

Improvement of Electrowinning Simulation Code (EcWinSim)

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1. Introduction

Several years ago, Korea Atomic Energy Research Institute (KAERI) developed the FORTRAN code named EcWinSim which is simple constant current electrolytic half-cell model for simulating spent nuclear material's behavior in molten salt and electrowinning system with liquid cadmium cathode (LCC) [1,2]. However, the original EcWinSim resulted in unreasonable outcomes with respect to mass balance in that a total amount of mass increases as electrochemical reaction progresses due to assuming that volumes of molten salt and liquid cadmium remain constant while nuclear elements are deposited. In this study, the formulation of governing equations for numerical algorithm is addressed again by using molality instead of molarity so that volume change is taken into account. Simulation results show that enhanced EcWinSim is far more reasonable than the original one because the mass of the electrowinning system should always remain constant over time.

2. Review of original EcWinSim

2.1. Background of model

An electrowinning process was considered to model and analyze the electro-transport of actinide and rare-earth elements by dynamic modeling taking into account the material balances and diffusion-controlled electrochemical reactions in a diffusion boundary layer at an electrode interface between the molten salt electrolyte and liquid cadmium cathode [1, 2]. The proposed modeling approach was based on the half-cell reduction reactions of metal chloride occurring on the cathode.

The reduction processes taking place at the electrode interface of a liquid Cd cathode are assumed to be rapid enough to bring about an instantaneous equilibrium. Thus, the following Nernst equation holds at the molten salt and cadmium interface of a liquid cadmium cathode for an element i :

$$E_i^e = E_i^0 + \frac{RT}{n_i F} \ln \frac{\gamma_i^{Salt} C_{i,s}^{Salt}}{\gamma_i^{Cd} C_{i,b}^{Cd}} \quad (i = 1, \dots, n) \quad (1)$$

where, E_i^e is the electrochemical equilibrium potential of i -th element, E_i^0 is the standard reduction potential, R is the gas constant, T is the operation temperature, n_i is

the number of equivalents per mole of i -th element in the salt, F is the Faraday constant, γ_i^{Salt} and γ_i^{Cd} are the activity coefficients of element in the eutectic molten salt and the LCC, respectively; $C_{i,s}^{Salt}$ and $C_{i,s}^{Cd}$ is the molarity concentrations (mole · cm⁻³) of i -th element at the salt side of the salt-LCC interface and at the LCC side of the salt-LCC interface, respectively.

The assumed concentration profile in the vicinity of a liquid cadmium cathode is as reported in the TRAIL model [3]. The cathodic current density carried by each element i can be approximated as follows:

$$i_i = n_i F D_i^{Salt} \frac{C_{i,b}^{Salt} - C_{i,s}^{Salt}}{\delta^{Salt}} = n_i F D_i^{Cd} \frac{C_{i,s}^{Cd} - C_{i,b}^{Cd}}{\delta^{Cd}} \quad (2)$$

where, i_i (A · cm⁻²) is the cathode current density carried by element i ; D_i^{Salt} and D_i^{Cd} (cm² · s⁻¹) are the diffusion coefficients of element i in the cadmium and salt, respectively; δ^{Salt} and δ^{Cd} (cm) are the diffusion layer thicknesses in the salt and cadmium, respectively.

For an activated polarization, the cathodic current density produced by an electrochemical reaction can be written by the Butler-Volmer equation as

$$i_i = i_{o,i} \left[\exp \left\{ -\frac{\alpha_i n_i F}{RT} \eta_i \right\} - \exp \left\{ \frac{(1-\alpha_i) n_i F}{RT} \eta_i \right\} \right] \quad (3)$$

where $i_{o,i}$ (A/cm²) is the exchange current density of the reaction that is the current density evaluated when the net current at the electrode is null; α_i is the transfer coefficient for the reaction; $\eta_i (= E^c - E_i^e)$ is the surface overpotential, where E^c is the variation in the cathode potential between the electrode and the electrolyte.

2.2. Drawbacks in original model

By assuming volume of LCC and salt remain constant regardless of reaction, mass balance equation was expressed as in the original equation

$$V^{Cd} C_{i,b}^{Cd,0} + V^{Salt} C_{i,b}^{Salt,0} = V^{Cd} C_{i,b}^{Cd} + V^{Salt} C_{i,b}^{Salt} \quad (4)$$

where $C_{i,b}^{Cd,0}$ and $C_{i,b}^{Salt,0}$ are bulk concentrations of i -th element at a previous time step in LCC and salt, respectively.

The above equation assumes that the volumes of LCC and salt remain constant but they must be revised to satisfy mass balance every time step as follows

$$V^{Cd,0}C_{i,b}^{Cd,0} + V^{Salt,0}C_{i,b}^{Salt,0} = V^{Cd}C_{i,b}^{Cd} + V^{Salt}C_{i,b}^{Salt} \quad (5)$$

where $V^{Cd,0}$ and $V^{Salt,0}$ are volumes in LCC at a previous time step and the bulk concentration of i -th element at a previous time step.

3. Improved EcWinSim

3.1. Molality instead of molarity

In order to consider the mass and volume change due to the material transfer as the electrochemical process progresses, the equations of system were reorganized using molality which is not affected by the volume and the temperate instead of molarity. Conversion from molarity to molality is possible by using the following equation

$$C_{i,b}^{Salt} = \frac{W_{Salt}^{Salt} L_{i,b}^{Salt}}{V^{Salt}} \quad (6)$$

where W_{Salt}^{Salt} is the mass of pure LiCl-KCl eutectic molten salt, $L_{i,b}^{Salt}$ is the molality (mole \cdot g $^{-1}$) of element i in the molten salt.

