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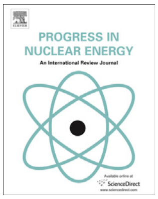

Kinetic model for electrorefining, part II: Model applications and case studies

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ABSTRACT

The model developed in Part I of the systematic study is applied to identify the kinetic features of materials flow in an electrorefinner. The most recent thermodynamic and electrochemical data reported are used in the present simulations. Both liquid and solid electrodes are considered. The main differences of the kinetics of materials dissolution/deposition between the liquid and solid electrode and the reasons for these differences are identified. The important factors that affect the evolution of electrorefining with operation are identified.

1. Introduction

In Pryprocessing, the major actinides, U and Pu can be recovered from the molten salt through electro-deposition at the cathodic electrodes of electrorefiner. Most uranium is deposited at a solid cathode, then plutonium together with minor actinides, and the remaining uranium are deposited at a liquid metal cathode (liquid Cd or Bi, in the present study, we focus on the liquid Cd cathode) (Nawada and Fukuda, 2005). The alkaline metals and most of rare earths cannot be electro-transported and continuously accumulate in the molten salt with operation. Therefore, during the electrorefining, the spent fuel composites are separated into four parts: pure uranium at the solid cathode, Pu together with minor actinides and a small amount of uranium at the liquid cathode, alkaline fission products in the molten salt, and noble fission products together with cladding hulls at the anode basket. The first two parts are products of the pyroprocessing (fertile or fissionable nuclear materials) and can be reused for new fuel fabrication, while the last two parts are wastes. The fission products in the salt bath can be removed by recycling the salt, and converted into a solid waste form.

Typically, an electrorefiner for pyroprocessing applications is composed of an anode (liquid or solid), a solid cathode for depositing most of the U, a liquid cathode for depositing Pu, MAs and some U, and molten salt which serves as transport bath. For enhancing mass transfer, stirring may be installed in the liquid phases (liquid electrodes and molten salt) as was done the design of MARK–IV electrorefiner (Li, 2002). For studying the kinetic features of electrorefining, the material transport from the solid or a liquid anode to the solid and liquid cathodes through the molten salt bath must examined. The simulation frame of the present study is given in Fig. 1. In the present simulation, the main components of a spent metallic fuel, U, Pu and Zr, are considered.

2. Parameter identification

LiCl–KCl (40% mol) and liquid cadmium have been found to be a good molten salt bath and a good liquid electrode for spent metallic fuel treatment. For applying the model developed in Part I (Zhang, 2013), the following parameters must first be identified: liquid salt and cadmium properties including density, viscosity, molar weight; actinide behaviors in the liquids including apparent potential, solubility, activity coefficient, diffusion coefficient and chemical interactions with the molten salt and cadmium.

The density (ρ) and dynamic viscosity (μ)can be expressed by:

$$\rho\left[\mathrm{g}/\left(\mathrm{cm}^3\right)\right] = A - BT \tag{1}$$

$$\mu\,[\mathrm{g}/(\mathrm{cm\ s})] = C\exp\left(\frac{E}{RT}\right) \tag{2}$$

where A, B, C and E in Eqns. (1) and (2) are constants. For the molten salt (Janz, 1967; Samuel, 2009):

$$A = 2.0233,\ B = 5.238\times10^{-4},\ C = 8.61\times10^{-4},$$
$$E = 20926.3;$$

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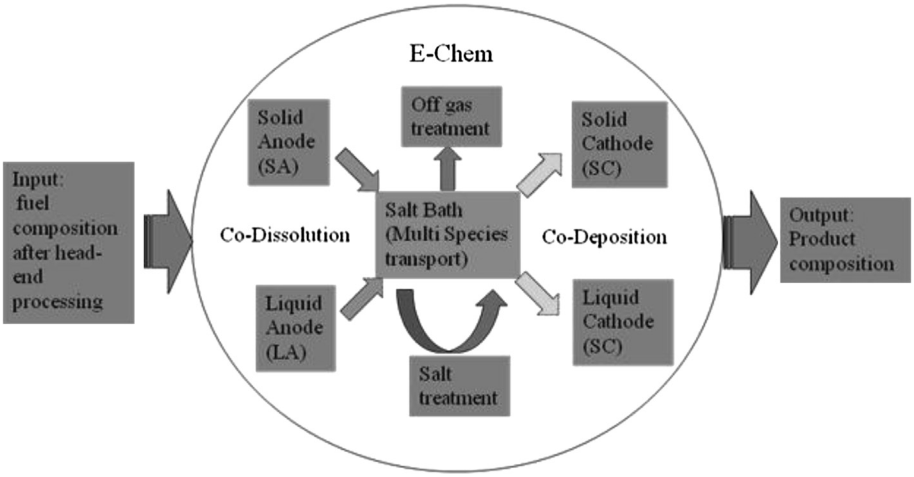

