



# Kinetics of reduction of nitric acid by electrochemical method and validation of cell design for plant application



Satyabrata Mishra, Falix Lawrence, C. Mallika\*, N.K. Pandey, R. Srinivasan, U. Kamachi Mudali, R. Natarajan

Reprocessing Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India

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## ABSTRACT

Employing electrochemical method, the concentration of nitric acid had been reduced from 4 to about 0.5 M, under constant current/potential conditions in batch mode, for the purpose of optimizing the process parameters for the destruction of nitric acid in radioactive liquid waste, with good energy efficiency. Based on the rate constants determined from the batch process, a cell assembly in cylindrical configuration was designed for the electro-reduction of nitric acid in continuous mode, in radioactive environment. The steady state concentration of the acid at the outlet was compared with that concentration calculated using model equation and the agreement between the two sets of data was found to be reasonable. Cyclic voltammetric runs were recorded to understand the reduction behavior of nitric acid on platinum electrode. The results revealed the reduction of nitrate ion to be a quasi-reversible process and for the scan rate of  $0.1 \text{ V s}^{-1}$ , values of  $3.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $1.37 \times 10^{-3} \text{ cm s}^{-1}$  were computed for the diffusion coefficient and heterogeneous electron transfer rate constant, respectively.

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## 1. Introduction

The high level liquid radioactive waste generated during the aqueous reprocessing of the spent fuels of Fast Breeder Reactors (FBRs) comprises the fission and corrosion products in about 4 M nitric acid, which is one of the major concerns in waste management, as substantial amount of liquid waste is produced. The objective of waste treatment is volume reduction to yield a small package, having a high specific activity of fission products. To reduce the volume of high level liquid waste (HLLW) and to control the corrosion in 304 L stainless steel waste tanks during subsequent storage of concentrated waste solution, it is desirable to reduce the nitric acid concentration to a lower value. Among the denitration processes for the treatment of highly radioactive waste solutions, methods such as Nitrate to Ammonia and Ceramic (NAC) process, electrochemical destruction, biological denitration, calcination, hydrothermal and chemical reduction are significant and studies performed using these processes for the denitration of low/high level liquid wastes have been reported in literature

reviews [1–5]. Biological denitration reduces nitrate to nitrogen or its oxides using a broad range of bacteria in the presence of reducing organic nutrients like methanol, methane, glucose and starch [6]. However, bacteria are sensitive to heavy metal ions and to changes in the composition of the influent stream. Though several reductants like sugar, molasses, phosphorous, glycerin, formaldehyde, formic acid and ethyl alcohol are available for chemical denitration, reduction of nitric acid involving a homogeneous reaction with formaldehyde [7–13] or formic acid [14–17] and denitration reaction with HCHO/HCOOH induced by nitrite [18–20] or catalysts like active carbon [21] and noble metal supported catalysts [22–24] have been investigated extensively, owing to the efficiency, simplicity and economic viability of this process. The reaction of HCHO with nitric acid is exothermic and it leaves no residual chemicals, as the products are gaseous  $\text{NO}_2$ , NO and  $\text{CO}_2$ . However, the reaction is initiated after a certain induction period. During this period, the auto catalyst,  $\text{HNO}_2$  accumulates in the solution up to a threshold concentration (in the range 0.01–0.1 M), beyond which the reaction develops rapidly. Denitration following the induction period can be violent that leads to uncontrollable process conditions and is a significant safety concern. The induction period is reported to depend on the concentration of nitric acid, nitrite content and temperature and can be considerably minimized or suppressed by passing gaseous  $\text{NO}_2$  through the acid prior to the addition of HCHO [7]. At  $100^\circ\text{C}$  and at acid concentrations above 3 M, the reaction is more or less

\* Corresponding author. Tel.: +91 44 274 80126.

E-mail addresses: [sbmishra@igcar.gov.in](mailto:sbmishra@igcar.gov.in) (S. Mishra), [felix@igcar.gov.in](mailto:felix@igcar.gov.in) (F. Lawrence), [mallika@igcar.gov.in](mailto:mallika@igcar.gov.in) (C. Mallika), [nkpandey@igcar.gov.in](mailto:nkpandey@igcar.gov.in) (N.K. Pandey), [rsrini@igcar.gov.in](mailto:rsrini@igcar.gov.in) (R. Srinivasan), [kamachi@igcar.gov.in](mailto:kamachi@igcar.gov.in) (U. K. Mudali), [rnr@igcar.gov.in](mailto:rnr@igcar.gov.in) (R. Natarajan).

instantaneous. At marginally lower temperatures, the induction period can be shortened by adopting a heterogeneous catalysed denitration in the presence of catalysts like Pt/SiO<sub>2</sub>, Pd-Cu, heavy metal ions such as V, Cr, Fe and U and activated carbon; nevertheless, the amount of solids introduced into the waste increases.

Electrochemical denitration offers an easily controlled and safe mode for the destruction of nitrate ions without adding corrosive chemicals [25–30]. Electrolytic reduction has been successfully employed for the removal of nitrate from ground water [31,32]. Reduction of nitrate ions in an electrochemical cell can be carried out under acidic, neutral or basic conditions [33–40] using a variety of electrodes [41–48]. Nevertheless, the reduction of nitrate in acidic solutions takes place at more positive potentials and hence, a more favorable process [27]. In the electrolytic method, nitrate and nitrite ions are reduced to the nitrogen-containing gases NO<sub>x</sub>, N<sub>2</sub>O, N<sub>2</sub> and NH<sub>3</sub> [27,49]. Baumgartner and Schmieder [50] reported that there exists a nitric acid limiting concentration of 3.8 M, below which nitrate reduction takes place only by the addition of cations such as Cu, Fe, Mn and Na. However, Mallika et al. [51] demonstrated that the limiting concentration of nitric acid can be extended up to 0.5 M in batch mode experiments, without the presence of metal ions.

