



Feasibility studies on the separation of ruthenium from high level liquid waste by constant potential electro-oxidation



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ABSTRACT

Ruthenium is one of the most abundant fission products in fast breeder reactors. It creates problems during the reprocessing of spent fuel and in the management and disposal of wastes, owing to the formation of highly volatile and radiotoxic $^{106}\text{RuO}_4$. Cyclic voltammograms of $[\text{Ru}(\text{NO})]^{3+}$ solution recorded at Pt electrode revealed that surge in anodic current occurs at about 1.25 V (vs Ag/AgCl) due to oxidation of Ru and water. Batch experiments were carried out for the separation of Ru as RuO_4 vapour from pure nitrosyl nitrate and simulated high level liquid waste (SHLLW) solutions by electro-oxidation method as a function of nitric acid concentration, temperature, applied potential and concentration of the redox mediator, Ce. The results indicated that separation percentage of Ru increased with increase in applied potential as well as temperature and decrease in acidity. In the presence of 0.04 M Ce at 1.65 V (vs Ag/AgCl), separation of 97% was obtained in 1 M HNO_3 after 10 h of electrolysis; however, only 58% could be separated from SHLLW solution under similar experimental conditions. Rate constants were calculated for the oxidation reaction of ruthenium and the energy of activation was determined to be 75.69 kJ/mol.

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1. Introduction

In the aqueous reprocessing of spent nuclear fuels by PUREX process, uranium and plutonium are separated by solvent extraction using 30% tri n-butyl phosphate (TBP) in n-dodecane. The high level liquid waste (HLLW) solution consists of radioactive fission products in nitric acid (Swanson, 1984). The HLLW is subjected to various waste management processes such as concentration, denitration and vitrification in order to reduce the volume of waste and to convert it into a solid vitrified body for safe disposal. Ruthenium is one of the most troublesome fission products because of its oxidation to highly volatile and chemically unstable radiotoxic $^{103}\text{RuO}_4$ and $^{106}\text{RuO}_4$ (McKibben, 1984). Ruthenium tetroxide decomposes to a non-volatile black deposit of ruthenium dioxide (RuO_2) on contact with the cooler parts of the surface of stainless steel equipment during the waste treatment and thus, the radiation dose of the plant increases. Deposition of ruthenium was observed to plug the off-gas piping of the equipment owing to appreciable

volatilization of RuO_4 during waste treatment. During vitrification of the waste, platinum group fission product metals (Ru, Rh and Pd) form precipitates as alloy and/or oxides in molten glass and Ru forms needle like electrically conducting RuO_2 crystals (Krause and Luckscheiter, 1991). Vitrification of HLLW was temporarily stopped in a nuclear reprocessing plant operated by Japan Nuclear Fuel Ltd (JNPL) due to problems arising from the sedimentation of platinum group metals in the glass melter, which had led to electric energy loss, local overheating, high viscous glass formation and unexpected low production rate of vitrified glass (Krause and Luckscheiter, 1991). Thus, separation of Ru species from the HLLW is desirable, prior to nuclear waste treatment for safe disposal.

Various methods reported in the literature for the removal of ruthenium from HLLW are volatilization, precipitation, solvent extraction, chromatography, sorption and electro-oxidation/reduction. A review of the various methods of separation of Ru available in literature with emphasis on applications in spent nuclear fuel reprocessing had been reported by the present authors (Swain et al., 2013a). Ruthenium could be separated by a simple and cost effective method using n-paraffin oil in the presence of ammonium ceric nitrate as oxidizing agent (Motojima, 1989; Swain et al., 2013b). The simple and inherently safe electrochemical

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method for the separation of Ru requires neither the addition of external reagents nor complicates the nuclear waste management operation. In the electrochemical method, Ru could be separated either by deposition as metal on the cathode (Ozawa et al., 2005; Jayakumar et al., 2005) or by electro-oxidation to RuO₄ at the anode (Motojima, 1990; Yoneya et al., 1995; Mousset et al., 2004). The separation yield of Ru by electro-deposition technique was observed to be very low and large portion of Ru remained in the solution, whereas, using electro-oxidation method removal of Ru was reported to be quantitative. Separation of Ru by electro-oxidation was carried out by Motojima (1990) and Mousset et al. (2004) by constant current mode using Pt anode. Motojima used cerium ions as the redox mediator in an undivided electrolytic cell and Mousset et al. had employed a porous ceramic diaphragm to separate the anode and cathode compartments and Ag was used as the redox catalyst. Yoneya et al. (1995) separated Ru quantitatively from HLLW by constant potential electrolysis and applying a potential of 1.85 V (against standard Ag/AgCl (SSE) reference electrode) to Pt working electrode in a divided electrolytic cell. A fundamental study on the constant potential electro-oxidation of Ru under various experimental conditions such as temperature and concentration of cerium was carried out by Sato et al. (2012) to improve the efficiency and rate of oxidation of Ru at lower potentials.

