

ELECTRO REDUCTIVE DISSOLUTION OF PLUTONIUM OXIDE- A PRELIMINARY STUDY

K. Dhamodharan¹, Anitha Pius^{*2}, Pradeep Kumar Sharma¹,
S. Pugazhendi¹ and V. Vijayakumar¹

¹Reprocessing Group, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603 102

²The Gandhigram Rural Institute -Deemed University, Gandhigram, Dindigul - 624 302

*dranithapius@gmail.com Tel No: +919443108504

[Received-06/05/2014, Accepted-21/05/2014]

ABSTRACT

Mixed Oxide with higher percentage of plutonium oxide is used as driver fuel for Fast Breeder Reactor. Spent fuel containing plutonium rich oxide discharged from reactor is generally dissolved in nitric and hydrogen fluoride acid mixture. Handling of resultant High Level radioactive Waste with corrosive fluoride is an important issue with respect to interim storage, volume reduction by evaporation and future geological repository. Relatively little information is available on dissolution of plutonium oxide under reducing condition. Present work involves generation of uranous by electrolysis of uranyl nitrate solution in nitric acid of concentration range 1.0 – 12 moles/litre with 0.5mole/litre hydrazine nitrate as stabilizing agent. Current efficiency as well as percentage conversion of uranyl to uranous was determined as function of nitric acid concentration. Stability of uranous in nitric acid of higher concentration was monitored with respect to time. Dissolution of plutonium oxide was carried out in presence of electrolytically generated uranous nitrate and without uranous nitrate in nitric acid medium. Dissolution rate of plutonium is found to be higher in a system with uranous nitrate than in system without uranous in nitric acid medium during dissolution of pure refractory plutonium oxide powder.

Key words: Dissolution of plutonium oxide, Stability of uranous, Electro reductive dissolution, Mixed oxide Fuel.

[I] INTRODUCTION

Spent fuel of different burn up from 25-155 GWd/Te with different cooling period discharged from Fast Breeder Test Reactor (FBTR) is being reprocessed in Compact Reprocessing of Advanced fuel in Lead mini cell (CORAL), Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam. Modified Purex process using 30% Tributyl phosphate diluted in heavy normal paraffin [1-3] is followed for separation of unused fertile and fissile material from fission

products. Though carbide, nitride and metallic fuel are called as advanced nuclear fuel for fast reactor, but fuel containing either UO₂ or mixture of UO₂ and PuO₂ is being used as nuclear fuel in commercial thermal as well as fast reactor. The reason may be due to strong lattice, high stability, ceramic nature, compatibility of oxide with clad and also availability of operational experiences of oxide form of nuclear fuel. In addition to above mentioned properties, oxide fuel maintains

constant O/M ratio at wide range of oxygen partial pressure under reactor operational condition. Hence thermal conductivity of fuel is not changed considerably with respect to increasing burn up during residence period in the reactor. As carbide fuel is prone to hydrolysis and oxidation and its fabrication is more difficult than fabrication of oxide fuel. In case of carbide, nitride and metallic fuel, swelling rate is more with increasing burn up and it induces fuel clad chemical and mechanical interaction when compare to oxide fuel. But the problem encountered in manufacture of nuclear fuel in the form of mixed oxide containing 25-30% PuO₂ especially for fast reactor and reprocessing of respective spent fuel discharged from reactor is extreme difficulty associated with dissolution in nitric acid medium. But dissolution of pure uranium oxide in nitric acid medium takes place more readily than mixed oxide containing higher percentage of plutonium oxide. Reason may be attributed that Gibbs free energy change involved in dissolution of plutonium oxide in nitric acid medium is found to be slightly positive and it is negative in case of uranium oxide. Hence concentrated nitric acid in range of 10-12M with 0.1M hydrogen fluoride is used for dissolution of plutonium oxide or mixed oxide fuel containing higher percentage of plutonium [4]. But presence of corrosive nature of fluoride ion in High Level radioactive Waste (HLW) becomes key issue during interim storage and complicating the ultimate disposal of PUREX process wastes.

