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Performance of Uranous nitrate and Acetohydroxamic Acid on the Partitioning of Plutonium and Uranium in Compact Reprocessing of Advanced Fuels in Lead Cells Reprocessing Facility

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ABSTRACT

A case study on the performance of uranous nitrate and acetohydroxamic acid on the partitioning of plutonium and uranium was studied. The loaded organics (30% tri-butyl phosphate in normal paraffin hydrocarbon as diluent) contains plutonium, uranium, and fission products such as Cs and Ru. Aqueous feeds containing 7 g/L uranous nitrate with 0.5 M hydrazine nitrate in 1 M nitric acid, and 0.3 M acetohydroxamic acid (AHA) in 1.5 M nitric acid were used as partitioning agents. Volume ratio of organic to aqueous was maintained as a unity. Gamma spectrum was taken from the lean organic and strip product to study the behavior of Ru and Cs distribution during partitioning. Uranous was found to be more effective in stripping plutonium, but it always contains the quantitative amount of uranium in the strip product. AHA, on the other hand, required more number of stages for effective partitioning but provides plutonium with the allowable amount of uranium in the strip product. Uranous was more effective in the decontamination of Cs, whereas both uranous and AHA were less effective in the decontamination of Ru.

Key words: *Nuclear fuel reprocessing, Acetohydroxamic acid, Uranous nitrate, Ruthenium and cesium.*

1. INTRODUCTION

Fast breeder reactor program is placed in the second stage of Indian Nuclear Power Program [1]. Reprocessing of fast breeder test reactor spent fuel was carried out in compact reprocessing of advanced fuels in lead cells (CORAL), an experimental facility using modified plutonium-uranium reduction extraction (PUREX) process [2]. PUREX process involves: (i) Decladding, (ii) dissolution, (iii) co-decontamination, (iv) partitioning and, (v) reconversion of U and Pu to their respective oxides.

Spent fuel rods are normally cut to pieces in pre-determined length, called as mechanical decladding. Then, the fuel alone is dissolved in concentrated nitric acid leaving the clad as a solid waste called HULL. Dissolved fuel is adjusted to chemical conditions suitable for solvent extraction. In PUREX process, 30% tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH) diluent is used as a solvent. In codecontamination step, U and Pu in the nitric acid medium are selectively extracted into the organic phase leaving fission product in the aqueous phase. U and Pu were separated to each other from loaded organic by selective stripping of Pu to the aqueous phase, which is called as partitioning step. Partitioned U and Pu in aqueous solutions are converted to solid oxides in reconversion step.

Selective stripping of plutonium from loaded organic containing both uranium and plutonium can be achieved through selective complexation or reduction of plutonium [3].

1 M H_2SO_4 in 1 M nitric acid [4] complexing reagent can be used for U and Pu partitioning. In which, SO_4^{2-} ion selectively complex Pu and leaving U in the organic phase. U complexation by SO_4^{2-} ion is avoided by salting out the effect of the nitrate ion. However, the corrosive nature of sulfate ion limits its widespread utility. Other mode of stripping of plutonium can be achieved through selective reduction. Ferrous sulfamate [5], uranous/hydrazine [6], hydroxylamine nitrate/hydrazine [7,8], etc. are some of the reducing agents. In ferrous sulfamate, ferrous ion converts to ferric ion and provide a single electron for Pu^{4+} to Pu^{3+} reduction. The following equation represents the reduction reaction using ferrous ion.

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$$Fe^{2+} + Pu^{4+} \rightarrow Pu^{3+} + Fe^{3+} \quad (1)$$

Sulfamate ion has a role of nitrite ion scavenger. It is also called as a stabilizer for produced Pu^{3+} ion. Since usage of ferrous sulfamate reagent results in high metal ion waste as ferric ion, which leads to limit the use of ferrous sulfamate.

