

## Preliminary Investigation of Simulating Electrode Potential for Process Monitoring-based Safeguards for Pyroprocessing

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### 1. Introduction

The safeguards-ability of nuclear fuel cycle facilities has to be ensured internationally. Traditional facilities have fulfilled their safeguards using the traditional mass balance based approaches and containment/surveillance systems. Pyroprocessing, however, may require the use of alternative safeguards technologies because of its unique design and process characteristics. Process Monitoring (PM), in this regard, has been suggested as a supplementary safeguards technology [1]. PM has been used in industry to consistently produce high quality products [2] and can provide advantage for nuclear safeguards with its capability to provide real time monitoring.

Electrorefining is a key unit process in pyroprocessing. In the electrorefining process, various elements (actinides, lanthanides, etc.) are dissolved out from spent fuel which acts as an anode. Simultaneously, uranium is selectively deposited on a cathode according to its electrochemical property. Because cathode potential changes as the deposited materials accumulate, monitoring electrode potential can be useful for safeguards through observations of the operating state [3]. To develop a method that distinguishes between a normal and off-normal operating states, two objects are needed. One is a methodology to distinguish the state of the process, and the other is a signal. Studies on examining the use of PM for pyroprocessing safeguards indicated the feasibility of using such approaches [4]. These studies indicated that electrode potential can serve the signal for safeguards purposes. However, as producing real signals using real process materials is impractical, using the tool of simulation with a computer code is needed in a related research.

In this study, to investigate the validity of simulating the electrode potential with a computer code, test case experiments were conducted to examine the differences between the results of simulation and experiment. Cathode potential was recorded during electrodeposition and the results were compared with simulation results. In the experiment, lanthanides (cerium and lanthanum) are used as surrogate materials instead of U or TRU elements.

### 2. Methods

In this section, the employed computer code (ERAD), experiment design, and operating conditions are described.

#### 2.1 ERAD

ERAD is a one-dimensional electrochemical kinetics and transport analysis code [5]. ERAD simulates various (i.e., major and secondary) phenomena related to electrorefining including the description of thermodynamics, kinetics, diffusion, anodic passivation layer, and solubility limit. ERAD uses three major equations to simulate the system. Each equation simulates a specific phenomenon: the Nernst equation defines the equilibrium potential; the Butler-Volmer equation addresses the reaction rate at the electrode surface; and finally, the diffusion equation, with a migration term, evaluates mass transfer near each electrode.

Input parameters, required to run the ERAD code, can be categorized into six groups based on their functions: the electrochemical property section, the operating condition section, the cell design/geometry section, the solver pack (LSODE) section, the output setting section, and the element property section. Among these six categories, two can be determined through the experiment. These include the electrochemical property group, which can be calculated using experiment results along with the electrochemical analysis, and the operating condition group. There are a variety of outputs from the ERAD. These outputs include composition changes of the cell (anode, cathode, electrolyte), and the electrode potential.

#### 2.2 Experiment

Experiments were performed in a glove box under an argon atmosphere, with less than 1 ppm of both oxygen and moisture.

The operating temperature measured by a chromel-alumel thermocouple was 773 ( $\pm 3$ ) K. The electrolyte, composed of 44 wt% LiCl-KCl eutectic. Two types of lanthanide element chloride were used at varying concentrations. These were melted in the alumina crucible. All reagents were ACS grade and purchased from Alfa-Aesar.

The electrochemical cell consists of three components: a working electrode, a counter electrode, and a reference electrode. The working electrode is a 1 mm diameter Molybdenum (Mo) wire. The immersed length of the working electrode is 2 ( $\pm 0.1$ ) cm. The counter electrode consists of a Ce rod (6.35 mm diameter

and 50 mm length) located in a stainless steel basket. An Ag/Ag<sup>+</sup> electrode was used as the reference electrode. It is composed of a silver (Ag) wire (0.5 mm in diameter), immersed in 1 wt.% AgCl in LiCl-KCl eutectic. The eutectic is in a mullite tube with outer and inner diameters of 6 mm and 4 mm, respectively. All electrodes were sheathed in alumina tubes to prevent electrical conduction between materials. A schematic of the electrochemical cell is shown in Fig. 1.

A potentiostat/galvanostat (Biologic, SP-150) with EC-lab software were used for the electrochemical analysis.

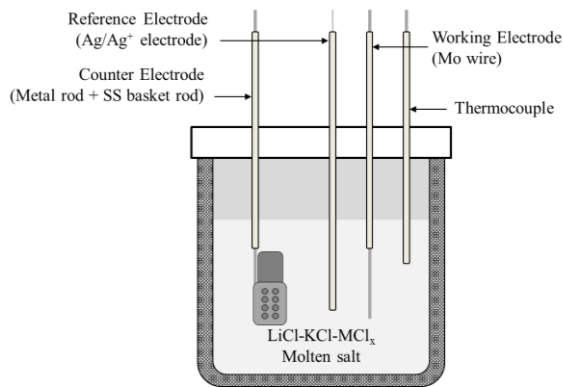


Fig. 1. The electrochemical cell design for experiment.

