

## **ELECTROCHEMICAL REACTIONS FOR TECHNETIUM RECOVERY AND ANALYSIS IN THE RADWASTES SOLUTIONS**

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The report is to summarize the R&D activities in IPC in co-operation with US DOE and CEA France in the field of the utilization of the electrochemical techniques for Tc recovery and analysis in the radwastes solutions of different origins.

In process of  $\text{TcO}_4^-$  ions electrochemical reduction in solutions 0,1-1,0 M  $\text{HNO}_3$  at SMDE two electrode reactions are observed. Diffusion controlled  $\text{TcO}_4^-/\text{Tc(III)}$  reduction occurs at the potentials 0,069 - -0,205 V/SCE. The second electrode reaction is perceived at the potentials about -0,71 V/SCE, weakly affected by the  $\text{H}^+$  and  $\text{NO}_3^-$  concentration in the electrolyte. This process is associated with the nitric acid destruction, catalyzed by Tc(III) ions. The process of the electrochemical denitration at graphite cathode ( $E=-0,6 - -0,8$  V/SCE) was found to be significantly accelerated in presence of  $2.0 \cdot 10^{-3}$  M Tc(VII) in the electrolyte. In the latter process Tc(VII) is partially reduced to Tc(V) and Tc(IV). The latter species are accumulated at the electrode surface in the form of low-soluble  $\text{TcO}_2 \cdot x\text{H}_2\text{O}$ .

In order to understand better the reduction mechanism of  $\text{TcO}_4^-$  ions at mercury electrode, the electrochemical techniques allowing to follow the changes in the polarographic waves in time were developed. The application of time resolved (3D) polarography and differential capacity measurements to the study of Tc(VII) reduction in 0,1 M acetate buffer solution ( $\text{pH}=3,5- 6,0$ ) allowed to conclude, that the Tc(VII)/(III) reduction wave which was described in literature, has to be associated with the successive VII  $\rightarrow$  V reactions, followed by disproportionation of Tc(V) and formation of Tc(IV) insoluble species, which are adsorbed on the electrode and reduced to Tc(III). The life time of Tc(V) species in acetate media was estimated.

Electrochemical method for Tc recovery from PUREX waste solutions (200 mg/l Tc(VII), 2-4 M  $\text{HNO}_3$ ) including catalytic destruction of nitric acid, followed by

Tc electrodeposition from formate buffer solution (pH=6,0 – 7,5, ionic strength - 0,5 – 1 M) at graphite electrode was developed. Electrolysis of this solution at  $E=-1,2 - -1,4$  V/SCE results in the reduction of Tc(VII) to  $TcO_2 \cdot xH_2O$  deposited at the electrode with recovery varying from 92 to 95 %. Capacity of the graphite electrode in this process achieved  $3,5 \text{ mg/cm}^2$ .

Electrochemical reduction of Tc(VII) ions at SMDE in solutions 0,1 – 6,0 M NaOH was studied using fast-polarography (TP), differential pulse polarography (DPP) and cyclic voltammetry techniques. In these solutions Tc(VII) is readily reduced to Tc(VI) at the potentials  $-0,775 - -0,705$  V/SCE, shifting towards positive direction with the increase of NaOH concentration in the electrolyte. Further reduction of  $TcO_4^{2-}$  ions is complicated by coupled disproportionation reactions of Tc(VI) and Tc(V). When the NaOH concentration is less than 2,0 M, Tc(IV) is found to prevail in the reduction products. The increase of the alkali concentration in the electrolyte results in the slow down of the Tc(V) disproportionation rate and consequently in the increase of Tc(V) part in the products of the electrochemical reaction.

DPP technique was used for the development of the analytical procedure for mutual quantitative determination of U(VI), Tc(VII) and Cr(VI) in the solutions of alkaline radwastes. Detection limit of this determination was at the level  $10^{-7}$  M and was weakly affected by the presence of carbonate and nitrate ions in the sample.

$TcO_2 \cdot xH_2O$  electrodeposition from the solutions 0,5 – 4,0 M NaOH, containing up to 2,0 M  $NaNO_3$  at Ni, Pt and stainless steel cathodes was studied. More than 98 % Tc recovery was observed at current density exceeding  $160 \text{ mA/cm}^2$ .  $NO_3^-$  ions reduction was observed simultaneously with Tc(IV) hydrous oxide electrodeposition, the yield of denitration process increasing with the growth of Tc(VII) concentration in the electrolyte.