In the case of hydroxylamine, its rate of reduction reaction is inversely proportional to the fourth power of acid concentration, which is shown by equation 2.

$$2NH_2OH + 4Pu^{4+} \rightarrow 4\ Pu^{3+} + N_2O + 4H^+ + H_2O \quad (2)$$

Therefore, hydroxylamine suits well for low acidity applications. Uranous-hydrazine reagent is commonly used as the partitioning agent in many countries because of its fast kinetics and does not introduce any foreign metal ions like iron, etc. Uranous-hydrazine reagent stripped solutions require extensive conditioning to convert the unused uranous U(IV) to uranyl (U(VI)) ions. Otherwise, it may lead to uranium-contaminated plutonium oxide product due to the co-precipitation of unconverted uranous ions. Partitioning by uranous also results in extra metal ion load to the reprocessing plant. Hence, any salt-free reagent applicable to uranium, plutonium partitioning is desirable. Acetohydroxamic acid (AHA) is one of the salt free reagents, and its performance in uranium and plutonium partitioning was studied with U and Pu loaded organic (30% TBP in NPH) in absence of fission products [9]. Nevertheless, its performance on actual loaded organic from the reprocessing plant with fission product contamination is yet to be studied. In the present work, the performance of uranous-hydrazine and AHA reagents in partitioning U and Pu from the actual loaded organic from CORAL reprocessing facility are compared. The distribution of the troublesome fission products Cs and Ru during partitioning with uranous and AHA are also studied.

2. EXPERIMENTAL

2.1. Chemicals and Reagents

Uranous nitrate was prepared from uranyl nitrate by electro-reduction using titanium cathode and platinum anode. Sigma–Aldrich makes acetohydroxamic acid (purity 98%) and AR grade nitric acid were used in all the experiments.

2.2. Analysis

Analysis of uranium in both aqueous and organic phases was done by a spectrophotometric method using pyridylazo resorcinol (PAR) as the chromogenic reagent [10]. Analysis of plutonium was carried out radiometrically using para electronics made alpha scintillation counter using ZnS/Ag scintillator. Liquid samples of known volume containing Pu is delivered on stainless steel (SS) metal disks, and it was dried in hot plate. Dried metal discs fired in Bunsen burner to fix the radionuclides strongly on the SS surface. Then, its radioactivity was counted using ZnS/Ag scintillator. Fission product gamma spectrum was taken using coaxial high-performance germanium (HPGe) detector for the organic and aqueous phases resulted during the partitioning by uranous and AHA. DSG brand HPGe detector and Maestro multi-channel analyzer (MCA) software were used for the gamma spectrum study.

2.3. Statistical Error Analysis

Plutonium values vary with relative standard deviation (RSD%)=2% in scintillation based radiometric determination. Uranium values vary with RSD%=5% in the spectrophotometric determination of uranium by PAR method.

2.4. Partitioning Studies

One of the loaded organic received from CORAL reprocessing facility was taken as the organic feed. The loaded organic feed was divided into two equal parts. One part was used for partitioning with uranous-hydrazine, and the other part was used with AHA as the partitioning agent.

The concentrations of U, Pu, and H^+ and the activity levels of the organic feed are as follows:

[U]:9.29 g/L; [Pu]:6.88 g/L; $[H^+]$:0.76N β activity: 3.358 mCi/L; γ activity: 1.568 mCi/L; α activity = 586 mCi/L

2.4.1. Partitioning study with uranous-hydrazine mixture

The concentrations in the aqueous feed are:

$[U^{4+}]$: 7.0 g/L; $[N_2H_4]$: 0.5 M; $[H^+]$:1.0 M; $[UO_2^{2+}]$: 5.33 g/L

Uranous concentration in uranous reagent was estimated by redox titrimetry using potassium dichromate as titrant and ferroin as indicator [11]. Acidity and hydrazine concentration of uranous reagent were analyzed by simultaneous determination of free acidity and hydrazine using oxalate complexation [12-14].

To a known volume of organic feed, an equal volume of uranous/hydrazine reagent was added in an extraction vial and equilibrated for 5 min in a vortex shaker. After settling, the organic and aqueous phases were centrifuged, and the concentration of uranium and plutonium were analyzed in both phases. The aqueous phase was separated, and one more contact was given with fresh uranous reagent to the organic phase for the purpose of quantitative stripping of plutonium. Fission product spectrum was also taken in each stage.

2.4.2. Partitioning study with AHA

The aqueous feed was 0.3 M AHA in 1.5 M nitric acid. This aqueous feed composition selected as per previous studies [15]. Partitioning experiments were carried out with 0.3 M AHA in 1.5 M nitric acid as the aqueous feed. Using the procedure described above, five contacts were given for the quantitative stripping of plutonium. In each contact, both organic and aqueous phases were analyzed for U and Pu. Fission product spectrum was also taken using HPGe detector (DSG made-coaxial type detector using Maestro MCA software).

