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Sequential Destruction of Dissolved TBP and Nitric Acid in Raffinate Streams of Nuclear Fuel Reprocessing by Electrolytic Technique

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Abstract: The acidity of the first cycle raffinate produced from CORAL (COmpact Reprocessing of Advanced fuels in Lead cells) is to be reduced from 4M to < 0.5M in order to reduce its volume by evaporation is achieved by electrolytic destruction of nitric acid using simulated raffinate solution. This method is developed for safe disposal of raffinate waste produced and its waste management, it is achieved using electrolytic cell containing platinum anode and titanium cathode, which in turn destroys the simulated solution of 3.85 N nitric acid containing 250 ppm of dissolved TBP is destructed to 0.7 M and 49 ppm respectively and the ~90 % of fission products and corrosion products are removed byelectro-depositionin the cathode at different temperatures with current efficiency of 67 to 80%.

Keywords: Destruction, Dissolved TBP, Nitric acid, nuclear fuel reprocessing, electrolytic method.

1 Introduction

Fast reactor fuel reprocessing plays a vital role in nuclear energy programme. The CORAL for reprocessing of spent fuel from FBTR (Fast Breeder Test Reactor) uses mixed carbide fuel which contains high content of plutonium with high specific activity and short cooled. The separation of uranium and plutonium from irradiated fuel is carried out by modified PUREX [1] process which generates first cycle high active raffinate waste contains fission product and corrosion products in 4M nitric acid. The raffinate waste is stored in stainless steel tanks until it is immobilized in glass matrixand the upper limit of concentration of nitric acid should be less than 6M, since more than 6M will increase severe corrosion problem. To reduce the amount of waste volume and to minimize the corrosion in the tanks during subsequent storage of high active waste solution, it is desirable to reduce the concentration of nitric acid and volume of the raffinate solution by 50% that to only by evaporation. If the acidity is brought down to < 0.5 M then the volume of the raffinate waste could be brought down efficiently by direct evaporation. Destruction of nitric acid by neutralization with sodium hydroxide is highly expensive and the salt content of the waste produced is large. If the direct evaporation is followed without reducing the concentration of nitric acid, the organics of dissolved TBP will undergo runaway reaction with nitric acid and form mixture of organic compounds called red oil at 130°C [2-4]. Thereforeproper control and safe evaporation is requiredto prevent the explosion and fire hazard when raffinate solution containing fission products and dissolved TBP in nitric acid is heated. Drobnic [5] explained glass making difficulties in the nitrates and decomposition of higher oxides of nitrogen (N_2O_3, NO_2, N_2O_4) and volatile radionuclide compounds such as RuO_4.
These off gases are removed by dissolving with water which also forms secondary nitric acid with some concentration. The lot of developmental works focused on thevarious methods to evaporate raffinate wasteare described in the literature by many investigators for the destruction of nitric acid in high active waste, using different reagents of chemicals such as formic acid [6,7], formaldehyde [8-10], sugar, diethyl oxalate, phosphorus, glycerin and organic complexing agents (citric acid, tartaric

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acid, EDTA and oxalic acid) followed by evaporation [11] and combined electrolytic/chemical methods [12-14]. However, most of the proposed methods require additional safety due to chemical and temperature dependent. Chemical destruction of nitric acid is accomplished with formaldehyde which increases the risk of safety concerns due to HCHO-HNO_3 explosion reaction. The reagent formaldehyde and nitric acid cannot be mixed before there action since otherwise the reaction will be too violent when it is heated and the reaction between formaldehyde and nitric acid is exothermic and the excess heat is evolved followed bylarge amount of gas is produced which cause pressure development in the reaction vessel. So care must be taken to make steady flow rate of formaldehyde by adding drop by drop and the temperature should be strictly maintained at 90ºC and subsequent removal of excess formaldehyde leads to secondary waste. This method increases in volumenot only require more time for evaporation, it also generates secondary waste solution for which concentrating and disposing is time consuming and more expensive despite safety problems. Process of treating nitric acid by direct electrolytic destruction of nitric acid by cathodic reduction and the reaction sequence, kinetics and mechanism for the reduction at cathode has been reported [15-27]. As an alternative to direct incineration of HLW using formaldehyde to destruct nitric acid, this electrolytic method of destruction has an advantage over the reaction with formaldehyde thatthe destruction process of electrolytic method operates at low temperatures there by reducing the possibility of explosion where formaldehyde is used in classical method and reduces volatilization of gaseous fission products. Present work describes the sequential destruction of nitric acid and ~200 ppm of dissolved TBP and the electro-deposition of most of the fission products and corrosion products in simulated raffinate waste by electrolytic method from room temperature to 60^0 C and the results are summarized in this paper.

