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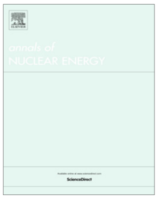

Development of a 1D transient electrorefiner model for pyroprocess simulation

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ABSTRACT

Development of an efficient 1-dimensional computer code to model mass transport and separation in electrorefining, a key component process of pyroprocessing, is described in this paper. A variety of phenomena occurring in electrochemical devices is reviewed along with examination of existing computer models to provide basis for new model development. Key processes and phenomena of importance were selected based on describing rate-limiting steps and separation efficiency of electrorefining. The developed model, named ERAD, describes time-dependent behavior of multi-component electrochemical systems with the capability of depicting anodic dissolution of spent nuclear fuel, non-hydrodynamic mass transport effects in the electrolyte, and cathodic deposition of materials. Utilization of the model is demonstrated through comparison with existing experimental data. For the purpose of model validation, model predictions are also compared with cyclic voltammetry and other experimental data.

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1. Introduction

Molten salt-based pyroprocessing technology is being examined internationally as an alternative to treat spent nuclear fuel over aqueous technology. The technology has been demonstrated in an engineering scale with irradiated fuel elements from the Experimental Breeder Reactor II (EBR-II) at the Idaho National Laboratory (INL, formerly Argonne National Laboratory – West). Currently the pyroprocessing facility at INL is used to treat all of fast reactor spent fuel elements from EBR-II before final waste disposal.[1] Pyroprocessing is also actively investigated in countries with on-going research programs on fast reactors. These include Russia, Japan, India, and South Korea. In the case of Russia, pyroprocessing has been used to treat spent fuels from fast reactors.

Pyroprocessing is a generic term for high-temperature methods. Rather than using water and organic compounds as solvents, molten salts (e.g. LiCl + KCl or LiF + CaF_2) and molten metals (e.g. cadmium, bismuth) are used as solvents in pyroprocessing. The method was first used in 1930 (Driggs and Lilliendahl, 1930) to separate uranium out of the mix of KUF_5 and UCl_4 in a molten salt system of NaCl–KCl. Electrodeposition of uranium from a BaCl–KCl–NaCl–UCl_3 melt was also confirmed as part of the Manhattan project in the early 1940s. But in comparison to aqueous technology, the product of pyroprocessing was not of high purity. Due to the inherently low decontamination factor for fission products, a large decay heat and high radiation field were present in the fuel product. Thus, this method was not chosen for the purpose of the Manhattan project.

The evolution of the modern pyroprocessing technologies in the US began in the mid-1980s at Argonne National Laboratory as part of the Integral Fast Reactor (IFR) Program Laidler et al., 1997. The work was to take advantage of the fact that pyroprocessing provides the potential for total actinide recycling without resorting to individual separation schemes providing built-in proliferation resistance to the fuel cycle. With pyroprocessing, an integral fuel cycle concept can be realized in which the irradiation, processing, and fabrication facilities are located on the same site, thus facilitating the necessary safeguarding effort. As the process does not use solvents containing hydrogen and carbon, which are neutron moderators, the risk of criticality accidents is lower.

In the current investigations on pyroprocessing, one of the main issues is to improve the efficiency of materials separation. Increased separation efficiency translates into more effective management of spent fuel and improved economic efficiency of nuclear materials recycling. In this regard, the effort to improve separation efficiency deals with design optimization of electrorefining (ER), the step to separate actinide elements from the fission products in the spent nuclear fuel.

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[1] This treatment was deemed necessary for the stability of the waste form as the fuel element contains metallic sodium as a bonding material. Metallic sodium reacts with water to form sodium hydroxide and hydrogen gas. The resulting solution is corrosive and the released gas may pose a pressurization and/or explosive hazard. Treatment by pyroprocessing will separate sodium as part of the metallic waste form.

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Design optimization of ER by using actual spent nuclear fuel materials is problematic for both technical and political reasons. Therefore, the initial effort to improve the efficiency of materials separation is typically performed by using computer models. Availability of a well-developed computer model provides a good basis for actual process design and optimization.

The purpose of this research work is to develop a simulation tool for ER process design and optimization. The new model should be computationally efficient to perform design optimization while being capable of describing important processes related to material separation.

For this purpose, major processes and phenomena involved in ER of spent nuclear fuel are reviewed to provide basis for the modeling effort. A new model was developed based on this review, and was tested against data appropriate for model validation.

2. Review of electrorefining and previous modeling work

The central element of the molten salt-based pyroprocessing process is ER, which separates actinide elements from the fission products present in spent nuclear fuel. Electrorefining is a widely used process in the minerals industry to purify impure metals.

Electrorefining of spent nuclear fuel in a molten chloride electrolyte takes place in two steps. First, metals at the anode are chlorinated through electrochemical reactions. Then, metal chlorides are selectively de-chlorinated at the cathode surface through more electrochemical reactions. Of the species present at the anode, the most active are chlorinated. Correspondingly, of the species present in the molten salt electrolyte, the most noble are dechlorinated at the cathode. Thus that most noble metal that can dissolve from the anode should ideally be the only metal deposited on the cathode.