3. RESULTS AND DISCUSSION

Comparison of the performance of U(IV) and AHA as a partitioning reagents

U(IV) partitioning

U(IV) reduces Pu(IV) to Pu(III) as follows:

$$U^{4+} + 2Pu^{4+} + 2H_2O \rightarrow 2Pu^{3+} + UO_2^{2+} + 4H^{+} \qquad (3)$$

Since the distribution coefficient of Pu(III) is less in 30% TBP system, Pu is back extracted into the aqueous phase. The values of uranium and plutonium distributed between the lean organic (organic phase resulted after equilibration) and strip product (aqueous phase resulted after equilibration) are given in Table 1.

Organic feed: [U]: 9.29 g/L; [Pu]: 6.88 g/L; [H^+]: 0.76 N; β activity: 3.358 mCi/L; γ activity: 1.568 mCi/L: α activity = 586 mCi/L

Aqueous feed: [U^{4+}]: 7.0 g/L; [N_2H_4]: 0.5 M; [H^+]: 1.0 M; [UO_2^{2+}]: 5.33 g/L

Number of iterations: 2

In the first contact, concentration of plutonium reduced from 6.88 g/L to 0.066 g/L in the organic phase. In the second contact, Pu concentration reduced to 0.007 g/L. However, uranium in the loaded organic increased from 9.29 g/L to 22.54 g/L. In the second contact, the uranium concentration in organic phase increased from 22.54 g/L to 24.40 g/L only. Remaining uranium (10.46 g/L) went along with the strip product.

The activity levels of Ru and Cs in the lean organic and strip product resulted from uranous partitioning experiments are given in Table 2.

Number of iterations: 2

Table 1: Distribution of U and Pu in uranous partitioning.

Contact no.	Lean organic		Strip product	
	U (g/L)	Pu (g/L)	U (g/L)	Pu (g/L)
1	22.54	0.066	0.100	6.800
2	24.40	0.007	10.46	0.058

It could be observed that Cs is not stripped by the uranous reagent. However, ruthenium is stripped around 50% within two contacts which is known from the presence of Ru in the strip product. Typical gamma spectrum of lean organics after first and second contact with uranous are shown in Figures 1 and 2, respectively.

Table 2: Activity levels of Ru and Cs in lean organic and strip product in uranous partitioning.

Description of sample	Activity (mCi/L)	
	^{106}Ru	^{137}Cs
Feed	1.974	0.237
Lean organic (1 contact)	1.752	0.219
Strip product (1 contact)	0.22	BDL
Lean organic (2 contacts)	1.015	0.218
Strip product (2 contacts)	0.740	BDL

BDL=Below detectable limit

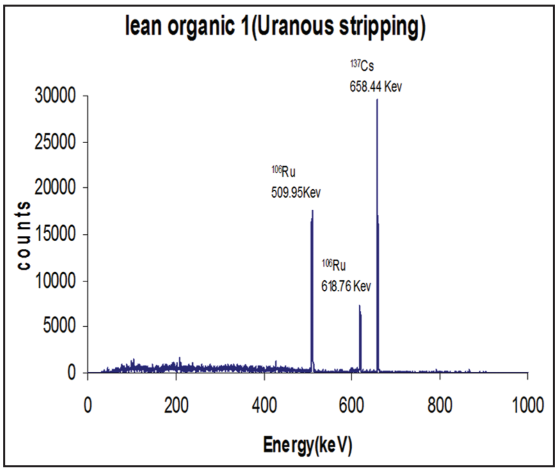

Figure 1: Gamma spectrum of lean organic resulted from first uranous contact.