Molarity containing equations (1), (2) and (4) can be changed by using molality concentration as follows

$$E_i^e = E_i^0 + \frac{RT}{n_i F} \ln \frac{\gamma_i^{Salt} L_{i,s}^{Salt} W_{Salt}^{Salt} V^{Cd}}{\gamma_i^{Cd} L_{i,s}^{Cd} W_{Cd}^{Cd} V^{Salt}} \quad (7)$$

$$i_i = n_i F D_i^{Salt} \frac{W_{Salt}^{Salt} L_{i,b}^{Salt} - L_{i,s}^{Salt}}{V^{Salt} \delta^{Salt}} \quad (8)$$

$$W_{Cd}^{Cd} L_{i,b}^{Cd,0} + W_{Salt}^{Salt} L_{i,b}^{Salt,0} = W_{Cd}^{Cd} L_{i,b}^{Cd} + W_{Salt}^{Salt} L_{i,b}^{Salt} \quad (9)$$

3.2. Numerical algorithm

Fortunately, the use of molality does not change the formulation for numerical calculation. To solve equations (3), (7)~(9), $n+3$ simultaneous nonlinear equations can be formulated in the following form.

$$\begin{aligned} F_1(E_1^e, E_2^e, \dots, E_n^e, E^c, V^{Salt}, V^{Cd}) &= 0 \\ &\vdots \\ F_{n+3}(E_1^e, E_2^e, \dots, E_n^e, E^c, V^{Salt}, V^{Cd}) &= 0 \end{aligned} \quad (10)$$

There are two more equations to solve than original EcWinSim due to regarding volumes of salt and Cd as solution variables. This can guarantee mass balance. Gauss-Newton algorithm was applied to solve the above simultaneous equation (10).

4. Results and discussion

The thermodynamic data and electrolytic parameters used in this calculation are shown in Table I. The original and revised EcWinSim are compared regarding ten elements deposited in LCC and diluted in LiCl-KCl salt as shown in Figs. 1 and 2, respectively. The total

mass of ten elements increases by 5% in the original EcWinSim due to the constant volume assumption. However, the revised EcWinSim shows that the mass is conserved. The use of molality concentration and consideration of volume change both make EcWinSim more reasonable than before.

Table I: thermodynamic and kinetic properties

	E_i^0	γ_i^{Salt}	γ_i^{Cd}	$i_{o,i}$	α_i	D_i^{Salt}	D_i^{Cd}
U	-2.476	3×10^{-3}	10^2	5×10^{-3}	0.5	1.03×10^{-5}	1.5×10^{-5}
Np	-2.676	3.1×10^{-5}	$10^{-2.1}$	5×10^{-3}	0.5	1.08×10^{-5}	1.5×10^{-5}
Pu	-2.783	2.8×10^{-3}	$10^{-3.8}$	5×10^{-3}	0.5	2.32×10^{-5}	1.5×10^{-5}
Am	-2.865	4.7×10^{-3}	$10^{-3.9}$	5×10^{-3}	0.5	1.10×10^{-5}	1.5×10^{-5}
La	-3.107	5×10^{-3}	$10^{-8.4}$	5×10^{-3}	0.5	8.00×10^{-6}	1.5×10^{-5}
Ce	-3.060	2.6×10^{-3}	$10^{-7.9}$	5×10^{-3}	0.5	8.00×10^{-6}	1.5×10^{-5}
Pr	-3.043	9.4×10^{-3}	$10^{-7.7}$	5×10^{-3}	0.5	1.00×10^{-5}	1.5×10^{-5}
Nd	-3.054	1×10^{-3}	$10^{-7.9}$	5×10^{-3}	0.5	1.10×10^{-5}	1.5×10^{-5}
Gd	-2.996	2.3×10^{-4}	$10^{-6.2}$	5×10^{-3}	0.5	1.00×10^{-5}	1.5×10^{-5}
Y	-3.076	4.5×10^{-6}	$10^{-6.1}$	5×10^{-3}	0.5	9.70×10^{-6}	1.5×10^{-5}

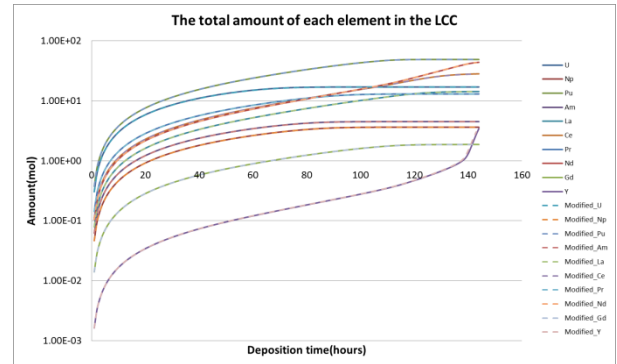


Fig. 1. Deposited elements in LCC

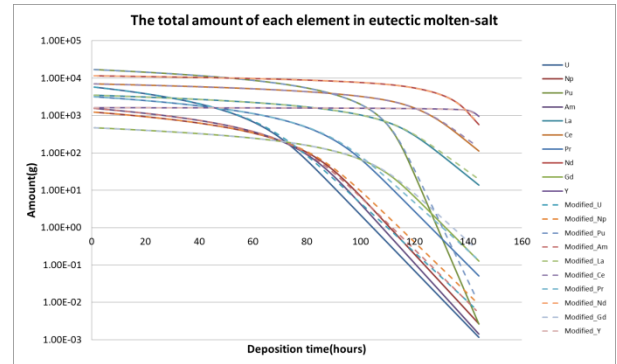


Fig. 2. Diluted elements in LiCl-KCl

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