2 Experimental

2.1 Reagents

All reagents are analytical grade. Millipore water is used for all reagents preparation and titrations. Nitric acid (Ranbaxy Chemicals, AR grade), sodium fluoride (GR 99.6%, Merck, Mumbai), and other chemicals (99%, S D Fine chemicals, Mumbai) are used.

2.2 Stock Solution

The simulated High Level Liquid Waste (HLLW) represents first cycle raffinate from the PUREX process of Fast Reactor Carbide fuel (based on FBTR Mark-I of burn up 155 GWd /t and one year cooled) dissolved in 4 M nitric acid. From the stock solution, 200 mL of solution is used as feed solution for electrolysis. 250 ppm of TBP is added to the above simulated solution and kept stirring for one hour to mix the TBP uniformly. The composition of the simulated raffinate stream is represented in Table .1

2.3 Instrumentation

A constant temperature water bath MIC-66A (±0.10ºC)

(Modern Scientific Instrument Company, Mumbai) used for the temperature controlled studies.

Table 1: Simulated fission product solution in 4M nitric. Acid.

Fission products	g/L	Fission products	g/L
$Ca(NO_3)_2$	2.608	$Ba(NO_3)_2$	0.922
$Fe(NO_3)_3{\cdot}9H_2O$	0.61	$Zr(NO_3)_2x{\cdot}H_2O$	2.479
$(NH_4)Mo_7O_{24}{\cdot}7H_2O$	2.052	$Pd(NO_3)_3$	2.317
$Sm(NO_3)_3{\cdot}6H_2O$	0.111	$Ce(NO_3)_3{\cdot}6H_2O$	2.383
Sb_2O_3	0.021	$La(NO_3)_3{\cdot}6H_2O$	1.300
Am, Cm, Np $(Nd(NO_3)_3$	0.265	$AgNO_3$	0.153
$Ru(NO_3)_3{\cdot}xH_2O$	3.085	$Al(NO_3)_3{\cdot}9H_2O$	0.862
$Nd(NO_3)_3{\cdot}6H_2O$	3.603	$Rh(NO_3)_3{\cdot}2H_2O$	1.104
$Gd(NO_3){\cdot}6H_2O$	0.092	$Sr(NO_3)_2$	0.352
$Cs(NO_3)$	2.061	$Cd(NO_3)_2$	0.097
$Pr(NO_3)_3$	0.951	$Y(NO_3)_3{\cdot}6H_2O$	0.363

Micro balance supplied by Sartorius Model CP 225D, analytical single pan, maximum capacity 160 g and 10 microgram sensitivity, readability and precision for all weighing operations. DC power supply unit Model IEPS 3010 by ITEK Engineers is used for electrolytic destruction experiments. To measure the absorbance of the solution using fiber optic aided spectrophotometer technique with 1 cm path length dip type probe made indigenously. All titration were performed on titration system model E526manufactured by Metrohm, Switzerland. pH adjustments were carried out using Chemlabs, digital pH-meter model Micro-07, Bangalore.

2.4 Experimental Procedures

The feed solution of 200 mL is added into the electrolytic cell to run the experiments. For experimental runs with 250 mL capacity of this cell, the electrolysis started by passing the constant current mode of one Ampere using DC power supply of voltage about 2-3 V is applied which is required to maintain a current density of about 80 mA/cm^2. During electrolysis, the platinum anode and titanium cathode are separated by ceramic diaphragm and the samples are collected from the electrolyzer for every one hour of electrolysis and analyzed for free acidity and TBP. The free acidity of all the samples are carried out by complexing the metal ions in the aliquot with sodium fluoride and titrating with standard sodium hydroxide using Bromothymol Blue indicator [24]. The analysis of TBP is determined by spectrophotometric technique using phosphomolydate as chromogenic agent and maximum numbers of fission products are analyzed by ICP-OES & AAS technique.