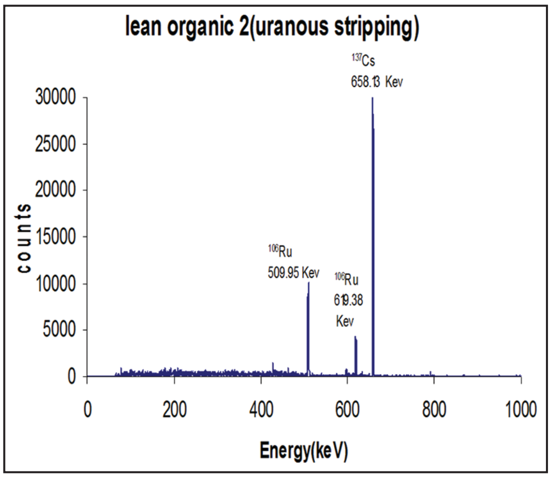

Figure 2: Gamma spectrum of lean organic resulted from second uranous contact.

3.1. AHA Partitioning

AHA reduces Pu(IV) to Pu(III) as follows:

$$2Pu^{4+} + CH_3CONHOH + 2H_2O \rightarrow 2Pu^{3+} + CH_3COOH + NH(OH)_2 + 2H^+ \quad (4)$$

From the results reported earlier [15], the optimum composition of AHA as partitioning reagent is chosen as 0.3 M AHA in 1.5 M nitric acid. The second part of loaded organic received from CORAL reprocessing facility was contacted with 0.3 M AHA in 1.5 M nitric acid. The distribution values of uranium and plutonium in lean organic and strip product are given in Table 3.

Table 3 reveals that in the first contact using AHA reagent with O/A ratio of one, concentration of plutonium in the organic and aqueous phase after equilibration were found to be 2.16 and 4.76 g/L, respectively. The distribution ratio of plutonium after equilibration was calculated as follows:

D_{Pu} = [Pu]Org./[Pu]Aq.

A distribution ratio value of plutonium was found to be 0.45 in our present experiment conducted with actual loaded organic resulted from CORAL reprocessing facility. However, the distribution ratio value of 0.16 was reported earlier when 4 g/L of plutonium in 30% TBP-NPH was scrubbed with 0.3 M AHA in 1.5 M nitric acid [15].

Karraker et al. [16] had reported the distribution ratio of plutonium using 0.3 M AHA in 1.71 M nitric acid equilibrated with 30% TBP to be 0.167. Carrott et al. [17] had intensively studied the distribution of plutonium with varying initial concentration of plutonium, AHA, and acidity. They obtained a value of 0.082 as the distribution ratio for 11.48 g/L of plutonium in the presence of 0.25 M AHA in 1 M nitric acid at 298 K. Tkac et al. [18] had also reported similar graphically represented results using various concentrations of nitric acid and AHA in presence and absence of lithium nitrate. The higher value of distribution ratio (0.45) in the first contact after equilibrating with AHA is attributed by the presence of degradation products of TBP and diluent in the organic phase in our experiments.

Table 3: Distribution of U and Pu in AHA partitioning.

Contact no.	Lean organic		Strip product	
	U (g/L)	Pu (g/L)	U (g/L)	Pu (g/L)
1	9.23	2.16	0.08	4.76
2	8.54	0.97	0.69	1.18
3	7.95	0.51	0.58	0.48
4	NA	0.25	NA	0.24
5	NA	0.12	NA	0.11

NA=Not analyzed, AHA=Acetohydroxamic acid

Concentration of plutonium requires to be decreased further in the organic phase. Hence, four more contacts with AHA reagent were given. Even after five contacts, Pu concentration decreased to 0.12 g/L only. Since the feed organic used in these experiments is the actual loaded organic from the plant, it contained the degradation products also.

Analysis of the lean organic [19] showed the presence of 1.6 g/L of dibutyl phosphate (DBP), which is the degraded product of TBP. Since the reduction of Pu(IV) to Pu(III) from Pu(IV):TBP solvated complex is much easier than that from Pu(IV):DBP complex [20], more number of stages are required for the quantitative stripping of plutonium using AHA reagent. The distribution ratio of Pu against contact number is plotted in Figure 3.

From the Figure 3, it is evident that the distribution ratio value increases with increase in the contact number and reaches a saturation value of almost 1 after third contact. This observation is contradictory to the behavior of plutonium partitioning using AHA in simulated feeds reported previously [9]. In the experiments conducted with simulated feed, distribution ratio of plutonium was almost constant ranging from 0.12 to 0.25 only. The activity level of ruthenium and cesium in the lean organic and strip product in the first and second contact resulted from a partitioning experiment using AHA are listed in Table 4.

