Transient modeling of spent nuclear fuel electrorefining with liquid metal electrode

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HIGHLIGHTS

- A transient model for multi-phase electrorefining of spent nuclear fuel is developed.
- Benchmark is conducted against a lab-scale experiment with liquid metal electrode.
- A good agreement is achieved for mass fraction at electrodes and bulk concentration.
- Sensitivity study evaluates effects of material properties and operating conditions.
- Uncertainty of current efficiency can cause some degree of disagreements.

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ABSTRACT

During the molten salt electrorefining of spent nuclear fuel, multiple phases such as oxide, solid metal, liquid metal, and molten salt often co-exist. Computational modeling can be a useful tool for understanding the reaction mechanism across the multiple phases. The new model has been developed and applied to a lab-scale electrorefining with liquid metal anode and solid cathode LiCl-KCl molten salt. The benchmark study predicts anodic dissolution and cathodic deposition of U and Pu with minor disagreements. In particular, the on-set of Pu deposition on the surface of the solid cathode is well estimated, which is important for the quality of U ingot and the safeguards of process. The underestimation of U deposition (~6%) and the overestimation of Pu dissolution (~7%) at the end of simulation are explained by unconsidered reaction species such as Np and Am from the liquid Cd anode, which overestimates the dissolution of Pu from the anode compared to the measured data. The sensitivity study also reveals the transition behaviors of electrochemical reactions for U and Pu on the solid cathode are changed by diffusion boundary layer thickness, transfer coefficients, and the difference of electrochemical potentials more sensitively than those of the liquid metal anode. For this specific experiment case, the thinner diffusion boundary layer improves the prediction of cathodic reactions particularly at the end of electrorefining.

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1. Introduction

Pyroprocessing has been developed in the United States, the European Union, Japan, and Korea as a potential option for treating spent nuclear fuel [1—9]. This process uses a high temperature molten salt electrolyte to recover U, Pu, and minor actinides. Initially developed for recycling spent metal fuel, this process has the potential of treating spent oxide fuel from light water reactors [10—12]. During the treatment, multiple phases such as oxide, solid metal, liquid metal, and molten salt often co-exist. Therefore, understanding the reaction mechanism of actinide and fission products across the multiple phases is critical for developing the pyroprocessing technology.

Among the steps of pyroprocessing, electrorefining uses solid and liquid electrodes immersed in molten LiCl-KCl to dissolve active elements from chopped solid metal segments of spent nuclear fuel, and selectively recovers U onto the solid electrode [13—17]. Afterwards, Pu and minor actinides are recovered from the electrolyte onto the liquid Cd electrode, together with residual U and some rare earth elements. During the electrorefining, it is

important to achieve high throughput while maintaining an acceptable quality in the product ingot [13]. Multi-species modeling of this process with experimental benchmarking can be a useful tool for understanding the reaction mechanism across the multiple phases. Furthermore, the models would eventually allow optimization of the operating conditions, such as geometrical configuration, applied current density, hydrodynamic conditions, termination point, product composition, and operation time.

For this purpose, several researchers have developed simulation codes [13–26], many of which have been benchmarked to the lab-scale experiment by Tomczuk et al. (1992) [27] at the Argonne National Laboratory (ANL), using liquid Cd anode and solid steel cathode. This experiment is among the few cases that report kinetic electrorefining data using U and Pu. However, experimental data presented in the paper only include neither a range of conditions, not precise values. Furthermore, there are limited explanations of the representativeness of the sampling and measurement errors. In addition, sources of disagreements between modeling and experiment are not fully discovered. Sensitivity studies of operating conditions and material properties are therefore necessary for understanding the experimental results and transient behavior of anodic and cathodic reactions.

In this paper, we develop a new kinetic model to simulate multi-species electrorefining in molten salt, and benchmarked it against the lab-scale experiment of Tomczuk et al. [27]. To ensure the reliability and reproducibility of the simulation results, sensitivity studies are conducted to calculate the impact of input properties with a wide range of uncertainties. The properties include diffusion boundary layer thickness, transfer coefficients, and the difference of electrochemical potentials. Section 2 describes the physics and mathematics of the model in detail. Section 3 presents the geometrical information and operational conditions of the benchmark cases. Section 4 reports the results of modeling and benchmarking. Section 5 discusses the results of benchmarking and sensitivity studies.