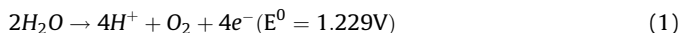
Development of electro-reduction process for implementation in the plant requires the understanding of the reaction mechanism, optimization of process parameters such as current density (*j*), type and size of electrodes, vessel configuration (with and without diaphragm) and geometry, design and fabrication of pilot plant scale cell setup and process performance test in the pilot plant equipment. In the present study, electrochemical reduction of 4 M nitric acid was carried out in a cylindrical cell configuration by batch mode, for the purpose of optimizing the process conditions for acid killing in the plant. Based on the data generated, an energy efficient cell design was made for operation in continuous mode in radioactive environment and the experimental and model predicted results had been compared. Also, the redox behavior of nitrate ion was investigated employing the potentiostatic electrolysis technique namely cyclic voltammetry (CV) and the kinetic parameters were determined.

## 2. Mechanism of reduction of nitric acid

Electrochemical reduction of nitric acid occurs according to the following reactions taking place at the electrodes [52,53].

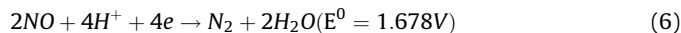
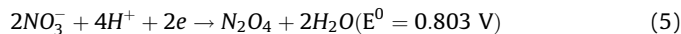
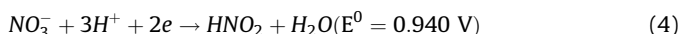
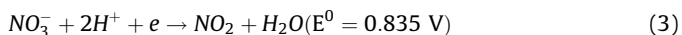
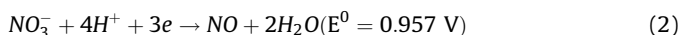
*At anode:*

Under the influence of an electrical potential, hydrogen ions are generated at the anode as per the reaction

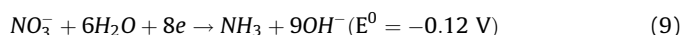
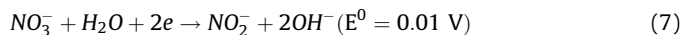


These hydrogen ions are transported with hydrated water to the cathodic compartment through the porous diaphragm, thereby increasing the concentration of anolyte acid. The migrated H<sup>+</sup> ions from the anodic compartment react with NO<sub>3</sub><sup>-</sup> ions at the cathode to produce H<sub>2</sub>O and NO<sub>x</sub>; hence, nitric acid concentration in the catholyte decreases. Other competing reactions also occur at the cathode.

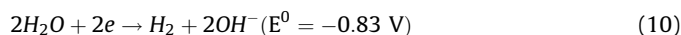
*At cathode:*



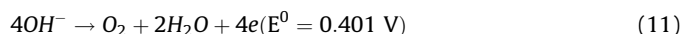
The following reactions have also been considered to proceed at cathode during electrolysis [54]:



Hydrogen evolution is the main parasitic cathodic reaction.



The main parasitic anodic reaction is oxygen evolution.



## 3. Experimental

### 3.1. Cyclic voltammetric studies

Nitric acid (AR grade; Hi-Pure Chemicals, Chennai) diluted with distilled water served as the electrolyte. Reduction of nitric acid was investigated by performing cyclic voltammetric experiments at 298 K in a standard three-electrode cell comprising Pt foil (Surface area, SA: 1.2 cm<sup>2</sup>) as counter electrode and standard Ag/AgCl in 3 M KCl (SSE) as the reference electrode. A platinum wire (SA: 0.146 cm<sup>2</sup>) served as the working electrode. The electrochemical system, Autolab Model PGSTAT 30 (Eco-Chemie, the Netherlands) equipped with Nova Software was used for applying the required potentials and for recording the voltammograms for the reduction of 4 M nitric acid at different scan rates.

### 3.2. Lab scale reduction experiments in batch mode

The cell assembly for the reduction of nitric acid in batch mode consisted of a cylindrical titanium (Grade II) vessel, which also served as the cathode. Titanium was chosen as the cathode material due to its excellent corrosion resistance as well as high hydrogen over potential. Pt-10% Ir gauze was used as the anode. The anode was inserted into a porous porcelain diaphragm tube, which in turn was placed inside the Ti cathode vessel. The purpose of the diaphragm tube was to separate the anode and cathode compartments, while allowing the ions of the two compartments to migrate through it. The geometric surface area of the cathode and anode were 307 and 45 cm<sup>2</sup> respectively. The schematic of the cell is given elsewhere [51]. Since the radiation tolerance of polymer separating membranes is not satisfactory, ceramic membranes are considered for use in radiation environment. Porous ceramic membranes in planar configuration were not commercially available; hence, cylindrical cell configuration was chosen in the present study. The catholyte and anolyte were 350 and 100 ml of 4 M nitric acid respectively. Electrical energy was supplied to the cell by means of a switch mode DC power supply. Experiments were conducted in constant current as well as constant voltage mode. The concentrations of acid in the anode and cathode compartments were determined during the course of

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