### 2.3 Operating Condition Development

For the purpose of nuclear safeguards, various operating conditions of electrorefining, including unintended situations, need to be considered. In this study, experiment conditions were designed based on the Nernst equation which defines an equilibrium potential as follows.

$$E = E^{\circ} + \frac{RT}{nF} \ln C_{ox}$$

where,  $E$  is equilibrium potential [V],  $E^{\circ}$  is formal potential,  $R$  is gas constant [8.314 J/mol·K],  $T$  is temperature [K],  $n$  is the number of electrons transferred,  $F$  is the Faraday constant [96,485 C/mol], and  $C_{ox}$  is the bulk concentration of reactant [mol/cm<sup>3</sup>]. Since  $R$  and  $F$  are constants and  $n$  is considered a constant, the equilibrium potential can be defined as a function of  $T$  and  $C_{ox}$ . Therefore, in the experiment, temperature and reactant concentrations are variables.

To investigate the validity of the computational model, electrode potential measurements were conducted using 6 test cases as shown in Table I. These test cases represent examples of abnormal operation conditions related with operating temperature and species concentration. The operating temperature can vary due to malfunction of the electrorefiner heater and was assumed to range between 450 and 550 °C. In terms of species concentration, the increase of Pu concentration relative to U concentration should be limited to prevent co-deposition of Pu on the cathode which could be related to an act of diversion. To represent this abnormal

condition, the cell composition was determined on 3 wt% of CeCl<sub>3</sub> and 3 wt% of LaCl<sub>3</sub>. On the other hand, for the normal operating case, the cell is composed of 3 wt% CeCl<sub>3</sub> in LiCl-KCl eutectic salt to clarify pure cerium deposition. The summarized cell compositions are listed below:

- 1) 3 wt% Ce – to deposit only Ce (normal situation)
- 2) 3 wt% Ce and 3 wt% La – to deposit both Ce and La (abnormal situation).

Table I: experiment test conditions

| Test | Temperature [°C] | Composition [wt%] |    |
|------|------------------|-------------------|----|
|      |                  | Ce                | La |
| 1    | 450              | 3                 | 0  |
| 2    | 500              | 3                 | 0  |
| 3    | 550              | 3                 | 0  |
| 4    | 450              | 3                 | 3  |
| 5    | 500              | 3                 | 3  |
| 6    | 550              | 3 </td <td>3</td> | 3  |

### 2.4 Analysis

The deposition experiment was conducted using Chrono-potentiometry (CP). Constant current (from -10 mA to -30 mA) was supplied to the cathode for 2 hours. Cyclic Voltammetry (CV), and Linear Polarization (LP) were applied to obtain the ERAD input parameters. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES; Agilent, Agilent ICP-OES 720) was employed to measure the composition of the deposits and electrolytes.

The deposit samples were prepared by cutting a 3 cm segment from the immersed portion of Mo electrode, and dissolving it in reverse aqua regia (HCl : HNO<sub>3</sub> = 1 : 3).

## 3. Results and Discussion

Fig. 2 is an example of the results comparing the experiment and simulation data for test case 5.

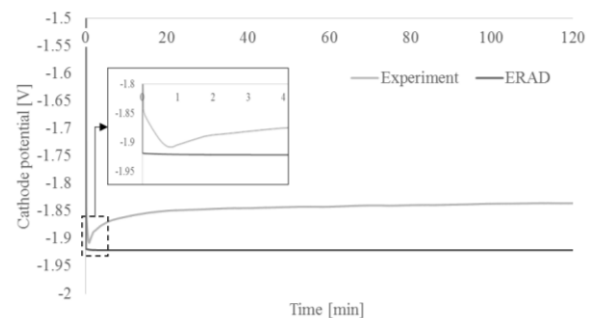


Fig. 2. Comparison result between experiment and simulation in test case 5.

The current density determines when and how much reduction occurs. When current is supplied constantly, the electrode surface area becomes an important factor since it determines the current density. In a real system, because of deposits, the electrode surface area increases

during the process. Therefore, the current density decreases gradually. However, with the ERAD, since the electrode surface area is fixed as a point value, the growth of the electrode's surface area is not described. Therefore, regardless of operation, the ERAD considers the surface area and the current density as constants. This discrepancy needs to be taken into account in the experiment and in the use of ERAD. In the experiment, the electrode potential was also slightly increased during the operation while in the simulation, the electrode potential was maintained constantly.

Another difference between the ERAD simulation results and experimental results is caused by the uncertainty in the standard exchange current density, which is an ERAD input parameter. This parameter is obtained by a LP analysis, and calculated via a Tafel plot. Because this analysis method is extremely sensitive to the variations of the experimental conditions and also analysis conditions, accurate and careful analysis are necessary with the use of multiple trials experiments.

Examining Figure 2 also indicates the presence of a dented portion in the display of the cathode potential from the experiment. This does not align with the ERAD simulation result. When the current is supplied, the reactant around the electrode is rapidly consumed and exhausted by the reduction reaction. If there is enough reactant surrounding the electrode, this phenomenon should not appear in the graphed data. However, since such short term behavior cannot be simulated by the ERAD, the resulting graph shows a plateau shape.

#### **4. Conclusions**

In this study, the validity of using the ERAD (a 1-D electrorefining simulation computer code) to simulate cathode potential was investigated by comparing experimental results with simulation results. Various test cases were designed based on the Nernst equation. The reasons for discrepancies were discussed. Even though the ERAD lacks accuracy, current results support the view that the code could acceptably simulate the cathode potential with the addition of further research. Future work will include experiments with more variations in conditions and will be conducted with the addition of a ternary system. Furthermore improvements will be investigated with the goal of increasing the similarity between experimental results and simulation results.

Electrode potential is a promising process monitoring parameter in pyroprocessing for safeguards. If the results can be acceptably improved, they will be used to produce data which simulates real process materials including TRU. Finally, it will provide an environment for developing acceptable PM methods.

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