2.5 Experimental Conditions

Experiments on electrolytic destruction of nitric acid are conducted under the following conditions:

Volume of electrolytic solution : 200 mL of ~3.8 M HNO_3
Dissolved TBP : 250 ppm
Anode material: Platinum Gauze: Size : 5 x 1 cm
CathodeMaterial: Titanium Foil: Size : 5 x 2.5 cm
Constant current mode : 1Ampere / hr
Voltage Range : 2.7-3.8 Volts
Current Density : 80 mA /cm^2
Initial concentration of nitric acid : ~ 3.8 M
Final concentration of nitric acid : ~0.7 (Limiting critical concentration)

2.6 Electrode Reactions

Overall electrode reactions are represented as follows
Anode reactions : $H_2O \rightarrow 2H^+ + 2e^- + [O]$
Cathode Reactions: $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$ (0.94 Volts)
$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$ (0.90 Volts)
Chemical Reactions: $HNO_2 + HNO_3 \rightarrow N_2O_4 + H_2O$
$N_2O_4 \rightarrow 2NO_2$
The experimental and electrolytic set-up is shown in Fig.1. (Inside the Fig.1.is close-up view of electrolytic solutions of feed and completion of electrolysis)

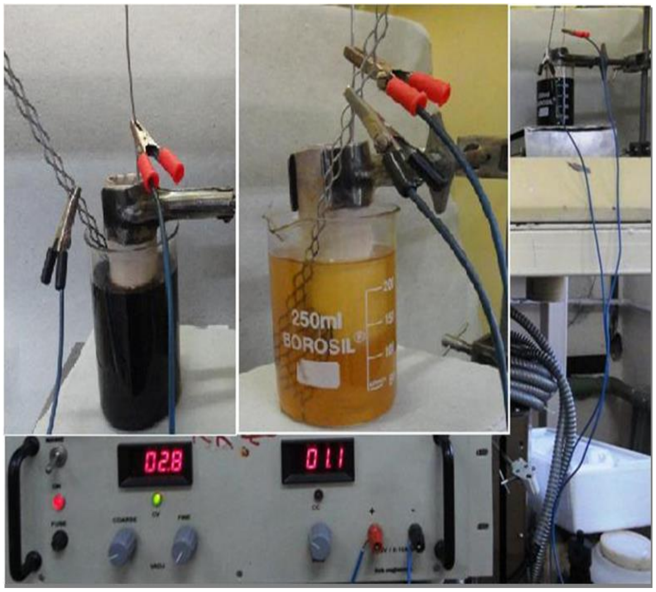

Fig.1: Experimental setup.

3 Results and Discussion

The acidity has been reduced from 3.8M to 0.7 M. After 31-38 hours of electrolysis the clear solution of pure orange yellow color indicates that the electrolyzed solution can be evaporated directly without any salt formation of fission and corrosion products since these concentrations are very low. The final nitric acid limiting concentration exists in 0.7M below which the reduction of nitric acid does not take place due to the NO^+ ion is present only in concentrated nitric acid to help destruction and it is expected that the formation of this above said ion is very low in dilute nitric acid from which only hydrogen is produced at cathode [17].

3.1 Color Variation with Decreasing Acidity

The feed solution which is in dark red color turns orange yellow (as shown in Fig.2) after the completion of 31-38 hours of electrolysis resulting in the acidity of 0.7 M. During experimental runs, the color of the solution varied from dark red to dark yellow at 3M and it finally changed to orange yellow color. Subsequently when the solution attains the acidity < 1.5M, it becomes turbid and black deposit (solids of fission products and corrosion products) is observed in the solution as well as on the surface of the cathode. The solution is filtered and after the electrode is cleaned, electrolysis continued until acidity attains to saturation level of 0.7M. The color variation as a function of decreasing acidity in the experiments is represented in Fig.3. Fig. 4 shows the graphical presentation of nitric acid destruction with respect to current efficiency. Overall current efficiency and time of electrolytic destruction is 80.68% and 36 hours. The efficiency of present method of destruction can be improved by regular washings of electrodes to prevent deposition at the electrode surface.

Fig.2: The different color of Initial feed solution and final solution after the destruction.