Hence electrochemical dissolution of PuO₂ in nitric acid under oxidizing condition was reported [5-7] to avoid fluoride ion in the dissolution step. In the electrochemical dissolution, soluble PuO₂²⁺ ion is formed by means of electron transfer reactions taking place between solid PuO₂ and strong oxidizing agents such as Ag²⁺ and Ce⁴⁺ in solution generated by continuous electrolytic process. As this method involves addition of external metal ion such as cerium or silver to enhance the dissolution kinetics, volume

reduction of HLW by means of evaporation technique is limited due to regeneration of respective metal salts in solid form. Further silver present as nitrate in HLW will lead to formation of molten silver in melting process. Molten silver if formed would be difficult to reintroduce into the glass matrix and could pose operating difficulties for the glass melter [8]. In case of Electro Oxidative Dissolution Technique (EODT), all most all plutonium in dissolver solution is converted into hexavalent state [9], and it requires additional electrolytic set up to convert hexavalent plutonium into extractable tetravalent plutonium by means of electrolytic reduction. Hence preliminary studies were taken up in laboratory to find the feasibility of dissolving plutonium oxide in nitric acid medium under reducing condition using uranous as reducing agent.

In order to dissolve PuO₂ in reducing condition, several reducing agents were already reported [10-12] and dissolution was carried out in hydrochloric acid and sulphuric acid medium under reducing condition. It was reported in available literature that standard redox potential of PuO₂/Pu (III) was 0.67V against SHE [13-15]. Hence dissolution of PuO₂ in reducing medium required the use of potential lower than 0.67V vs SHE and resultant reducing agent must be stable in nitric acid of higher concentration. Therefore UO₂²⁺/U⁴⁺ redox couple was found to be suitable reagent to form soluble Pu (III) from PuO₂ solid surface. As uranium is present always in the fuel, external addition of uranium is not required. Nitric acid concentration plays vital role in the kinetics of dissolution of PuO₂ and dissolution rate is always enhanced with nitric acid concentration. Hence systematic studies were carried out to generate uranous in nitric acid of different concentration. And stability of uranous in nitric acid of higher concentration was monitored with respect to time. Then effect of uranous in nitric acid medium on dissolution of

plutonium oxide was determined and results are presented in this paper.

[II] EXPERIMENTAL

2.1 Apparatus

Electrolytic cell consists of a beaker with teflon lid having provision for inserting electrodes, thermometer and condenser. This condenser is connected to ejector type scrubber system to remove off gas. It consists of caustic scrubber, safety trap, filter, ejector and pressure regulating valve for maintaining uniform suction rate. This set up was installed in a Glove Box and it meets required safety criteria to handle plutonium in the form of solid as well as liquid. Platinum wire and titanium mesh with 25cm² area were used as anode and cathode respectively for electrolysis. DC power supply unit at constant current mode with voltage range from 0-10 volt supplied by EM Electronic Pvt Ltd was used for electrolysis. Fiber Optic spectrophotometer with a wave length of range 300-1100nm supplied by Ocean Optics make USB 4000 model was used for determination of oxidation state of uranium during electrolysis.

2.2 Chemicals and Reagents

Uranium oxide powder of nuclear grade supplied by Nuclear Fuel Complex (NFC), Hyderabad was used to prepare uranium stock solution. All reagents were analytical grade and prepared in double distilled water obtained in glass distillation assembly. Chemicals of AR grade were used to prepare standards, reagents for quantitative determination and dissolution studies. Nitric acid (AR,Merck), potassium dichromate (AR, Merck) sodium hydroxide(AR,SD Fine Chem Ltd) potassium hydrogen phthalate (AR,Merck), potassium oxalate (AR, Merck) were used. Plutonium oxide powder used in this study was nuclear grade and it was obtained by calcination of plutonium (IV) oxalate cake at 500°C after reprocessing of spent fuel discharged from FBTR. This spent fuel discharged from FBTR was irradiated with burn

up of 155 Gwd/Te and taken for reprocessing after two years ex-vessel cooling period.