Diffusive mass transfer often limits reaction rate in electrochemical systems. In particular, diffusion affects the concentration at the electrode surface. At electrode surfaces, a thin laminar fluid layer is formed (within 2 μm to 1 mm of the surface). The only way that material can cross this boundary is via diffusion and electromigration. This is because flow is parallel to the electrode, and there is no turbulence.

As the anode is composed of impure fuel, some of the impurities will remain on the surface of the anode after the uranium is dissolved away. These impurities form an additional barrier to mass transfer. This layer of metallic impurities will be referred to as a passivation layer, since it inhibits the uranium chlorination reaction. The layer's properties will change depending upon anode composition.

Many models have been developed over the years to describe the ER process. Initially the models were relatively simple, and were based primarily on the concepts of thermodynamics and diffusion. Gradually models have become more sophisticated to handle many other phenomena.

For example, as part of the Integral Fast Reactor program, Johnson developed a model based on chemical equilibrium to predict electrorefiner behavior at Argonne National Lab (ANL) Johnson, 1988. A few years later in 1991, ANL developed PYRO—one of the first computer models of uranium electrorefiners developed. It also relied solely upon thermodynamic considerations to produce predictions. Despite its simplicity, it helped to improve the ability to optimize ANL's electrorefiner operations (Ackerman, 1991).

TRAIL is a model developed by CRIEPI (Central Research Institute of Electric Power Industry) in Japan based on describing thermodynamics and steady state diffusion. The electrodes were lumped into single points (Kobayashi and Tokiwai, 1993), implying that only electrodes lying along equipotential planes can be modeled accurately. Therefore, TRAIL is good for electrorefiners operating in the steady state, with electrodes along equipotential planes.

Shortly after, DEVON was developed as an extension to TRAIL and includes the effects of the electrolyte resistance on electrodes that are not on equipotential surfaces. In this upgrade, the electrodes are modeled in two dimensions in order to show more detail. Results compared well to measured cell potentials, but they did not account for activation overpotential. This may mean that the predicted potential distributions are slightly skewed. Nonetheless, it appears to be a useful code when the assumptions are met (Kobayashi et al., 1997).

Nawada and Bhat developed a model that relies upon thermodynamic analysis and does not rely upon electrochemical properties such as standard potential. Rather, it relies on Gibb's free energies and equilibrium constants. It also includes the solubility constraint for metals dissolved in liquid cadmium electrodes. The approach divides the system operation into several modes of operation where unique sets of equations can be solved. It is specific to electrorefiners that include only uranium and plutonium, although it can be generalized with modification (Nawada and Bhat, 1998).

Ahluwalia went farther and developed a more sophisticated model, the General Purpose Electrochemical Simulator (GPEC). It considers both Butler–Volmer kinetics and steady state diffusion. GPEC is user friendly due to a system to create cells with numerous electrodes of various types (Ahluwalia et al., 2001, 1999).

REFIN was developed in an effort to relax the steady state assumption and to include electromigration in the analysis. REFIN appears to be the most capable code available that does not engage in the computational expense of calculating effects related to electrode geometry such as fluid flow and potential distribution. Despite being a transient code, REFIN was tested against slowly moving data, and not against quickly moving data (Park, 1999).

Recent research by Iizuka focuses on the passivation layer that forms on anodes rich in zirconium. This layer was found to significantly alter system behavior by both limiting the anode dissolution rate, and creating the potential for noble metals to dissolve in the salt if that limiting rate is exceeded. Iizuka developed a conceptual model for this by modeling the passivation layer as a diffusion barrier. His first attempt to model dissolution of zirconium-rich fuel did not match the data because the anode potential was shifted by 200 mV (Iizuka et al., 2005). Later, he introduced a second diffusion barrier to better reproduce the data (Iizuka, 2010). Regardless of the discrepancy's origin, this model contains important components which should be included in any model attempting to model zirconium-rich fuel being electrorefined for more than a few minutes.

In recent years, focus has shifted to account for phenomena in a more integrated fashion, including the effects of fluid flow. Many of the recent models rely on CFD and FEM models. One hallmark of these simulations is the long computation time required for their completion. Most are constructed by including some set of electrochemistry relations in a CFD analysis. However, there are many levels of detail which can still be included in a 3D model, and there is more work to be done in this area (Choi et al., 2010; Lee et al., 2008, 2009; Song et al., 2010; Kim et al., 2012; Li and McNelis, 2012; Ruhela et al., 2010; Reddy et al., 2010; Agarwali et al., 2010; Ghosh et al., 2009). To remedy this situation there have been some attempts to model behavior in 2D (Hoover et al., 2009, 2011; Kim et al., 2013).

While there are several computer codes developed to predict the behavior of ER, each is unique in its own way. While some of the new modeling approaches in 2D or 3D are useful to describe the details of the process by combining effects of fluid flow and electrochemistry, they are either computationally burdensome or specific to a given design. Most of the less computationally intensive models have issues such as modeling capability, code execution, or validation. For example, TRAIL had the last large

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