

## EVALUATION OF HYDROXYUREA AS A PARTITIONING AGENT IN FAST REACTOR FUEL REPROCESSING PLANT - BATCH COUNTER CURRENT EXTRACTION STUDIES

P. Sivakumar<sup>1</sup>, S. Meenakshi\*<sup>2</sup> and P. Govindan<sup>1</sup>

<sup>1</sup>Reprocessing Group, Indira Gandhi Centre for Atomic Research, Kalpakkam-603 102, India

<sup>2</sup>Gandhigram Rural University, Gandhigram-624302, India

\*Email: drs\_meena@rediffmail.com Tel: +91 (44) 27480099; Fax: +91 (44) 27480207

[Received-24/11/2013, Accepted-07/12/2013]

### ABSTRACT:

Reprocessing of spent fuel from Fast Breeder Test (FBTR) reactor is being carried out at CORAL (COmpact Reprocessing of Advanced fuels in Lead shielded cells) Kalpakkam. Partitioning of Uranium and Plutonium is being carried out by oxalate precipitation method. A process based on the reduction of plutonium to inextractable form by Hydroxyurea followed by extraction of uranium using 30% TBP by batch counter current method is studied for the separation of uranium and plutonium. Extraction of Uranium is carried out in batch mode to draw McCabe-Thiele diagram and from this the number of stages required to achieve the desired degree of extraction of uranium with particular A/O ratio is arrived. The above parameters are verified in batch counter current extraction method by taking simulated concentration of co-decontaminated U/Pu from the fission products in the fast reactor fuel reprocessing plant.

**Keywords:** Hydroxyurea, PUREX process, Fast reactor Fuel reprocessing, Partitioning.

### [I] INTRODUCTION

Fast Breeder Test Reactor (FBTR) reactor at Kalpakkam has been operating successfully with mixed carbide (70% Pu and 30% U) as a driver fuel. The spent fuel of this reactor at various burn ups ranging from 25 GWd/te (Giga Watt day/tonne) to 154 GWd/te were processed in the facility called COmpact Reprocessing of Advanced fuels in Lead shielded cells (CORAL) by modified PUREX process using 30% TBP (Tri-n-Butyl Phosphate as extractant in HNP diluents or n-dodecane [1-3]. TBP extracts uranium and plutonium leaving bulk of fission products to aqueous waste. In PUREX process, partitioning of uranium and plutonium is carried out by selectively reducing  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  using

a suitable reducing agent. Since the distribution ratio of  $\text{Pu}^{3+}$  is fairly low, it is inextractable in 30% TBP [4]. Several partitioning agents have been reported. Uranous ( $\text{U}^{4+}$ ) is used as partitioning agent for uranium and plutonium separation. Its requirement is more than the stoichiometric amount of plutonium [5-7], because of the parasitic reaction of nitrite on  $\text{U}^{4+}$  and  $\text{Pu}^{3+}$  which decreases the stability of  $\text{Pu}^{3+}$  in the organic phase. As the concentration of plutonium in fast reactor fuel reprocessing plant is high, requirement of uranous is very high for the partitioning of uranium and plutonium, which in turn increase the plant load. In situ electrochemical production of uranous for the

partitioning of uranium and plutonium [8] method is having inherent disadvantages such as fouling of electrodes etc. and hence cannot be used for the plant application. Ferrous Sulphamate [5, 9] has been extensively used as partitioning agent. It is unstable with respect to changes of acidity and temperature. The redox potential of Fe(II)/Fe(III) is very nearer to Pu(III)/Pu(IV) and hence higher concentration of ferrous sulphamate is needed for the complete reduction of Pu(IV). Oxidation of  $\text{Fe}^{2+}$  and  $\text{Pu}^{3+}$  by  $\text{HNO}_2$  is significant even in the presence of sulphamic acid hence 20-40 times the stoichiometric quantity is required for the partitioning of uranium and plutonium. Also this causes corrosion and adds salt contents to the waste. Use of Hydroxylamine nitrate/ Hydrazine [10, 11] require minimum acidities, there may be increased chances of plutonium polymerization. These reagents are less stable at higher acidities. In CORAL, partitioning of uranium and plutonium is being carried out by oxalate precipitation method. Plutonium forms solid plutonium oxalate whereas uranium forms soluble uranyl oxalate. Uranium also forms solid oxalate along with plutonium when uranium concentration exceeds its solubility limit. It requires more number of washing cycles and hence increases in generation of the radioactive liquid wastes. Moreover this is a batch process. Because of these disadvantages, development of an alternate method of partitioning especially for FBR fuels is inevitable. It has been reported in the literature that Hydroxyurea [12-14] a salt free reducing agent is a potential candidate to reduce Pu(IV) to Pu(III) and also destroys nitrous acid devoid of any holding reductant. Our earlier studies show the applicability of hydroxyurea (HU) in the partitioning of uranium and plutonium and the effect of various parameters such as uranium concentration, HU molarity, acidity etc [15-16] in the partitioning of uranium and plutonium are also studied extensively. Based on the advantages of our earlier experiments, a study for the partitioning of U and Pu in aqueous medium is carried out with Hydroxyurea as reducing agent by taking