3.2 Current Efficiency and Time of Electrolysis with Increasing Temperature

During the course of electrolysis, the temperature is varied from room temperature to 60^0C with increments of 10^0C. It was observed that there is no prominent change in the acidity inferring that the destruction of acid has not taken place but only evaporation occurs at increasing temperatures. In these experiments with different temperatures at 25^{0}C, 40ºC, 50ºC and 60ºC in 31-38 hours of electrolysis, the destruction in the limiting acid concentration at titanium cathode occurred with decreasing current efficiency from 81% to 66% down by 15% at increasing temperatures. To get maximum current efficiency, the voltage was maintained around 2-4 volts in all the experiments. It has been observed that the destruction time of electrolysis is longer with increasing temperatures. The reduction in current efficiency is attributed to the competing reaction of NO_3^- reduction and hydrogen evolution. The data are given in Table.2

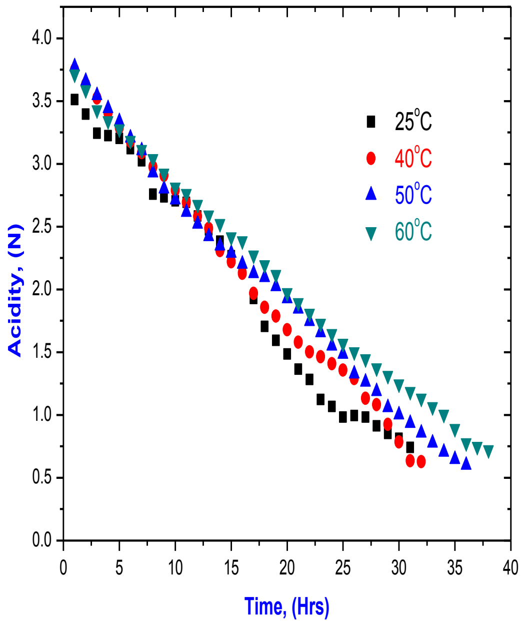

Fig.3: Concentration of nitric acid as a function of time at different temperatures.

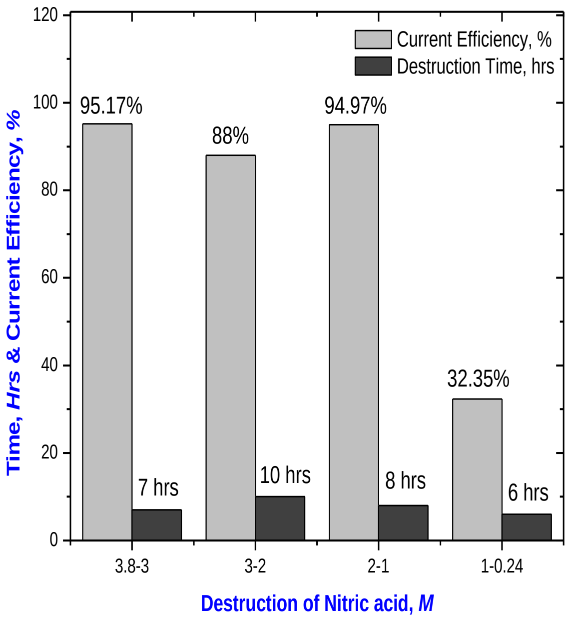

Fig. 4: Destruction of nitric acid with respect to current efficiency.

Table 2: Effect of temperature with respect to current efficiency.

Exp. No	Temp (ºC)	Duration of electrolysis (Hrs)	Acidity, (M)	Current efficiency (%)
1	27	31	3.852	81
2	40	32	3.842	81
3	50	36	3.838	69
4	60	38	3.820	66

3.3 Destruction of Dissolved TBP

It is observed from the experimental studies that the concentration of dissolved TBP is decreased from 250 ppm to 49 ppm in the catholyte which is confirmed after the analysis of TBP by spectrophotometry. Typical calibration graph for phosphate determination at 831 nm is represented in Fig.5. This is unique because the organics are always destroyed mainly in the anolyte. But in our experiments the organics are destroyed in the catholyte. This may be due to oxygen evolution occurs owing to the oxidation of water by electrolysis and destroys the concentration of dissolved TBP to 49 ppm and could be brought down to 5 ppm after reversing the polarity of electrodes. The destruction of dissolved TBP with respect to time and different current are shown in Fig.6.

3.4 Rate of Destruction with Decreasing Acidity

The rate of destruction is very low at < 1M due to hydrogen evolution at cathode and oxygen evolution at anode because of water electrolysis and it is almost no destruction has taken place at <0.7 M due to the formation of fission product deposits in cathode.

3.5 Electro-Deposition of Fission Products

During electrolysis, the black particles of fission products are observed and deposited on the surface of cathode when the acidity becomes < 2 M. Subsequently the electrode was removed and assembled back after thorough washing of cathode. This was necessitated due to voltage drop caused by the deposition of fission products as reported by previous authors [23-26] and continued the electrolysis .The sample is collected after the completion of electrolysis and the solution on the analysis of concentration of fission

Products and corrosion products carried out by ICP-OES and AAS techniques confirmed the deposition The results are shown in table.3.The results confirmed that 90 % of fission products are removed from the simulated raffinate solution.