2.3 Experiment

Concentrated uranyl nitrate stock solution was prepared by dissolving known weight of U₃O₈ in 10M nitric acid in a glass beaker at 50-60°C by heating on a hot plate. This stock solution was used throughout the experiment after giving required dilution. Depending on the concentration of uranium, either Davis and Gray method or spectrophotometric method using Pyridyl Azo Resocinol as chromogenic agent [16, 17] were used for analysis of stock solution and samples generated during experiment. Feed solution of 0.1M uranium in 1-12M nitric acid was prepared by addition of known volume of uranium stock solution and nitric acid. Exactly 50 ml of each feed solution with different acid concentration was taken in a glass beaker and electrolyzed using Ti mesh as cathode and Pt wire as anode after addition of 5mL of hydrazine at constant current mode for three hours. Concentration of uranium in feed solution before and after electrolysis was carried out by redox titrimetry procedure. Similarly feed solution with 0.1M uranyl nitrate solution in 8M nitric acid containing 1M hydrazine nitrate was electrolyzed for 5 hours continuously. Samples were drawn at regular intervals of time after commencing the electrolysis. Free acidity and hydrazine in the electrolyzed samples were determined simultaneously using potassium oxalate as complexing agent as per procedure [18, 19]. Concentration of uranous in this sample was analysed by redox titrimetry procedure. Change in concentration of uranous after 5 hrs electrolysis in 10M nitric acid was followed by taking UV-Visible spectra with respect to time after giving suitable dilution.

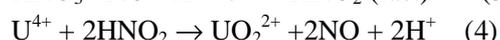
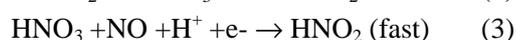
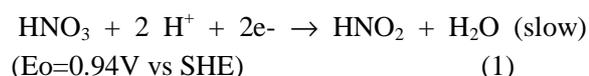
Exactly 1.053g of plutonium oxide was weighed and transferred quantitatively into Teflon beaker with 125ml of 8M HNO₃ containing 0.042M uranyl nitrate and 1.0M hydrazine nitrate. Electrolysis of this solution was carried out in

constant current mode by passing 2 Amp current using titanium mesh cathode and platinum wire anode. The voltage required to sustain 2 Amp current in the cell was applied which ranges from 4-5V. Solution temperature was maintained at 70-75°C for 16 hours during electrolysis. Ejector system and cooling water to condenser were operated for scrubbing the off gas and condensation of liquid vapor generated respectively in dissolution of plutonium oxide. Destruction of hydrazine during electrolysis was compensated by addition of 5 mL of hydrazine nitrate at end of 4hours. Samples were drawn at 4 hours intervals of time and analyzed for plutonium. Before sampling, electrolysis of solution was stopped, cooled and made up to 125mL by addition of 8M nitric acid. Radiometric counting method was followed for the determination of Pu content in the samples. In another experiment, nearly same quantity of PuO₂ (0.981g) was dissolved in 8M nitric acid at 70-75°C with constant stirring for 16 hours. Pu was determined in the samples taken at different intervals of time. Concentration of Pu in different samples was further analyzed by direct spectrophotometric method after addition of sodium nitrite to convert all Pu into Pu (IV). . Apparatus used for carrying out reductive dissolution is shown in Fig. 1a and corresponding schematic is represented in Fig 1b.

[III] RESULT AND DISCUSSION

The current efficiencies for production of uranous as a function of the nitric acid was studied in detail and the results are given in figure.2a Data in figure 2a indicate uranous formation from uranyl nitrate solution decrease with increasing nitric acid concentration and the conversion drastically falls down above 7 M. Uranous formation was negligible when acidity of feed solution was increased to 12M. It may be due to strong oxidizing nature of concentrated nitric acid. This decrease in the uranous production with increasing acidity of feed solution is

attributed to the increased parasitic reaction of the NO_x gases, hence leading to the formation of uranyl ion from uranous as per chemical reaction (4). Data in Fig 2a also inferred variation of current efficiencies with acidity of feed solution. This decreased current efficiency is also attributed to use of current for the parasitic reaction such as formation of nitrous acid and can be expressed as the following reactions according to previous study [20].



The autocatalytic decomposition of nitric acid can be suppressed by the addition of hydrazine as holding reductant to prevent the accumulation of HNO₂ as per equation (5).



Absorption Spectra of Uranous in 10 M nitric acid taken as a function of the time after completion of electrolysis is given in Fig 2b. The absorbance at 660nm in Fig 2b was used to calculate change in uranous concentration in the sample and it indicates that concentration of uranous decreases with respect to time. This decrease is due to slow oxidation of uranous in nitric acid. Though concentration of uranous is decreased with respect to time in absence of electrolysis in 10 M nitric acid, it was found stable, generated in nitric acid by electrolysis and it can be used as reductant to produce more soluble form of Pu (III) from surface of the plutonium oxide.

