INL/EXT-10-20002

International Nuclear Energy Research Initiative Development of Computational Models for Pyrochemical Electrorefiners of Nuclear Waste Transmutation Systems

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INTERNATIONAL NUCLEAR ENERGY RESEARCH INITIATIVE

Development of Computational Models for Pyrochemical Electrorefiners of Nuclear Waste Transmutation Systems

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Collaborators: University of Idaho and Seoul National University

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Research Objectives

In support of closing the nuclear fuel cycle using non-aqueous separations technology, this project aims to develop computational models of electrorefiners based on fundamental chemical and physical processes. Spent driver fuel from Experimental Breeder Reactor-II (EBR-II) is currently being electrorefined in the Fuel Conditioning Facility (FCF) at Idaho National Laboratory (INL). And Korea Atomic Energy Research Institute (KAERI) is developing electrorefining technology for future application to spent fuel treatment and management in the Republic of Korea (ROK). Electrorefining is a critical component of pyroprocessing, a non-aqueous chemical process which separates spent fuel into four streams: (1) uranium metal, (2) U/TRU metal, (3) metallic high-level waste containing cladding hulls and noble metal fission products, and (4) ceramic high-level waste containing sodium and active metal fission products. Having rigorous yet flexible electrorefiner models will facilitate process optimization and assist in trouble-shooting as necessary. To attain such models, INL/UI has focused on approaches to develop a computationally-light and portable two-dimensional (2D) model, while KAERI/SNU has investigated approaches to develop a computationally intensive three-dimensional (3D) model for detailed and fine-tuned simulation.

Research Progress

Database Compilation and Experimental Measurements

The assessment of accurate thermodynamic and electro-kinetic data of the involved species in electrorefining process is of high importance in order to boost the reliability and credentials of the computational models. During FY-10, to further aid the development/validation of the models, the rotating cylinder hull (RCH) cell with aqueous electrolyte (see Fig.1) was used as a means to further generate electro-kinetic data. The RCH cell is widely acknowledged as a useful experimental tool for the investigations of various electrochemical deposition behaviours. The RCH cell allows the control of aqueous electrolyte fluid dynamics and the mass-transport of reaction species while providing various electrochemical signals. The deposition behaviour of uranium to a rotating cathode shares much commonality with the metal (e.g., copper) deposition behaviour of the aqueous RCH cell. Thus, the aqueous RCH cell enabled us to examine a wide range of electrochemical behaviours and was useful to validate the developed models for molten salt electrorefining system indirectly without needing additional electrorefiner processing data.

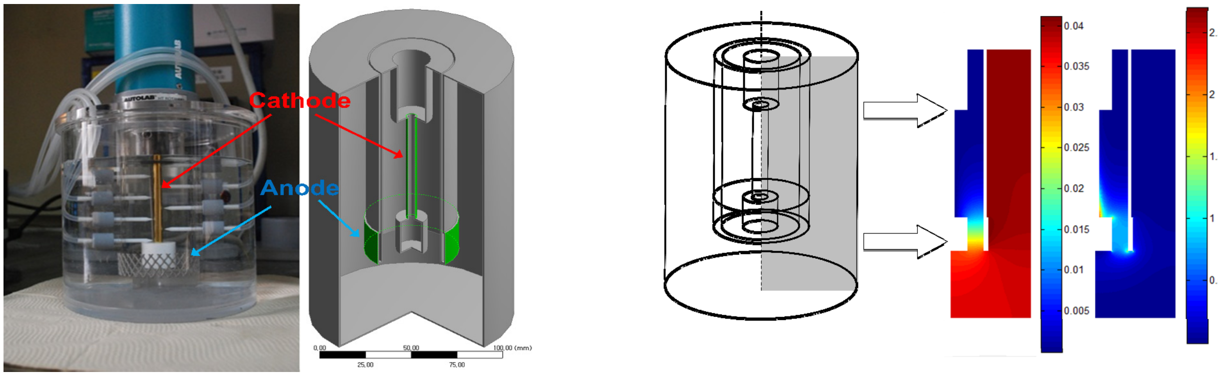


Figure 1. Aqueous rotating cylinder Hull (RCH) cell equipment and the associated model

