to CMPO phase to avert the undesirable third phase formation during the extraction of trivalent metal ions from HAW by CMPO. In addition the solvent systems proposed for trivalent actinide separation invariably employed organic phase modifiers, such as polar extractants and long-chain alcohols to overcome such undesirable third phase formation. Although the addition of phase modifier averted the problem of third phase formation, it should be noted that they resulted in the generation of aqueous and organic wastes in significant quantities. The chemical and radiolytic degradation of phase modifier in conjunction with radiolytic products of solvent complicates the hydrodynamics of the process and burdens the management of spent organic waste. Therefore, it is desirable to employ an extractant that operates without the need of phase modifier for minor actinide partitioning, and also simplifies the existing flow-sheet.

8. Diglycolamides

In the previous decade, the CHON based extractant, namely diglycolamides, containing three oxygen donor atoms in a molecule have become popular for efficient

separation of trivalent metal ions from nitric acid medium. Among the various diglycolamides, the symmetrical derivatives, namely *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) and *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) have been extensively studied for trivalent actinides separation. However, these diglycolamides have some specific drawbacks such as third phase formation and extraction of unwanted fission product metal ions. From the process point of view and waste minimization it is desirable to employ an extractant that operates without the need of any phase modifier for minor actinide partitioning from HLLW.

9.   Unsymmetrical diglycolamides

In this context, we developed several unsymmetrical diglycolamides (UDGA) and studied for the extraction of trivalent metal ions from nitric acid medium [12,13]. In contrast to symmetrical DGAs such as TODGA and TEHDGA, the alkyl groups attached to the UDGAs are different. Among the various UDGAs studied, the *N,N,*-didodecyl-*N',N'*-dioctyl-3-oxapentane-1,5-diamide, trivially called as didodecyl-dioctyl-diglycolamide (D^3DODGA) was identified a promising reagent for trivalent actinide partitioning. It offered significant advantages over the other existing symmetrical DGAs. The dodecyl group in conjunction with the octyl group present in D^3DODGA, not only retained the excellent extraction properties of TODGA, but also surmounted the problem of third phase formation during the extraction of trivalent metal ions from 3-4 M nitric acid. Our studies have shown that D^3DODGA does not require any phase modifier during the extraction of trivalent actinides from 3-4 M nitric acid as there was no third phase formation in 0.1 M D^3DODGA/n-DD even equilibrated with 600mM of Nd(III) in 3 M nitric acid [13].
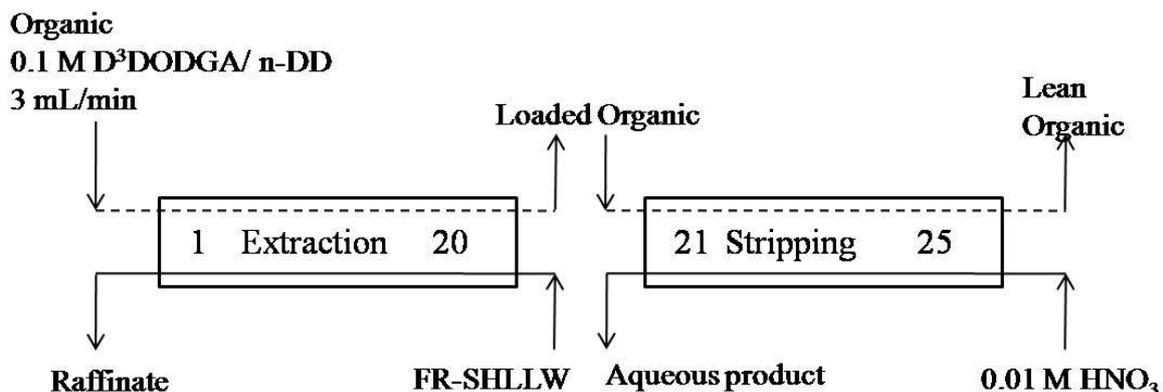

FIG. 2. Proposed flow-sheet for partitioning of trivalent actinides from FR-HLLW using modifier-free unsymmetrical diglycolamide, 0.1 M D^3DODGA/n-DD. The numbers 1 to 25 represents each mixer and settler.

10.   Mixer-settler studies with FR-SHLLW using UDGA

As a consequence, we studied the extraction and stripping behavior of various metal ions present in the fast reactor simulated high-level liquid waste (FR-SHLLW) using a modifier-free solvent phase composed of 0.1 M D^3DODGA in *n*-DD. The details are described elsewhere [14]. The results revealed the possibility of using 0.1 M D^3DODGA /*n*-DD for the separation of trivalent actinides from simulated and genuine wastes. The separation of trivalent americium from fast-reactor (FR) simulated high-level liquid waste (SHLLW) in a mixer-settler mode was then taken up and demonstrated using a modifier-free

organic phase containing 0.1 M D^{3}DODGA in *n*-DD. The extraction of Am(III) was accompanied by the co-extraction of all lanthanides and unwanted metal ions such as Zr(IV), Y(III), and Pd(II) from FR-SHLLW. The co-extraction of unwanted metal ions was minimized by adding a suitable aqueous soluble complexing agents such as trans-1,2-diaminocyclohexane-*N,N,N'N'*-tetraacetic acid (CyDTA) to FR-SHLLW. The stage profiles in a mixer-settler showed that Am(III) was extracted in 7-8 contacts. Depending upon the distribution ratio of trivalents the preferential loading of lanthanides in 0.1 M D^{3}DODGA/*n*-DD was achieved in the order Eu(III) > Sm(III) > Am(III) > Nd(III) > Pr(III) > Ce(III) > La(III). All the extracted metal ions were back extracted (> 99.9 %) in 3-5 contacts with 0.01 M nitric acid. Based on the mixer-settler studies with FR-SHLLW, the flow-sheet shown in *FIG*. 2. has been proposed for trivalent actinide separation.

11.   Conclusions

Group separation of trivalent metal ions from fast reactor HAW (155 GWd/Te) was demonstrated using the TRUEX solvent. The results confirmed near quantitative separation (> 99.9%) and recovery (>99%) of trivalents (Am+Ln) from high active waste. The trivalents were extracted in six stages and stripped in 10 stages using CA formulation in a mixer-settler run. Nearly 20 – 25 % of radioruthenium was carried to lean organic phase and called for cleanup of the solvent phase before recycling. Decontamination of radioruthenium can be performed by contacting the lean organic phase with sodium carbonate solution and anion exchange resin. A method was developed and demonstrated for the mutual separation of Am(III) and Eu(III) from the TRUEX product by using 0.1 M HDEHDGA/n-DD. Quantitative extraction of Am(III) and Eu(III) was achieved in 2 contacts at pH 3. The recovery of Am(III) alone from the loaded organic phase was achieved using 0.01 M DTPA-0.025 M CA at pH 1.5. Later, group separation of trivalents from FR-SHLLW was demonstrated with the use of CHON based, modifier-free solvent phase composed of D^{3}DODGA in *n*-dodecane. The method based on D^{3}DODGA was found to be simple and offered significant advantages over the existing methods in terms of waste minimization and waste disposal.

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