

Electrochemical Modelling of Copper Electrorefining in Lab Scale and Pilot Plant Scale

Jinimol Joy¹, D. Sujish^{1*}, B. Muralidharan¹, G. Padmakumar¹ and K.K. Rajan¹

Fast Reactor Technology Group, Indira Gandhi Centre for Atomic Research,

Kalpakkam, India

*Corresponding author: 207, PPES, CTD, FRTG, IGCAR, Kalpakkam, sujish@igcar.gov.in

Abstract: Pyrochemical reprocessing is a non-aqueous method for reprocessing spent metallic fuels. Electrorefining is an important step in pyrochemical reprocessing. Ambient Temperature ElectroRefiner (ATER) is a facility to demonstrate the various mechanisms and associated interlocks. Here the electrolysis of copper in acidified copper sulphate electrolyte will be carried out. Electrodeposition of copper was also numerically simulated using the secondary electrodeposition module of COMSOL and validated with the experimental results. The modelling of electrorefining of copper was done for pilot plant scale. The current density for the cathode geometry and the time required for deposition of one batch of copper was also estimated. This paper details the lab scale studies, validation of simulation and further prediction of current densities for pilot plant scale.

Keywords: Copper deposition, Secondary current distribution, current density, Electrorefining.

1. Introduction

Electrorefining is an important step in pyrochemical reprocessing which is a non-aqueous method for reprocessing spent metal fuel. A preliminary demonstration facility has been erected to demonstrate the various mechanisms and associated interlocks. Here the electrolysis of copper in acidified copper sulphate electrolyte will be carried out to demonstrate the electrorefining process. Laboratory scale experiments were conducted in this regard to understand the copper electrorefining process. Electrodeposition of copper was numerically simulated using a commercial multiphysics code COMSOL. The current density in each case was calculated. Current density (CD) plays an important role in electrodeposition. It depends on various factors such as composition, temperature, distance between electrodes, geometry of electrodes etc.

As deposition and current density are directly proportional, for getting maximum deposition, we have to enhance CD. The experimental and theoretical current densities for various operating conditions were compared and there was very close agreement in the results. Based on the above results the modelling of electrorefining of copper was done for the as built ATER vessel. The current density for the cathode geometry was calculated and the time required for deposition of one batch of copper was also estimated.

2. Secondary current distribution

The current density, i at any point inside the cell was determined from the gradient of local potential, ϕ according to Ohm's Law^[1]

$$i = -\sigma \nabla \phi$$

where σ is the electrolyte conductivity. The potential distribution in the electrolyte was described by the Laplace equation.

$$\nabla^2 \phi = 0$$

Depending on the characteristics of the boundary conditions on the cathode, three types of current distribution models (primary, secondary and tertiary) can be specified. For a primary current distribution, the surface potential of the working electrode, V was set equal to the potential of the solution adjacent to the electrode, ϕ_o .

$$V = \phi_o$$

Primary current distribution is the current distribution that is completely controlled by the resistivity of the electrolyte solution between the working and counter electrodes. It assumes both charge transfer and mass transport conditions are negligible. The secondary current distribution is the current distribution that is controlled by the resistivity of the solution and the charge-transfer resistance of the electrode reaction occurring on the working electrode (cathode) where concentration gradient is negligible. The

concentration of copper ions is assumed similar at the cathode surface and bulk electrolyte. Under these conditions, the local current density can be related to the local overpotential, η on the electrode. The overpotential is the potential difference between the electrode and the solution adjacent to the electrode.

$$\eta = V - \phi_0$$

Large charge-transfer resistance (that is, a slow reaction), compared to the solution resistance, tends to make the current distribution more uniform. Secondary current distribution interface describes the current and potential distribution in an electrochemical cell under the assumption that the variations in composition are negligible in the electrolyte. In secondary current distribution case, Butler Volmer approximation can be used for the electrochemical kinetics.