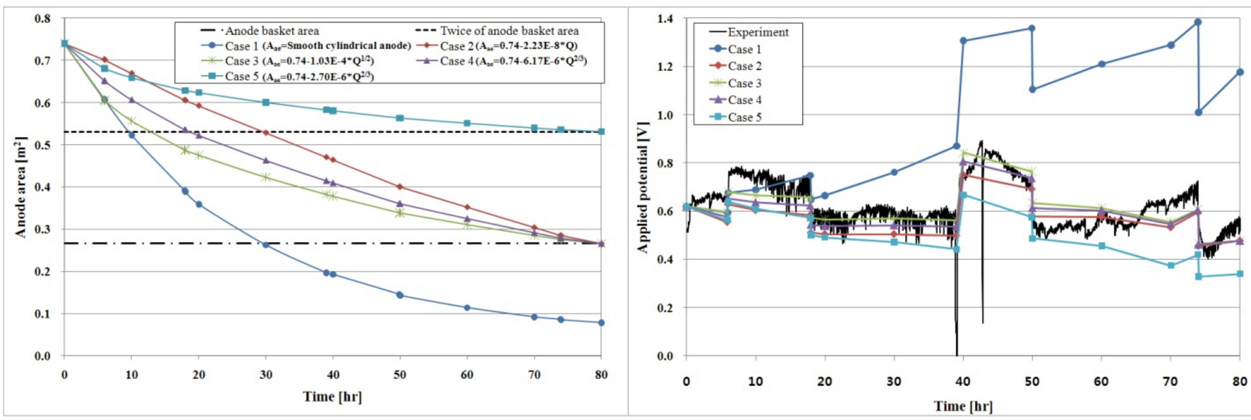
Besides active data synthesis with the RCH cell, detailed conditions and parameters for a Mark-IV electrorefiner experiment were compiled and distributed to the participants for the validation of the developed models. It is very important to note, however, that this only included conditions and not actual results. The project participants were asked to simulate the experiments. This would allow for both cross-validation of the models and for comparison to experimental data by INL-only (to only be reported to the other participants at a later date contingent upon approval for export control by the U.S. government.

3D-Model Development

During FY-2010, KAERI/SNU continued the development of a 3D electro-fluid dynamics model of the Mark-IV electrorefiner. The model framework combines electrochemical behaviors (solved with REFIN) and molten salt fluid dynamics (solved with ANSYS-CFX) effectively. FY-2010 efforts were focused on accurately simulating the cell potential of the Mark-IV electrorefiner by examining various anode surface profiles. The cell potential is the summation of potentials incurred from various interconnected phenomena. The developed 3D model accounts for anode potential (E_{anode}), cathode potential ($E_{cathode}$), ohmic drop (IR_{Ohmic}), cathodic overpotential (η_c), and anodic overpotential (η_a). Uranium is the primary metal being electrochemically active throughout the process. Thus, it is reasonable to assume that the active surfaces of the anode and the cathode would be uranium metals throughout the process. For this reason, it is assumed that anode potential offsets cathode potential. Then, the applied potential is represented as the summation of overpotentials and ohmic drop. That is, $E_{applied} = \eta_a + IR_{Ohmic} + \eta_c$.

The prescribed overpotentials and ohmic drop are functions of the current densities. As the total current information is only available, it is important to model effective electrode surface area profiles accurately in order to simulate the precise evolution of the current densities, in turn, overpotentials and ohmic drop. While using a growing cylinder to model the effective cathode surface area profile, SNU/KAERI considered five effective anode surface area profiles.