Dissolution rate of PuO₂ increased with fourth power of nitric acid between 7-14M. Hence nitric acid of higher concentration was chosen as medium for electrolysis of uranyl nitrate solution to generate U (IV). Data given in the Fig 3a

indicate that initially rate of formation of uranous in 8M nitric acid is more with time of electrolysis up to 3 hours. After three hours, uranous concentration in the solution was remaining constant irrespective of further electrolysis. During electrolysis concentration of hydrazine decreases exponentially with respect to time of electrolysis and it is given in Fig 3b. This decrease in concentration of hydrazine is due to scavenging action of HNO_2 produced during electrolysis as well as decomposition at electrode surface (anode). This decrease in hydrazine may accelerate oxidation of uranous and hence uranous generation remains constant after 3hours. But overall formation of uranous was not decreased below 50% in nitric acid of higher concentration. Data given in the Fig 3b also indicate that hydrazine addition is required after 5 hours in order to maintain the uranous concentration.

Results of preliminary studies on the dissolution of the plutonium oxide powder in presence of uranous and absence of uranous in 8M nitric acid under similar temperature are given in Fig 4a. Concentration of Pu in samples taken at 16 hours in reducing condition was found to be 0.015moles/L corresponding to 48% of initial weight PuO_2 and it is found to be 10 times higher than dissolution of PuO_2 carried out in nitric acid alone. In dissolution carried out in nitric acid medium at 70-75°C, plutonium concentration is found to be 1.67×10^{-3} moles/L in samples taken at 16 hours. As molar absorption coefficient of Pu (III) is lesser than Pu (IV), direct UV-Visible spectrum of Pu samples was taken at different intervals time after converting all Pu (III) into Pu (IV) by sodium nitrite addition and it is shown in Fig 4b. Spectrum in Fig 4b indicates that concentration of Pu increases with increasing dissolution time in presence uranous ion. Results of present study indicate that it is feasible to dissolve plutonium oxide under reducing condition using electrolytically generated uranous as reducing agent in nitric acid medium. But

parameters need to be optimized for the quantitative dissolution of plutonium oxide powder.

[IV] CONCLUSION

In reprocessing industries for recovery of unused U/Pu from spent fuel discharged from nuclear reactor, nitric acid medium is used for dissolution as well as solvent extraction steps. Hence generation and stability of suitable reductant in nitric acid is essential for carrying out reductive dissolution plutonium oxide. Present studies indicate that tetravalent uranium is found to be suitable agent and it can be used as promoter for dissolution of plutonium oxide in nitric acid medium. Continuous electrolysis can be adopted to generate tetravalent uranium from U (VI) in nitric acid with hydrazine as holding reductant. As concentration of hydrazine is decreased with time of electrolysis, hydrazine addition is required in order to maintain the concentration of uranous during dissolution of plutonium oxide. Under reducing condition, dissolution rate of PuO_2 was increased and it was found much lesser in dissolution carried out with nitric acid in absence of reductant of Pu (IV). Though presence of uranous in dissolvent may enhance the promotion effect for PuO_2 dissolution, the rate of dissolution is still lower than conventional dissolution method using nitric acid and hydrogen fluoride as dissolvent. But this method avoids use of corrosive fluoride as catalyst for dissolution of PuO_2 and introduction of foreign metal ion such as cerium, silver and cobalt being used as oxidant in electro oxidative dissolution technique.

ACKNOWLEDGEMENT

Authors are highly indebted and extended their sincere thanks to Dr. R. Natarajan, Distinguished scientist & Director, Reprocessing Group, Shri A. Ravishankar, Associate Director and Dr R.V.Subba Rao, Laboratory Superintendent, Reprocessing Group for their valuable suggestion

and encouragement during course this work. The valuable contribution during experiment from Miss D. Jayanthi, Miss. Poongodi, Shri Raj Kumar, Shri.Aravind Kumar Meena, and Shri K.Prasad Rao Kari of Chemical Laboratory, RPOD/RpG are greatly acknowledged.

