7. SUMMARY AND SCOPE FOR FUTURE WORK

7.1 SUMMARY

Ruthenium (Ru) is a rare transition metal element belonging to the platinum group of the periodic table. It is produced as a fission product in nuclear reactors in large quantity due to the fission of uranium and plutonium and is one of the most troublesome fission products creates problems during nuclear fuel reprocessing and waste management processes due to its complex chemistry and formation of highly volatile radiotoxic ruthenium tetro-oxide (RuO$_4$). Ruthenium is having wide industrial application whereas it is scarce in nature. Since significant quantity of Ru is produced as fission product and most of them are nonradioactive it can be separated and recovered after eliminating the radioactivity associated by cooling the fuel for 10-20 years then spent nuclear fuel can be recognized as an alternate source of Ru. In order to solve the problems both in nuclear fuel reprocessing and waste management and also for industrial applications there is increased interest on the separation and recovery of ruthenium. The work presented in this thesis deals with the development of chemical and electrochemical methods for separation and recovery of Ru from high level liquid waste. A summary of the results is given below.

Removal of Ru from high level liquid waste was carried out by chemical volatilization method using ammonium ceric nitrate oxidizing agent in presence of n-paraffin oil. Separation of ruthenium by electrochemical oxidation in a constant current mode was studied using undivided and divided electrolytic cell in presence of redox mediator cerium. Feasibility of separation of ruthenium from high level liquid waste by constant potential electro-oxidation was carried out. The reduction behavior of [RuNO]$^{3+}$ in nitric acid medium was studied by various electroanalytical techniques.
7.1.1 Separation of ruthenium by n-paraffin hydrocarbon

The volatilisation behaviour of ruthenium tetroxide was made use of in the removal of ruthenium from the high level liquid waste. Separation experiments was conducted by mixing Ru bearing nitrate, nitrosyl nitrate or SHLLW solutions with NPH in the presence of ACN as oxidizing agent for Ru, revealed that separation of about 80-90% Ru from Ru(NO$_3$)$_3$ and SHLLW (containing Ru in the form of Ru(NO$_3$)$_3$) solutions was possible with 0.04 M ACN in 4M nitric acid. About 80% of Ru could be separated from ruthenium nitrosyl (RuNO) solutions, at low concentration of nitric acid in the range 0.5–1M using 0.02–0.04M Ce(IV) as the oxidizing agent and at ambient temperature. The black ruthenium powder removed during this study was characterized by XRD, TEM and XPS techniques and is found to be amorphous RuO$_2$ and oxy-hydroxide species of Ru(IV). The ketonic group formed in the used NPH upheld the reduction of RuO$_4$ to RuO$_2$ by the alkane.

7.1.2 Separation of ruthenium by electro-oxidation

Separation of Ru was carried out by anodically oxidizing Ru to volatile RuO$_4$ using undivided and divided electrolytic cell. Separation up to 95% Ru could be achieved from ruthenium nitrosyl (RuNO) solution in 1M nitric acid when electrolysis was conducted for 10 h with the anodic current density as 20 mA/cm$^2$ at 318 K and with 0.02 M cerous ions using undivided electrolytic cell. Under identical conditions, the amount of Ru separated from SHLLW was only 54 %, due to the interference of nitrite ions present in the waste. A divided cell with glass frit as diaphragm eliminated the interference caused by nitrite ions. In the divided cell 74 and 80 % of Ru was separated from pure RuNO solution and SHLLW respectively in 4M HNO$_3$ solution after electrolyzing for 10 h at 20 mA/cm$^2$ anodic current density, without any redox mediator. Compared to nitric acid and sodium hydroxide, n-paraffin oil above the electrolyte
served as a better trap for gaseous RuO$_4$, thereby preventing the deposition of RuO$_2$ on the wall of the vessel. In the present method of separation of Ru by applying constant current quantitative separation of was possible both from [RuNO]$^{3+}$ solution as well as SHLLW, however the current efficiency of the system was very low.

7.1.3 Feasibility study on the separation of ruthenium by constant potential electro-oxidation

From cyclic voltammograms of [RuNO]$^{3+}$ solution recorded at Pt working electrode and Ag/AgCl reference electrode it was revealed that oxidation of both Ru to RuO$_4$ and water is occurring simultaneously after 1.25 V(vs. Ag/AgCl). The separation % of Ru was increased with increase in applied potential, increase in temperature and decrease in nitric acid concentration, however the faradaic efficiency was found to decrease with increase in applied potential, temperature and nitric acid concentration. Maximum % of Ru from RuNO solution was achieved at a applied potential of 1.65 V (vs. Ag/AgCl) and 1M nitric acid solution whereas the Faradaic efficiency decreased from 63% to 29% and 11% with increase in applied potential from 1.25 V to 1.45 V and 1.65 V (vs. Ag/AgCl). The decrease in faradaic efficiency at higher potential and temperature might be due to faster and predominant oxidation of water than Ru under these experimental conditions. The presence of redox mediator cerium increases the separation of Ru whereas Faradaic efficiency was found to be lower than that without Ce under same experimental conditions. Maximum of about 97 % Ru was separated from RuNO solution in presence of 0.04M Ce at 1.65 V(vs. Ag/AgCl) applied potential however in case of SHLLW it was about 58 % under same experimental conditions which might be due to simultaneous oxidation of Pd present in it.
Rate constants for oxidation of Ru from RuNO solution were calculated from the analysis of overall rate data. The rate of oxidation of Ru was faster at higher applied potential and 1M in acidity and also in presence of redox mediator Ce. Compared to the presence of redox mediator Ce the rate of oxidation of Ru was still faster at higher temperatures (i.e. 323 and 333 K). The activation energy was calculated from the temperature effect on the oxidation of Ru from RuNO solution in 1M nitric acid at 1.25 V(vs. Ag/AgCl) applied potential and was found to be 18.09 kcal/mol.

7.1.4 Electroanalytical studies on the reduction of \([\text{RuNO}]^{3+}\) in nitric acid

The redox behavior of \([\text{RuNO}]^{3+}\) species in nitric acid medium were investigated by cyclic voltammetry and chronopotentiometry at both Pt and GC working electrodes. A quasi-reversible one electron reduction of \([\text{RuNO}]^{3+}\) was observed at both GC and Pt. The diffusion coefficient \((D_0)\) of \([\text{RuNO}]^{3+}\) species in the order of \(10^{-8}\) cm\(^2\).s\(^{-1}\) was estimated by CV and CP techniques and the heterogeneous electron transfer rate constant \((k_s)\) for reduction of \([\text{RuNO}]^{3+}\) in the order of \(10^{-5}\) cm.s\(^{-1}\) was estimated using Klingler and Kochi equation using Pt and GC working electrode.

7.2 SCOPE FOR FUTURE STUDIES

The parametric studies conducted for the separation of Ru chemical and electrochemical volatilization method can be implemented in the plant for the removal of Ru from the actual HLLW. Presently only batch processes for chemical and electrochemical method of separation have been carried out, continuous processes have to be designed, optimized and operated. Although quantitative separation of ruthenium was possible by electrochemical method, the energy efficiency of the method was less in case of SHLLW hence studies ought to be carried out to enhance the efficiency of the method by altering factors such as anode material, additives
etc. Further studies on the electrolytic reduction and oxidation of ruthenium nitrosyl complexes in nitric acid medium since very less data available due to it complex chemistry. Designing suitable electrolytic cells and demonstrating the performance of these cells in separating Ru from simulated HLLW are also within the scope of future work.