Figure 2 shows the evolution of the considered anode surface area profiles (Fig. 2 (a)) and the associated cell potential calculation results compared to the measured data (Fig. 2 (b)). All profiles have the same initial effective area, which is the summation of fuel pin segment areas. The first case assumes a shrinking smooth cylinder model with respect to the transferred charges. The second case considers the linear retraction of anode surface area. The final effective anode area is assumed to be that of metal anode basket without perforations. The third and fourth anode surface area profiles examine nonlinear retraction rates of the second case. The fifth case assumes that the final anode surface area would increase to twice of the anode basket area. The rationale is that local redox processes may incur the roughness of anode basket surface, which may entail the increased effective anode surface area. Root Mean Square Deviation (RMSD) evaluation revealed that the third case (square root retraction rate) gives the best fitting result among the considered cases.



(a) (b)

Figure 2. (a) Anode surface area profiles and (b) the corresponding cell potential calculations

<u>Model Validation with RCH cell</u>

Equipped with data generated from the RCH cell, 2D and 3D models were developed by INL/UI and KAERI/SNU, respectively. The models calculate the potential and the current distributions throughout the cell. In principle, both modeling approaches involve solving the Laplace equation ($\nabla^2\phi = 0$) to give potential (ϕ) distribution over the defined RCH cell geometry. Then, ohm's law ($-\kappa\nabla\phi = j_{cell}$) is applied to calculate the current (j_{cell}) distribution, where κ is electrolyte conductivity. At the non-electrode boundaries, it can be assumed that there is no current flow; therefore, the Neumann boundary condition ($\nabla\phi = 0$) is applied. At the anode, the current distribution is assumed to be uniform at the applied current density. The cathode boundary condition takes into account the electrochemical overpotentials and the ohmic drop.

Figure 3 (a) shows the measured potential values for the RCH cell referenced to various vertical cathode locations. Also shown are the corresponding calculated potentials for various current density operations with KAERI/SNU 3D model. The graph shows good agreement between the measured potentials and the corresponding calculated values. Figure 3 (b) and Figure 3 (c) show the current distributions calculated from INL/UI 2D model and KAERI/SNU 3D model, respectively. For the 2D model, there are some issues in calculating the current distributions at the higher applied currents approaching the limiting current due to limited memory of the computer used for performing the calculations. The result will be updated soon using better computing equipment. Regardless of minor numerical issues, the general trends reveal excellent agreement between the models throughout the considered operating conditions. This reinforces the validity of the both modeling approaches.

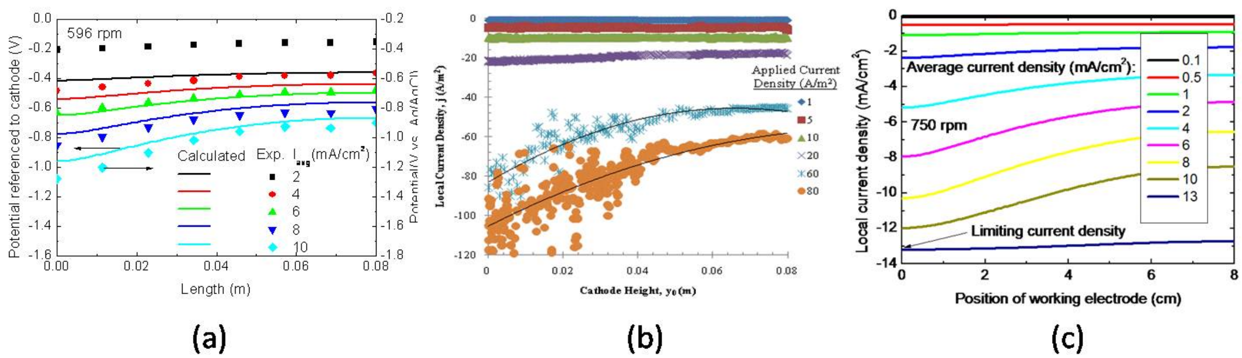


Figure 3. RCH cell cathode potential measurements and calculation results with models