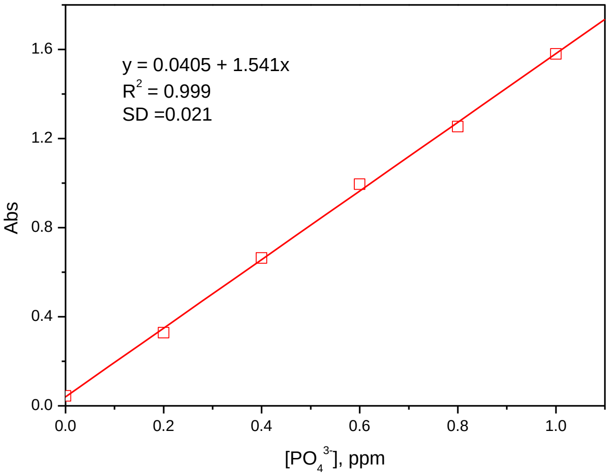

Fig.5: Calibration graph for PO_4^{3-} by spectrophotometry at 830 nm.

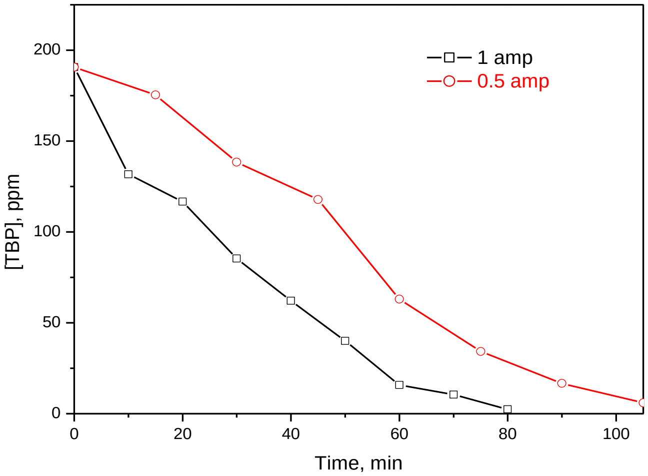

Fig.6: Destruction of dissolved TBP with respect to Time and current.

Table 3: Analysis of simulated fission product solution by ICP-OES and *AAS Technique.

Fission products	I	II	III	Fission Products	I	II	III
Nd	3868	90	98	Rh	1104	80	96
Ru	3085	360	88	Ba	922	260	72
Ca	2608	290	89	Al	862	60	93
Zr	2479	48	98	Fe	610	55	91
Ce	2383	350	85	Sr	352	82	77
Pd	2317	46	98	Ag	153	>4	97
Mo	2052	290	86	Cd	97	6	94
Cs*	2061	730	65	Gd	92	20	78
La	1300	240	82				

I . mg/L taken in the simulated solution,
II. mg/L remained in the final solution,
III. Percentage of fission products removed /deposited

4 Conclusions

The low temperature operating electrolytic system and the ability of the process to destruct nitric acid containing raffinate waste makes the process an attractive alternate destruction method to direct incineration by the addition of neutralizing agent formaldehyde for HLLW contains fission products thus reducing cost and apparatus requirements. This method is simple, economical, easy to handle, efficient and the salt content of the waste solution is considerably reduced. Using this method of cathodic deposition by the separation of some of the fission products and corrosion products give valuable solution to recover most of the fission products in the raffinate can easily converted to small amount of solid and the recovery of fission products from high level liquid raffinate waste stream can be converted to low level waste which proves efficient management of HLLW and the Gamma dose of this liquid waste could be brought down to workable limit since Glass Matrix demands reduction in waste volume loading through the recovery of fission products by this acid destruction method. The significant amount of noble metal fission products Ru, Rh and Pd gives problem in vitrification steps can be avoided. It is also applicable to homogeneous continuous destruction of all the range of nitric acid. Recovery of plutonium from high active waste streams using ion exchange after destruction of nitric acid is possible. This method not only reduces the overall toxicity of the waste but also the final volume to be disposed off. The electrochemical process are more expensive in terms of consumables the straight forward incineration when applied to waste. But if the waste to be destructed are more troublesome fission products with highly radioactive, the economics of electrolytic reduction process compared to direct incineration of raffinate waste becomes more favorable [28].

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