the simulated concentration U/Pu in batch counter current mode. Various parameters are optimized and the results are given in this paper.

## [II] EXPERIMENTAL PART

### 2.1. Reagents and chemicals

A stock solution of plutonium nitrate was prepared by dissolving  $\text{PuO}_2$  in 12 M nitric acid containing 0.1 M HF. A stock of uranium was prepared by dissolving uranium oxide powder in nitric acid. From this, required concentrations of uranium solution in 4 M nitric acid were prepared. Feed solution having the composition of 11 g/L plutonium and 10- 120 g/L of uranium in 4M nitric acid containing 0.1 M HU was prepared for extraction isotherm studies. 11 g/L plutonium and 21.5 g/L of uranium in 4M nitric acid containing 0.1 M HU was prepared for counter current extraction studies. Hydroxyurea of E Merck, sodium nitrite of AR grades were used. DM water was employed for making the reagents.

### 2.2 Solvent Extraction Studies

Known volume of solutions containing different concentrations of uranium and fixed concentration of plutonium in 4M  $\text{HNO}_3$  containing 0.1M HU are equilibrated with 30% TBP with the aqueous to organic (A/O) ratio of 4. Organic and aqueous phases are analysed for uranium and plutonium to construct the uranium extraction isotherm.

Batch wise counter current extraction is carried out by equilibrating uranium and plutonium mixture in 4M  $\text{HNO}_3$  with 30% TBP with the A/O ratio of 4.

### 2.3. Analyses

Uranium was analysed by Davis Gray [17] method after evaporation nearer to dryness or spectrophotometric method using Pyridyl Azo Resorcinol (PAR) [18] as chromogenic agent (after destroying HU by sodium nitrite) depending upon its concentration. Plutonium was analyzed by alpha radiometric method.

[III] Uranium Extraction isotherm and McCabe-Thiele diagram

The extraction of uranium and plutonium is based on the formation of neutral organic phase

complexes, such as  $UO_2(NO_3)_2 \cdot 2TBP$  and  $Pu(NO_3)_4 \cdot 2TBP$ . Pu is reduced to inextractable  $Pu^{3+}$  by the addition of HU followed by the extraction of uranium .

The number of stages required to achieve desired degree of separation, can be determined by constructing a McCabe-Thiele diagram. The diagram is constructed by determining the equilibrium isotherm for extraction via experiments. The equilibrium isotherm can be obtained by mixing an aqueous solution and organic solution until equilibrium is reached. After phase separation the aqueous phase and organic phases are analysed for the uranium concentration.

Graphical representation of the concentration of uranium in the organic phase and aqueous phases at equilibrium is called as uranium extraction isotherm. Using the extraction isotherm, McCabe-Thiele diagram is drawn. The McCabe-Thiele diagram consists of the equilibrium curve, Operating line for particular A/O ratio and vertical line starting from the X axis for particular feed uranium concentration. Operating line starts from origin and its slope varies with the A/O ratio.

Using the McCabe-Thiele diagram, the number of counter-current stages required to achieve the desired degree of extraction of uranium with the required A/O ratio can be obtained. MATLAB programme has been used for constructing McCabe-Thiele diagram, to predict the number of stages and A/O ratio required for the extraction of uranium in such a way that the loss of uranium in the aqueous phase should not have interference in the partitioning of uranium and plutonium by oxalate precipitation method. McCabe-Thiele diagram is drawn using the expected feed uranium and Plutonium concentration of fast reactor fuel reprocessing plant is shown in Fig. 1.