2. Method

2.1. Physical model

An electrorefining cell consists of the molten salt electrolyte, anode, and cathode. Depending on the type of process, the anode and cathode can be either solid or liquid. Species such as U, transuranic elements (TRU), and fission products in the anode are dissolved into molten salt in ionic forms, except the noble metals that do not easily form chlorides. The dissolved metal ions are transported to the surface of the cathode mostly through convection and diffusion. Among the dissolved metal ions, U is the first to be reduced and deposited on the cathode surface in metallic form. The electrochemical kinetics, electrochemical thermodynamics, and ion transport are closely coupled in this process.

2.2. Mathematical model

2.2.1. Governing equations: mass transport

The ion transfer from the anode to the cathode through molten salt electrolyte is governed by the Nernst-Planck equation, which is based on the conservation of mass and describes the motion of a charged chemical species in molten salt. The mathematical time-dependent form of the Nernst-Planck equation for the j-th ionic species is equations (1) and (2).

$$\frac{\partial C_j}{\partial t} = -\nabla \cdot J_j \tag{1}$$

$$J_j = -D_j \nabla C_j + C_j v - \frac{z_j F}{RT} D_j C_j \nabla \phi \tag{2}$$

C_j is the species concentration (mol cm^{-3}), J_j is the mass flux (mol s^{-1} cm^{-2}), D_j is the diffusivity (cm^2 s^{-1}), v is the velocity of the molten salt medium (cm s^{-1}), z is the valence of the ion. F is Faraday's constant (C mol^{-1}), R is the gas constant (J K^{-1} mol^{-1}), T is the temperature (K), and ϕ is the electrical potential (V).

The ion transport can occur through diffusion in the first term at right side of equation (2), convection in the second term and electromigration in the third term. In equation (2), electromigration can be ignored within the bulk electrolyte, by assuming there is sufficient supporting electrolyte. Park (1999) [18] showed that the U transport by electromigration is sufficiently small compared to that of diffusion within the diffusion boundary layer. When the convection term can be separately calculated, equation (2) can be simplified to a one-dimensional (1D) equation similar to Fick's second law:

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} \tag{3}$$

These assumptions allow us to solve the ion transport by calculating only diffusion with the Nernst diffusion boundary layer thickness. In this case, ion transport is mostly governed by convection in the bulk electrolyte, and by diffusion in the diffusion boundary layer. Generally, the Nernst diffusion boundary is very thin compared to the size of electrodes [13]. Its thickness can be determined by experimental correlations [28] or analyzed by computational fluid dynamics (CFD) codes [14].

2.2.2. Boundary conditions: mass flux

The boundary conditions of electrorefining are the dissolution of metal species from the anode into the molten salt, and the deposition of ionic species from the molten salt onto the cathode. Both boundary conditions are electrochemical reactions (i.e., oxidation and reduction). The sources and sinks on the surfaces of electrodes for electrical charge can be calculated by using Faraday's law according to equation (4), which converts the current density to mass flux:

$$m_j = \frac{i_j}{z_j F} \tag{4}$$

where m_j is the mass flux of ionic species j from or to the electrode (mol s^{-1} cm^{-2}), and i_j is the corresponding current density (A cm^{-2}). m_j from equation (4) is used as the Neumann boundary condition for the anodic and cathodic reactions to obtain equations (5) and (6), respectively:

$$m_j^a = \frac{i_j^a}{z_j F} \tag{5}$$

$$m_j^c = -\frac{i_j^c}{z_j F} \tag{6}$$

2.2.3. Electrochemical kinetics for mass flux

To determine the mass flux of ionic species at the anode and cathode, their current densities have to be determined first. The current densities of electrochemical reactions in electrodes are calculated by equations (7) and (8). We ignore the reverse reactions for both anode and cathode, but both equations are still concentration-dependent relations of the current and potential.