Number of iterations: 2

Cesium was stripped quantitatively by AHA reagent in first contact. This can be explained by simple replacement of H^+ ion in AHA by Cs^+ ion through ion exchange process. In the case of ruthenium, around 19% was stripped in first contact, and further stripping was not significant. The gamma spectra of lean organic

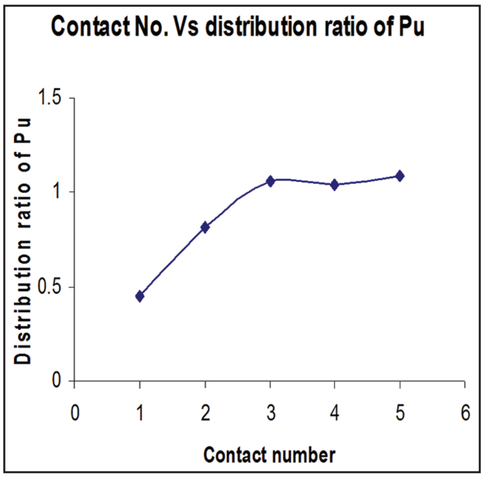

Figure 3: Contact number versus distribution ratio of Pu in acetohydroxamic acid partitioning.

after first and second contact with AHA are shown in Figures 4 and 5, respectively.

4. CONCLUSIONS

While comparing the performances of uranous-hydrazine and AHA as partitioning agents, uranous is undoubtedly more effective than AHA in stripping plutonium from loaded organics even in the presence of solvent degradation products. However, it has the disadvantage of higher uranium loading in the partitioning cycle and the additional step of converting U(IV) to U(VI). AHA, on the other hand, requires more number of stages than uranous reagent owing to the presence of solvent degradation products. While comparing the stripping of Ru and Cs, uranous is found to be less effective in Cs stripping whereas AHA is less effective in stripping of Ru.

Table 4: Activity levels of Ru and Cs in lean organic and strip product in AHA partitioning.

Description of sample	**Activity (mCi/L)**	
	^{106}Ru	**^{137}Cs**
Feed	1.974	0.237
Lean organic (1 contact)	1.379	0.065
Strip product (1 contact)	0.375	0.162
Lean organic (2 contacts)	1.153	BDL
Strip product (2 contacts)	0.054	BDL

BDL=Below detectable limit, AHA=Acetohydroxamic acid

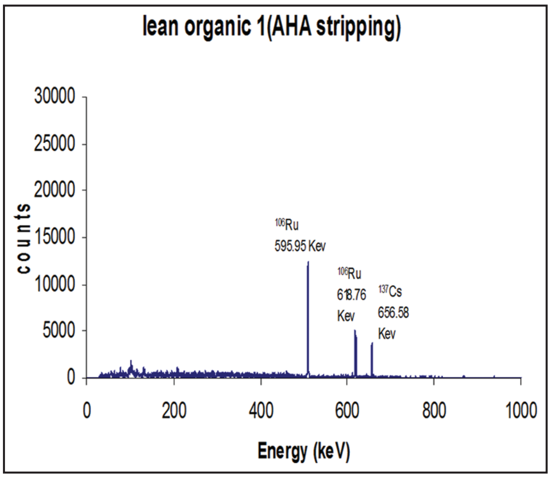

Figure 4: Gamma spectrum of lean organic after first contact with acetohydroxamic acid.

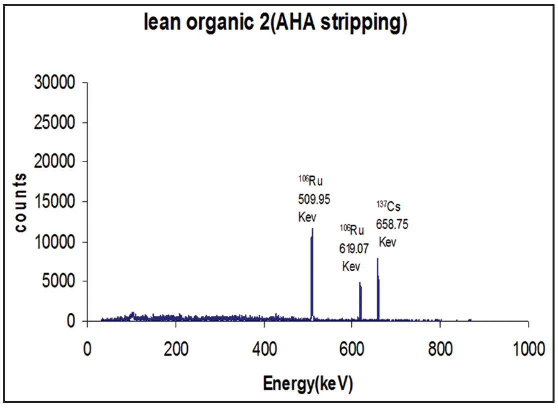

Figure 5: Gamma spectrum of lean organic after second contact with acetohydroxamic acid.

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***Bibliographical Sketch**

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