A parametric study on the separation of Ru by constant potential electro-oxidation of pure [Ru(NO)]³⁺ solution and simulated HLLW at different applied potentials, nitric acid concentration, temperature and redox mediator, Ce was conducted in the present work. The efficiency in the separation of Ru by electro-oxidation and kinetic parameters for the oxidation of Ru were also determined.

2. Experimental details

2.1. Chemicals

Standard solutions of ruthenium nitrosyl nitrate with the concentration of Ru as 160 ppm in 1, 2 and 4 M nitric acid were prepared by diluting commercially available ruthenium nitrosyl nitrate solution (1.7% Ru in 9 M nitric acid; supplied by M/s. Arora Matthey Ltd., Kolkata). Nitric acid supplied by M/s. Fischer Chemicals Ltd., Chennai (AR grade, 69–71%) was used in all the experiments. Cerium (III) nitrate hexa hydrate (AR grade, Min. assay: 99%) procured from M/s. SDFCL, Mumbai was used as the redox mediator during electrolysis.

A synthetic HLLW solution simulated with fission and corrosion product elements envisaged in the reprocessed waste of the spent mixed carbide fuel of fast breeder test reactor (FBTR) at Kalpakkam, was prepared in 4 M HNO₃. The chemical form of the elements and their concentration in the simulated waste solution are reported elsewhere (Satyabrata et al., 2010). The waste solution thus prepared was diluted suitably to adjust the concentration of ruthenium to be 160 ppm (the concentration of Ru in the actual waste) in 4 M HNO₃.

2.2. Cyclic voltammograms of ruthenium nitrosyl nitrate in nitric acid

Solutions of ruthenium nitrosyl nitrate (containing 20 mM of Ru) in different concentrations of nitric acid were prepared for performing cyclic voltammetric (CV) experiments in order to understand the electro-oxidation behaviour of [RuNO]³⁺ in acidic medium. Voltammograms were recorded for these solutions at 298 K in a standard three-electrode cell comprising a Pt (surface area: 0.42 cm²) or Au wire (surface area: 0.2 cm²) as working electrode, Pt plate as counter electrode and a standard Ag/AgCl

reference (SSE) electrode. Autolab Model PGSTAT-30 (Eco-Chemie, the Netherlands) electrochemical system equipped with General Purpose Electrochemical Software was used. Cyclic voltammograms were recorded at the potential scan rate of 50 mV/s, starting with the anodic scan followed by reversal of the scan at the anodic switching potential in the range 0–1.8 V (vs SSE). De-oxygenation of the test solution prior to the scans was done by flushing with argon and the results were analyzed after IR compensation.

2.3. Cell assembly for electro-volatilization

Ruthenium was separated by electro-oxidation using a platinum mesh (surface area: 34 cm²) working electrode (WE), platinum mesh (SA: 20 cm²) counter electrode (CE) and double junction Ag/AgCl reference electrode (RE) (supplied by M/s. Metrohm India Ltd., Chennai) in a divided cell with glass frit as diaphragm (Fig. 1). The electro-oxidation studies were performed by chronoamperometric method at various applied potentials, temperatures and in the presence of the redox mediator, Ce. Catholyte (10 ml) and cathode were kept inside the glass frit, which was fused to a glass tube suspended from the centre of the lid. Anolyte (50 ml), Pt mesh working electrode and Ag/AgCl reference electrode were placed outside the glass frit in the cell vessel. The RuO₄ vapour produced owing to the oxidation of ruthenium at anode was absorbed in gas wash bottles containing 0.5 M NaOH solution. During electrolysis, samples of the anolyte were drawn at regular intervals of time for analyzing the concentration of Ru. Estimation of ruthenium was by Inductively Coupled Plasma-Optical Emission Spectroscopic (ICP-OES, Jobin Yvon, France) analysis and the standards were produced by M/s. MBH Analytical Ltd., UK.

3. Results and discussion

Separation percentage of Ru by anodic oxidation was calculated using Equation (1):

$$\text{Separation\%} = \frac{[\text{Ru}]_{\text{Initial}} - [\text{Ru}]_{\text{Final}}}{[\text{Ru}]_{\text{Initial}}} \times 100 \quad (1)$$

Faradaic efficiency is defined by the relation,

$$\eta = \frac{\Delta m}{\Delta m^0} \times 100 \quad (2)$$

where, Δm is the number of moles of ruthenium oxidized in the experiment and Δm^0 is the number of moles of ruthenium which would be oxidized theoretically as per Faraday's law for the passage of Coulombic charge.

Δm can be calculated from Faraday's 1st law as follows:

$$\Delta m = \frac{i \cdot \Delta t}{nF} = \frac{C}{nF} \quad (3)$$

where, Δm is the number of moles of the material oxidized, i is the current in ampere, Δt is the time in second, C is the charge passed in coulomb, n is the number of electrons transferred and F is the Faraday's constant.

3.1. Oxidation potential and cyclic voltammetry of ruthenium nitrosyl nitrate

The CV of [Ru(NO)]³⁺ solution of (a) various concentrations of Ru in 1 M nitric acid, (b) 20 mM Ru in various concentrations of nitric acid and (c) at different temperatures were recorded at platinum electrode with the potential sweeping rate of 50 mV/s, in

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