The rate of a reaction and the driving force η_s (also called as surface overpotential) is related by the Butler-Volmer equation which is of the form

$$i = i_0 \left[e^{(\alpha_a F \eta_s) / RT} - e^{(-\alpha_c F \eta_s) / RT} \right]$$

The first term in the above equation is the rate of the anodic direction and the second term is the rate of the cathodic direction. The difference between these two gives the net rate of reaction. The parameter i_0 is called the exchange current density (analogous to rate constant in chemical kinetics). The parameters α_a and α_c are called the anodic and cathodic transfer coefficients and they usually have values between 0.2 and 2.^[2]

The domain equations for the electrodes and the electrolyte are the following:

$$\nabla \cdot i_k = Q_k$$

and

$$i_k = -\sigma_k \nabla \phi_k$$

where Q_k denotes a general source term and in this model source term is zero. k denotes an index that is l for the electrolyte or s for the electrode, σ_k denotes the conductivity in S/m and ϕ_k the potential in V. For uniform electrolyte composition, the sum of the fluxes of all charged species yields the following expression for the current density vector:

$$i_l = -\sigma_l \nabla \phi_l$$

where σ_l denotes the electrolyte conductivity and ϕ_l the potential in the electrolyte. The analogous equation is defined by the interfaces for current conduction in the electrodes:

$$i_s = -\sigma_s \nabla \phi_s$$

The difference between the interfaces lies in the description of the electrochemical reactions. The rate of electrochemical reactions can be described by relating it to the activation overpotential. For an electrode reaction, with index m , the activation overpotential, denoted η_m , is the following:

$$\eta_m = \phi_s - \phi_l - E_{eq.m}$$

where $E_{eq.m}$ denotes the equilibrium potential for reaction m . In the Secondary Current Distribution interface, the electrochemical reactions are described as a function of the overpotential. The interface uses several relations for the charge transfer current density and the overpotential. The most general expression is of Butler-Volmer type.

3. Use of COMSOL

3.1 Lab scale Modeling

The lab scale experiments for copper electrorefining were carried out. Numerical simulation of copper electrorefining was also carried out using COMSOL. The geometrical model and mesh details are shown in Figure 1. A typical plot of current density with time is shown in Figure 2. The experimental and numerical current densities were found to be matching.

3.2 Pilot plant scale Modeling

Figure 3 shows the ATER geometry used for the simulation. The ATER vessel is 1300mm in diameter. The centre to centre distance between the anode and the solid cathode is 700mm. The anode basket is modeled as porous electrode with porosity 0.4. Accordingly Copper rodlets are dump packed into the anode basket to a height of 103mm in all the four legs. A voltage of 1V is applied externally to the anode. This is modeled

using an external depositing electrode. The cathode is a cylindrical rod of 65 mm diameter and it has been modeled as the second external depositing electrode with external voltage zero. Acidified copper sulphate has been modeled as an electrolyte with electrical conductivity 44 S/m. The other inputs to the model include exchange current density which is 16A/m², Anode transfer coefficient which is 0.5 and cathode transfer coefficient 1.5. Number of participating electrons is 2 and the equilibrium potential at reference temperature of 298.15K is given by the relation $0.34 + (0.0591/2) \cdot \log(0.6)$. The simulation is time dependent and is executed for 20 days with a time step of 86400s. Meshing of the geometry is done by extra fine physics controlled meshes. The electrolyte current density on the cathode surface is evaluated.

4.1 Results of Lab scale Modeling

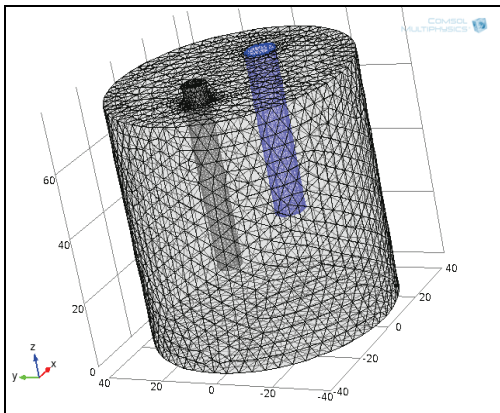


Figure 1. Geometry and mesh details of lab scale model.

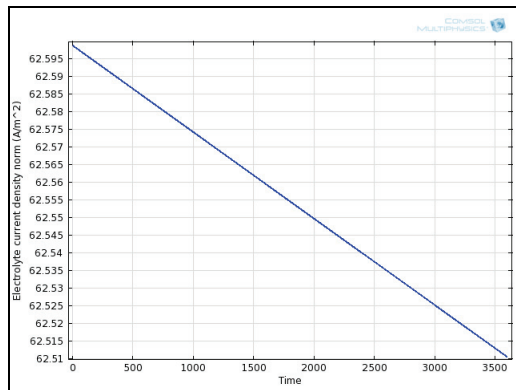


Figure 2. Typical current density plot on cathode.

The simulation was done for three different operating conditions of applied cell voltage, deposition time and distance between the electrodes. It was found that the experimental and model current densities are almost matching for the three operating conditions. The electrolyte potential was found to be constant in the entire electrolyte medium. The average electrolyte current density around the cathode was evaluated to be 62.55 A/m².