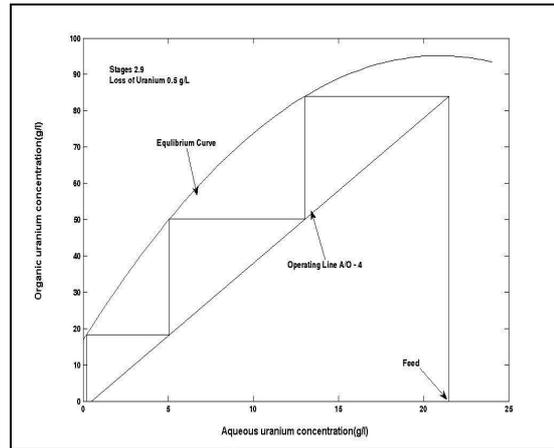


Fig: 1. Uranium: 10-120 g/L; Pu : 11g/L ; H+ : 4M in 0.1M HU

**[IV] BATCH COUNTER CURRENT EXTRACTION STUDIES WITH URANIUM AND PLUTONIUM MIXTURE**

The result such as number of stages required for the required degree of extraction of uranium with A/O ratio is verified by running a batch counter-current extraction. The counter-current flow of aqueous and organic streams is shown in Fig. 2 for a three stage contacting system.

The number of stages and A/O ratio is predicted by McCabe-Thiele diagram is verified by performing batch counter current extraction of uranium in an extraction vial.

The extraction sequence for 3 stages counter current in batch mode is given Fig. 3. In each stage the aqueous and organic phases are equilibrated for 10 minutes and allowed to separate the phases.

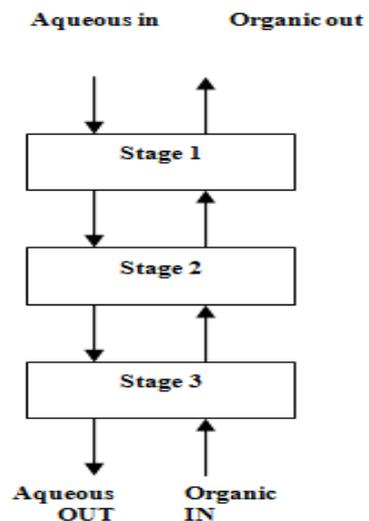
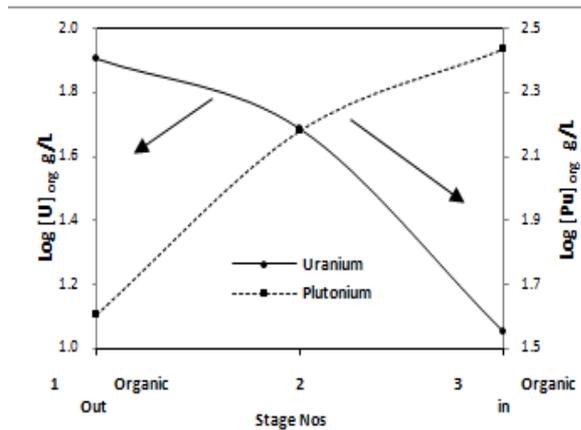


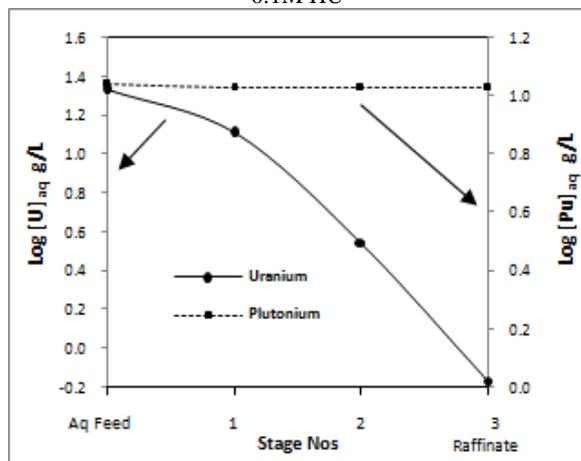
Fig: 2. Three stages counter current flow of Aqueous and Organic streams

After first set of extraction A3 is removed and A2 is poured into O3, A1 is poured into O2. To the left out O1 fresh aqueous (FA1) is added and this process is repeated for 3 more time. The resulting final aqueous samples such as FA1, FA2, FA3 and organic samples such as FO1, FO2 and FO3 are analysed for uranium and plutonium

A graph is plotted by taking stage numbers in the X axis and the organic phase concentration of uranium in the primary Y axis and organic phase concentration of plutonium in the secondary Y axis respectively. The plot is shown in Fig 4. Similarly a graph is plotted by taking stage numbers in the X axis and the aqueous phase concentration of uranium in the primary Y axis and aqueous phase concentration of plutonium in the secondary Y axis respectively. The plot is shown in Fig. 5