REFERENCE

1. R. Natarajan, IANCAS Bulletin, 14 (2), (1998)27
2. Natarajan R, Baldev R (2007), "Fast reactor fuel reprocessing technology in India", *Journal of Nuclear Science and Technology* 44 (3):393-397
3. Lanham W B., Runion T C., (1949),"Purex process for Plutonium and Uranium Recovery" USAEC, ORNL, 479
4. G.SCOTT BARNEY, "The kinetics of PuO₂ dissolution on Nitric-HF Acid Mixture", *J.Inorg.Nucl.Chem.*,Vol 39, issue 9(1977)1665-1669.
5. Yury Zundeleovich, " The mediated electrochemical dissolution of plutonium oxide: kinetics and mechanism", *Journal of Alloys and Compounds*, 182:115-130 (1992)
6. Jack L. Ryan, West Richland; Lane A.Bray, Richland; Allyn L.Boldt, Kennewick, all of Wash, "Dissolution of PuO₂ or NpO₂ using electrolytically regenerated reagents", United States Patent, Patent Number: 4686019, dt. Aug.11,1987
7. D.E. Horner, D.J. Crouse, J.C. Mailen, "Cerium-Promoted Dissolution of PuO₂ and PuO₂ – UO₂ in Nitric Acid", ORNL/TM-4716
8. E. C. Smith, B. W. Bowan II, I. Pegg, L. J. Jardine, Joule-Heated Ceramic-Lined Melter to Vitriify Liquid Radioactive Wastes Containing Am241 Generated From MOX Fuel Fabrication in Russia, UCRL-CONF-206437
9. A. Palamalai, S. K. Rajan, A. Chinnusamy,M.Sampath,P.K. Varghese, T.N.Ravi, "Development of an Electro-Oxidative dissolution Technique for Fast Reactor Carbide fuels", *Radiochimica Acta*, 55(1991)29-35.
10. Dhanpat Rai, Yuri A, Gorby, Jim K Fredrickson, Dean A. Moore and Mikazu Yul, "Reductive dissolution of PuO₂ (am): The effect of Fe(II) and Hydroquinon", *Journal of solution chemistry*, Vol 31, No 6, P 433 (2002)
11. S.I. Sinkov, G.J. Lumetta, "Sonochemical Digestion of High Fired plutonium Dioxide samples", PNNL-16035 (2006)
12. K.Dhamodharan, Anitha Pius, Pradeep Kumar Sharma, S.Pugazhendi, M. Venkataraman and R.V. Subbarao, "Fesibility study for use of uranous as reductant fro reductive dissolution of PuO₂ in nitric acid", *International Conference on Vistas in Chemistry* (2011) 46-47.
13. Dhamodharan K Anitha Pius, Pugazhendi S, Pradeep Kumar Sharma and Subba Rao R.V "Effect of Uranous in Dissolution of PuO₂ in nitric acid medium", *National Conference on Interface Between Chemical Sciences and Technologies* (2011) 33
14. Akihiko Inoue, "The mechanism of Mediated Electrochemical Dissolution of Semiconducting Metal Oxide Particle", NSTI, Nano Technology, ISBN 978-1-4398-3415-2 Vol.3 (2010)
15. W.Davies, W.Gray, (1964) "A rapid and specific titrimetric method for the precise determination of uranium using iron(II) sulphate as reductant", *Talanta*, 11 PP 1203-1211
16. R.V.Subba Rao, K.Damodaran, G.Santosh Kumar, T.N.Ravi, (2000) "Determination of uranium and plutonium in high active solutions by extractive spectrophotometry", *Journal of Radio analytical and Nuclear chemistry*, Vol.246, No.2. 433-435
17. Booman, G.L., Eillo, M.G., Kimball, R.B., Cartan, F.O., Rein, *J.E: Anal.Chem.* 30,284 (1958)
18. ORNL Master Analytical Manual , TID-7015 (1960)
19. G. Linzbach, G. Kreysa, "Micro kinetic investigation of the electrochemical reduction of uranyl ions in acid solutions", *Electrochim. Acta*, 33 (1988)1343
20. A.D. KELMERS, D.N. BROWNING," Hydrazoic acid distribution between TBP-dodecane and nitric acid solutions", *Inorg. Nucl. Chem. Lett.*, 13(1977) 505

ELECTRO REDUCTIVE DISSOLUTION OF PLUTONIUM OXIDE- A PRELIMINARY STUDY



Fig. 1a. Apparatus used for dissolution of PuO₂.