4.2 Results of Pilot plant scale Modeling

The applied cell voltage is 1V, deposition time is 18 days and distance between the electrodes is 700mm. The Variation of current density along the cut line that passes through electrodes is shown in Figure 4. Surface plot of Electrolyte current density around cathode is shown in Figure 5. Current density around cathode is increasing from top to bottom as effective distance between electrodes is decreasing. Maximum Current density is seen at bottom portion which is facing the anode with a value of 312 A/m². The surface average current density around the cathode was evaluated by the surface integration of local current densities and found to be 143.47A/m².

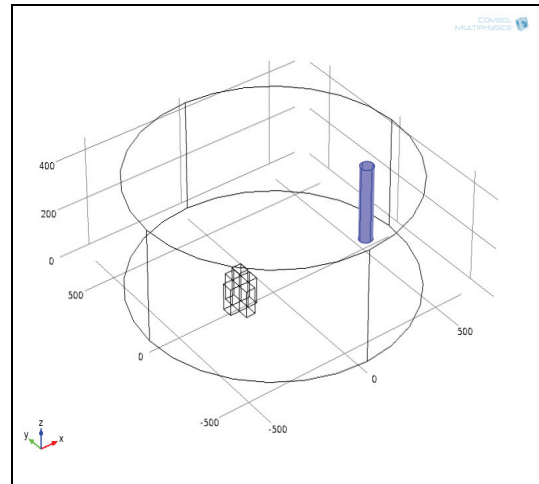


Figure 3. Geometrical model of pilot plant scale copper electrorefining.

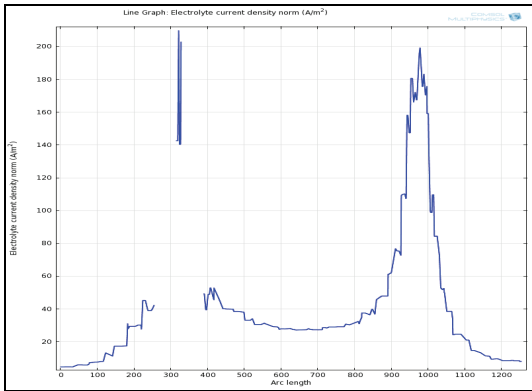


Figure 4. Current density plot along a cut line

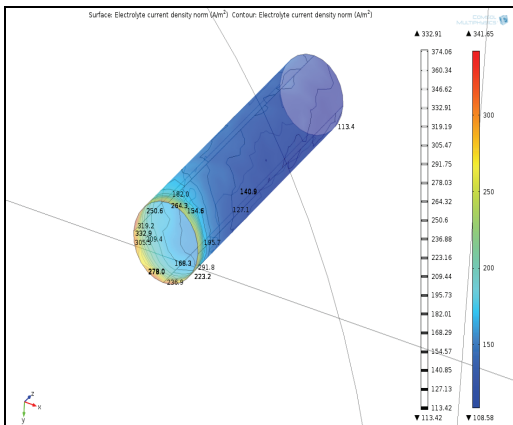


Figure 5. Contour plot of current density on the cathode surface.

5. Conclusions

The secondary electrodeposition module of COMSOL was used to simulate the electrodeposition of copper in laboratory scale. The model was validated by evaluating the experimental and theoretical current densities at various operating conditions. The same module has been used here to evaluate the current density for as built ATER. The current density for this system is around 143.47 A/m^2 . Accordingly the time taken to deposit of 5 kg of copper on the solid cathode would be 20 days.

8. References

1. C.T.J. Low, E.P.L. Roberts and F.C Walsh, Numerical simulation of the current,potential and concentration along the cathode of a rotating

cylinder hull cell, *Electrochimica Acta* 52, pp 3833 (2007)

2. John Newman, Karen E. Thomas-Aleya,*Electrochemical systems*, Chapter 8, pp 216, Ed.3, Mc. Graw Hill (2005)

3. COMSOL multiphysics, Electrodeposition module.

4. Jinimol Joy, Copper Electrodeposition to simulate Electrorefining for Pyroprocessing, M.Tech Thesis- June 2012.

5. Jinimol Joy, D.Sujish, B.Muralidharan, B.P.Reddy and G.Padmakumar, 'Modelling and validation of copper electrorefining in laboratoryscale',FRTG/CTD/PPES/99519/3020/R-A.