**Fig. 4.** Organic phase stage profile  
Feed: Uranium- 21.5 g/L ; Pu- 11g/L ; H<sup>+</sup>- 4M in 0.1M HU



**Fig. 5.** Aqueous phase stage profile  
Feed: Uranium- 21.5 g/L ; Pu- 11g/L ; H<sup>+</sup>- 4M in 0.1M HU

**4.1. Recovery of uranium in each stage**

The expected concentration of uranium in each stage of the organic phase is calculated from the following expression

$$(X_{in}-X_{out}) = m (Y_{out} - Y_{in})$$

$$m=O/A=(X_{in}-X_{out})/(Y_{out} - Y_{in})$$

$$A/O=(Y_{out} - Y_{in})/(X_{in} - X_{out})$$

$$Y_{out} = A/O * (X_{in} - X_{out}) + Y_{in}$$

Where  $X_{in} = 21.5 \text{ g/L}$  ;  $X_{out} = \text{Raffinate out of each stage}$  ;  $A/O = 4$  ;  $Y_{in} = \text{organic inlet of each stage}$  ;  $Y_{out} = \text{organic outlet of each stage}$ . The calculated and actual concentration of uranium in each stage of the organic phase is given in Table 1.

Stage	Uranium in Aqueous (g/L)		Uranium in Organic phase (g/L)			Recovery %
	$X_{in}$	$X_{out}$	$Y_{in}$	Theoretical $Y_{out}$	Actual $Y_{out}$	
3	3.5	0.68	0	11.28	11.28	96.8
2	12.8	3.5	11.28	48.48	48.5	
1	21.5	12.8	48.5	83.3	80.3	

**Table 1.** Recovery of uranium in each stage

**4.2. Stage efficiency calculation**

Efficiency of extraction in each stage is calculated using the expression as given below.

$$\text{Efficiency} = (Y_{out} - Y_{in}) / (Y_{Eq} - Y_{in})$$

Where  $Y_{in}$  and  $Y_{out}$  are the inlet and outlet concentrations of uranium in the organic phase of each stages.

$Y_{Eq}$  is calculated from the equation obtained in extraction isotherm and the equation is  $22.84\ln(X)+20.02$  where  $X$  is the concentration of uranium in aqueous phase leaving the respective stage.

- Stage 1 Efficiency =  $(11.28-0)/(11.2-0)=100 \%$
- Stage 2 Efficiency =  $(48.5-11.28)/(48.6-11.28) = 100 \%$
- Stage 3 Efficiency =  $(80.3 - 48.5)/(78.25-48.5) = 106 \%$

**[V] RESULTS AND DISCUSSIONS**

Data in Fig.1 show the equilibrium and operating line of A/O ratio of 4. It indicates that

three stages are required to achieve the required degree of extraction of uranium.

Data in Fig.4 show that the concentration of uranium in the aqueous phase is decreasing with number of stages and at the end of three stages the aqueous raffinate is having the concentration of 0.68 g/L (initial uranium concentration) with the condition arrived from McCabe-Thiele diagram. This is in good agreement with the parameters predicted from McCabe-Thiele diagram. The remaining 3% of uranium going along with the plutonium stream is compromised in the oxalate precipitation of plutonium. Data in Fig.4 also show that more than 99% of the plutonium is present in the aqueous stream and only ppm level of Pu is present in the organic phases.

Data in Table 1 indicate that the expected and actual concentrations of uranium in the organic phases are not varying significantly and the cumulative extraction of uranium in the three stages is 97%.3% of

Data in Fig.5 show that the concentration of uranium in the organic phase is increasing with number of stages and at the end of three stages the organic outlet is having the concentration of 80.3 g/L of uranium. Data in Fig.5 also indicate that Pu present in the organic stream is decreasing as a function of number of stages, which implies that with the increasing the loading of uranium, concentration of Pu in the organic phase decreases due to the non availability of free TBP for uptake of Pu. The concentration of uranium and plutonium in the organic outlet is 80.3 g/L and 40 mg/L respectively. The residual Pu in the organic phase is still to be reduced by appropriate scrubbing the organic phase with 0.1M HU in HNO<sub>3</sub>. Uranium present in the aqueous plutonium stream is quite low and hence is not interfering in the oxalate precipitation of plutonium.

#### [VI] CONCLUSIONS

Reduction of plutonium by hydroxyurea followed by extraction of uranium upto saturated loading reduces the plutonium contamination in the organic phase. Scrubbing of organic phase

with hydroxyurea still reduces the plutonium retention in the organic phase. Addition of sodium nitrite destroys Hydroxyurea and also converts Pu<sup>3+</sup> to Pu<sup>4+</sup>. Oxalate precipitation of this conditioned plutonium indicates that hydroxyurea is not interfering in the reconversion stages of Pu.