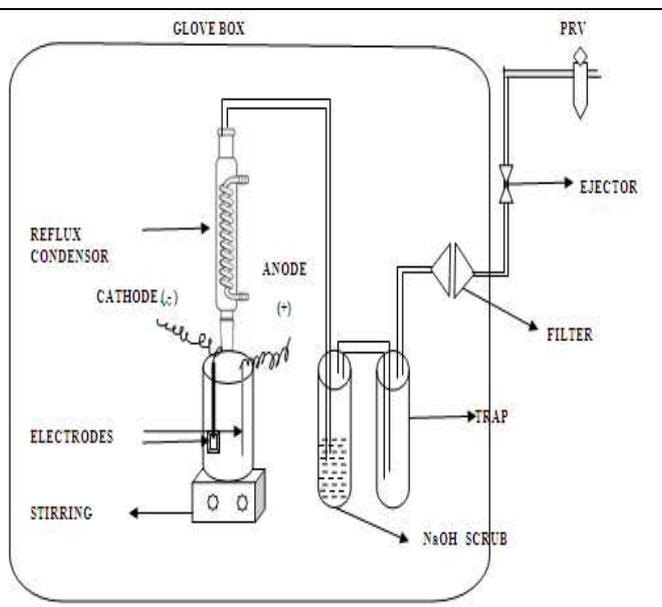


Fig. 1b. Schematic of dissolution apparatus.

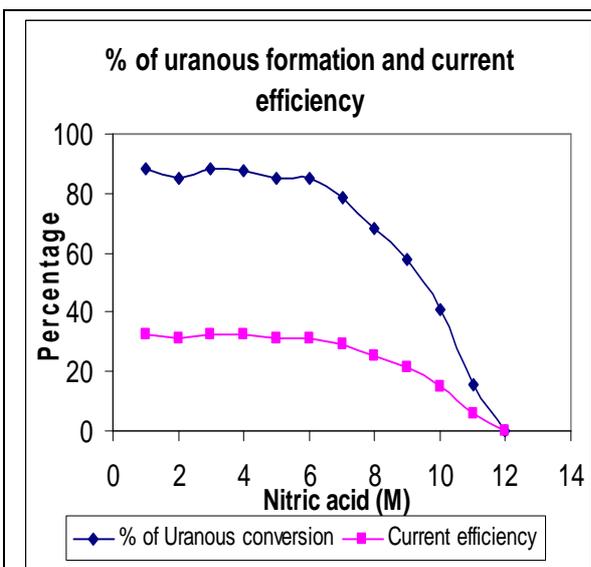


Fig.2a. Variation in % of Uranous production and current efficiencies as a function of nitric acid concentration.

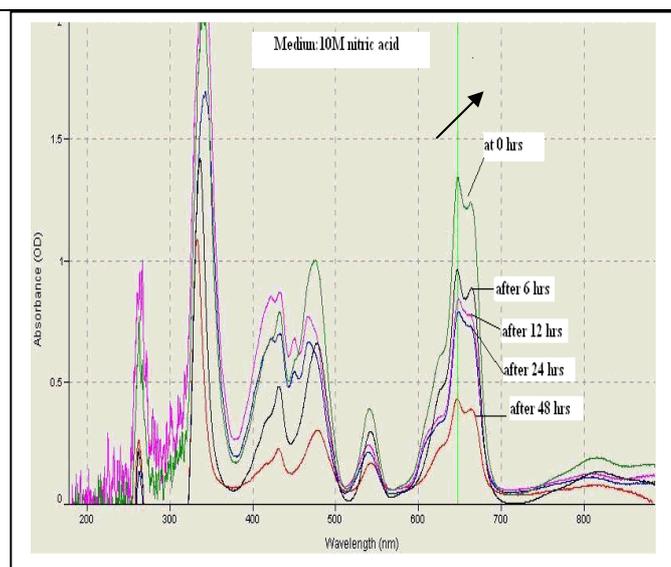


Fig.2b. Absorbance variation at $\lambda_{max} = 660\text{nm}$ as a function of time.

ELECTRO REDUCTIVE DISSOLUTION OF PLUTONIUM OXIDE- A PRELIMINARY STUDY

