

Analysis of a Molten Salt Electrolysis with a Liquid Cadmium Cathode

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1. Introduction

A pyrochemical processing has become one of the promising technologies for the volume reduction of a PWR spent fuel. Molten salt electrochemical method is envisaged as one process in which the actinides are separated from the bulk of fission products in a molten salt electrolyte by using a liquid cadmium cathode [1,2,3]. To obtain a better understanding of the electrochemical behavior in this process, a mathematical model would be useful not only to predict the operational variables but also to control the electrochemical parameters.

In this study, an equilibrium and electrotransport model of a pyrochemical process was proposed and discussed with respect to the recovery and reconstitution of the actinide group from the thermochemical data.

2. Calculation Model

At an electrowinning operation of 723K, the activation and reduction processes taking place on the electrode interface of a liquid cadmium cathode are assumed to be so rapid as to bring about an instantaneous equilibrium. Thus, the following Nernst equation holds at the salt-cadmium interface of a liquid cadmium cathode for an element i :

$$E_i = E_i^o + \frac{RT}{n_i F} \ln \left(\frac{\gamma_i^{\text{salt}} X_{i,cs}^{\text{salt}}}{\gamma_i^{\text{Cd}} X_{i,cs}^{\text{Cd}}} \right) \quad (1)$$

where, E_i (V) is the cathode potential, E_i^o (V) is the standard potential of element i ; R (=8.314 J·mol⁻¹K⁻¹) is the gas constant, T (K) is the temperature; n_i is the number of equivalents per mole of i in the salt; F (=96,500 C·mole⁻¹) is the Faraday constant; γ_i^{salt} and γ_i^{Cd} are the activity coefficient of i in salt and cadmium, respectively; $X_{i,cs}^{\text{salt}}$ and $X_{i,cs}^{\text{Cd}}$ (mole·cm⁻³) are the concentration of i at the salt and cadmium side of the cadmium-salt interface, respectively.

The model assumes uniform concentrations of the elements in the salt and cadmium, except in the vicinity of the electrode interfaces. The mass transfer is modeled by a diffusion layer theory, in which the concentration gradients in the vicinity of the electrode surface are approximated as linear with in a thin diffusion layer [4,5,6].

The assumed concentration profile in the vicinity of a liquid cadmium cathode is shown in Figure 1. The cathodic current density carried by each element i can be calculated as follows:

$$I_i^c = n_i F D_i^{\text{salt}} \frac{X_{i,b}^{\text{salt}} - X_{i,s}^{\text{salt}}}{\delta_c^{\text{salt}}} = n_i F D_i^{\text{Cd}} \frac{X_{i,s}^{\text{Cd}} - X_{i,b}^{\text{Cd}}}{\delta_c^{\text{Cd}}} \quad (2)$$

where, i_i^c (A·cm⁻²) is the cathode current density carried by element i ; D_i^{Cd} and D_i^{salt} (cm²·s⁻¹) are the diffusion coefficient of element i in the cadmium and salt, respectively; $X_{i,b}^{\text{salt}}$ and $X_{i,b}^{\text{Cd}}$ (mole·cm⁻³) are the bulk concentration of i in the salt and cadmium phase, respectively; δ_c^{salt} and δ_c^{Cd} (cm) are the diffusion layer thickness in the salt and cadmium, respectively.

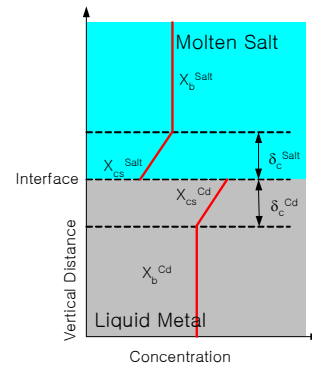


Figure 1. Diffusion layer model for the liquid cadmium cathode.

3. Numerical Approach and Discussion

If the cathodic potential E_c is given, the concentration of element i on both sides of the cathode surface ($X_{i,cs}^{\text{salt}}$, $X_{i,cs}^{\text{Cd}}$) can be determined by solving Eqs.(1) and (2) under given bulk concentrations ($X_{i,b}^{\text{salt}}$, $X_{i,b}^{\text{Cd}}$). Then the current density or each component can be calculated by Eq.(2). This calculation is iterated by changing different values of E_c until the sum of the calculated current components agrees with the total cathodic current applied:

$$I^c = \sum_i I_i^c \quad (3)$$

In a multi-component equilibrium system, the distribution of the elements between the salt and the liquid cadmium is governed by Eq.(1) and a material balance. Figure 2. shows that the actinide elements could be separated from a salt containing rare earths by adjusting the cell potential.

The calculated results about the mass transfer indicate that the behavior of actinide elements in an electrotransport can be explained well by a diffusion layer model in the molten salt electrolyte and liquid

cadmium cathode. The diffusion layer thickness in the vicinity of the electrode is determined from a polarization due to the exhaustion of elements on the electrode surface.

Based on this approach, the modeling will become useful for the design and operational strategy to be adopted for an electrowinning process.

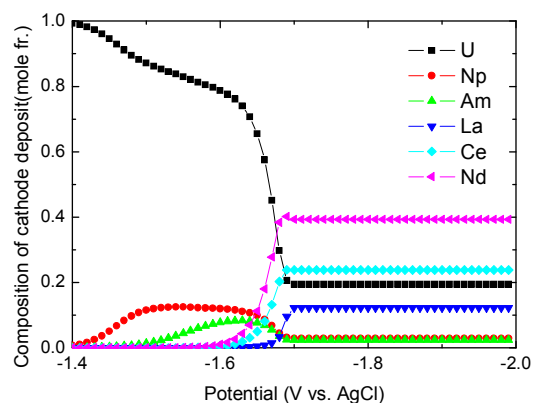


Figure 2. Composition of element deposit on the liquid cadmium cathode by potentiostatic electrolysis at 450°C.

4. Conclusion

An equilibrium and electrotransport model of a pyrochemical process was proposed and discussed with respect to the recovery and reconstitution of the actinide group. A diffusion layer model explains the behavior of the electrotransport from the molten salt electrolyte to the liquid cadmium cathode well.

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