Fig. 1. Thej modeling objectives of EChem model.

and for liquid cadmium (Crawley, 1968; Battezzati and Greer, 1989):

$$A = 8.388, \ B = 1.2205 \times 10^{-3}, \ C = 0.003, \ E = 10900.$$

Knowing the density and dynamic viscosity, the kinetic viscosity is calculated by $\nu = \mu/\rho$.

There are numerous sources for chemical and thermodynamic data for the actinides and fission products in the molten salt KCl–LiCl mixture. The present model will use the most recent data. The apparent potential, the activity coefficient, and diffusion coefficient are temperature dependent, and can be generally expressed by:

$$E^{ap}_{(i^{n_i+}/i^{0})\text{vs}(\text{Cl}^-/\text{Cl}_2)}[\text{V}] = A_1 + B_1 T \tag{3}$$

$$\log\gamma = A_2 + \frac{B_2}{T} \tag{4}$$

$$D\left[\left(\text{cm}^2/\text{s}\right)\right] = D_0 \exp\left(-\frac{E_D}{R\,T}\right) \tag{5}$$

For uranium, U^{3+} (Zhang, Submitted, 2012):

$$A_1 = -2.9429, \ B_1 = 5.8724 \times 10^{-4}$$

$$A_2 = -0.08463, \ B_2 = -2076.1$$

$$D_0 = 2.291 \times 10^{-3}, \ E_D = 32550$$

For the apparent potential and the activity coefficient of Pu^{3+} (Roy and et al., 1996):

$$A_1 = -3.3183, \ B_1 = 7.0443 \times 10^{-4}$$

$$A_2 = 1.7692, \ B_2 = -3203.8$$

For the diffusion coefficient of $PuCl_3$ Shirai and et al., 2001).

$$D_0 = 1.528 \times 10^{-2}, \ E_D = 33423.9$$

D_0 and E_D are obtained by fitting the data reported in the reference using Eq. (5).

Thermal and chemical properties of some actinides in liquid cadmium have been also measured, but the available data are much sparser than those for molten KCl–LiCl. A diffusion coefficient for U in liquid cadmium was developed (Willit et al., 1992):

$$D_0 = 2.160 \times 10^{-4}, \ E_D = -17100$$

There is no such correlation for the diffusion coefficient of Pu in liquid cadmium. In the present simulation, this coefficient is assumed to be the same as the diffusion coefficient of U.

The activity coefficient of U and Pu in liquid cadmium was measured and calculated by Johnson (1974; Johnson and Feder 1962). The data reported are fitted by Eq. (5). For U:

$$A_2 = 3.7589, \ B_2 = -1364.79$$

and for Pu:

$$A_2 = 4.2506, \ B_2 = -6124.62$$

Knowing the activity coefficients of Pu and U in the liquid cadmium, the apparent potential at the liquid cadmium electrode of the two elements can be calculated using the apparent expression developed in part I.

Another important parameter that must be identified in the present simulation is the solubility of actinides in the molten salt and the liquid cadmium electrode. Generally, the solubility can be expressed by:

$$\log S[\text{mol fraction}] = A_3 + \frac{B_3}{T} \tag{6}$$

where A_3 and B_3 are constants. Based on our best knowledge, there are no data for the solubility of U and Pu in the molten salt. Iizuka and Moriyama (2010) thought that the solubility of U could be as high as 1.3 at% at 773 K. The concentration of U and Pu in the molten salt for pyroprocessing application is much less than this value. Therefore, it is assumed that Pu and U won't be saturated in the present study. However, future models should include the effects of saturation in the separation processes.

The solubility of U and Pu in liquid cadmium has been reported (Johnson, 1974; Johnson and Feder, 1962). Using Eq. (6) to fit the available data, one obtains for U:

$$A_3 = 3.2126, \ B_3 = -3893.44$$

and for Pu

$$A_3 = 1.3394, \ B_3 = -2387.62$$