#### ACKNOWLEDGEMENTS

Authors express their sincere thanks to Shri. R.Natarajan, Director, Reprocessing Group and Shri. A.Ravishankar, Associate Director, Reprocessing Plant Operations Group and Shri.V.Vijayakumar, Head, Reprocessing Plant Operations Division for their keen interest and constant encouragement throughout the work. The helpful discussion with Dr. R.V.Subbarao is highly remarkable. The contribution of Shri Ananthanarayanan, Shri. S.Suman and Shri Shrivankumar of Chemical Lab, RpG is gratefully acknowledged.

#### REFERENCES

1. M.Venkataraman, R.Natarajan and Baldev Raj, CORAL: A stepping stone for establishing the Indian Fast Reactor Fuel Reprocessing Technology, Proceedings of GLOBAL 2007, held at Boise, Idaho, 208-216
2. R Natarajan, Challenges in Fast Reactor Fuel Reprocessing, Indian Association of Nuclear Chemists and Allied Scientists Bulletin, 27-32, 14 (2), 1998.
3. Nuclear chemical Engineering, Benedict. M., Pigford. T.M. and Levi. H.W, Second Edition McGraw Hill Book Co., New York (1981)
4. Veena Sagar, K. Venugopal Cherty and D.D.Sood, Extraction of Pu(III) by TBP in presence of Uranium, Solvent Extraction and Ion Exchange, 18(2) 307-317 (2000)
5. Kjeller Report Reprocessing of fuels from present and future power reactors, Advanced course organized by the Netherland's-Norwegian Reactor school September 1967.
6. W W Schulz, L L Burger, J D Navratil, Science & technology of Tributylphosphate: Vol 3, CRC Press USA, (1990)
7. Sawant RM, Rastogi RK, Chaudhuri NK (1998) Study on the extraction of U (IV) relevant to PUREX process. J Radioanal Nucl Chem 229:203

8. IGC Newsletter-Vol-85, July-2010 Process Modeling of In-situ electrochemical partitioning of Uranium and Plutonium in PUREX process.
9. D.D.Sood, and S.K.Batil, Chemistry of Nuclear Fuel Reprocessing: Current Status , Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 203, No. 2 (1996) 547-573
10. Plutonium partitioning in the purex process with hydrazine stabilized hydroxylamine nitrate, G.L.Richardson, J.L.Swanson, June 1975, HEDL-TME-75 30
11. S. L. Yarbrow, S. B. Schreiber, E. M. Ortiz, R. L. Ames Journal of Radioanalytical and Nuclear Chemistry, Vol. 235, Nos. 1 2 (1998) 21 24
12. Zhu Zhaowu, He Jianyu, Zhang Zefu, Zhang Yu, Zhu Jianmin, Zhen Weifang Journal of Radioanalytical and Nuclear Chemistry, Vol. 262, No. 3 (2004) 707-711
13. Zhu Zhaowu, He Jianyu, Zhang Zefu, Zhang Yu, Zheng Weifang Journal of Radioanalytical and Nuclear Chemistry, Vol. 260, No. 3 (2004) 601-606
14. P.Sivakumar, S.Meenakshi, S.V.Mohan, R.V.Subba Rao and M.Venkataraman, Modified TTA Method for the Determination of Plutonium, Journal of Radioanalytical and Nuclear Chemistry, Volume 294, Number 1(2012), pp 93-96
15. P.Sivakumar, S.Meenakshi and R.V.Subba Rao, Partitioning of Plutonium and Uranium in Aqueous medium using Hydroxyurea as reducing agent, Journal of Radioanalytical and Nuclear Chemistry Volume 292, Number 2 (2012), pp 603-608
16. P.Sivakumar, S.Meenakshi and R.V.Subba Rao, Purification and recovery of Plutonium from Uranium oxide obtained in the Fast reactor fuel reprocessing plant using Hydroxyurea as reductant,Journal of Radioanalytical and Nuclear Chemistry, Volume 291, Number 1(2012), pp 763-767
17. A rapid and specific titrimetric method for the precise determination of uranium using iron(II) sulphate as reductant, W.Davis and W.Gray, Talanta, 1964 Vol (II) pp 1203-1211
18. T.M.Florence, Yvonne, Farrar, Spectrophotometric determination of Uranium with 4-(2 pyridyl azo) resorcinol, Anal.Chem, 1963, 35, 11 pp 1613-1616.

**Fig: 3.** Scheme for three stages of counter current extraction in batch mode

