Kinetic model for electrorefining, part I: Model development and validation

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ABSTRACT

Electrorefining is the key process of the pryprocessing for treatment of spent nuclear fuels. In the present study, a kinetic model for electrorefining is developed. The model has the capability to predict the kinetic features of materials dissolution/deposition at anodes/cathodes of the electrorefiner and the evolution of the partial currents of the species involved, the potentials of the electrodes, and species concentrations in the molten salt. The model takes into account the changes of the surface areas and the volumes of the electrodes related to materials dissolution and deposition. The model is validated by compared with available experimental data. This article, focusing on the model development and validation, is Part I of the systemic study on development of the pyroprocessing model. Part II of this study will focus on the applications of the model.

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1. Introduction

Pyroprocessing technology was originally developed for treatment of used metallic fuels in the U.S. and of used oxide fuels in Russia, respectively (Pyrochemical Separations In Nuclear Applications, 2004). From the 1950s to the 1970s, pyroprocessing was focused on the separation of the main fuel constituents, U and Pu, from the fission products. However, pyroprocessing was found to not completely separate the fissile materials from the fission products, which was thought to be a disadvantage at the time (Goff and Simpson, 2009). After the aqueous process, PUREX, came into use for processing nuclear spent fuels from light water reactor, research on pyroprocessing was greatly scaled back.

With increasing non-proliferation concerns, the incomplete separation feature of pyroprocessing was recognized to be an advantage to proliferation resistance over PUREX process. In the mid-1980s, pyroprocessing research was resumed in the U.S. as part of the integral fast reactor (IFR) program. The research focused on the recycle of the metallic fast reactor fuel which was an actinide-zirconium alloy (Goff and Simpson, 2009). After 1994, the technology was applied to process the EBR-II spent fuel, and through 2007 about 3.7 metric tons of the spent fuel was treated at the

Idaho National Laboratory (INL) (Inoue and Koch, 2008). The technology was also proposed to separate actinides for recycling in the accelerator-driven transmutation of nuclear waste (ATW) system (Li, 1997). Most of Pyroprocessing research in the U.S. was carried out at INL and at the Argonne National Laboratory (ANL).

Since late 1980s and early 1990s, more countries have launched research programs for the development of the molten salt chemistry and technology for pyroprocessing applications. Asian countries involved in the research include Japan, India, China and South Korea, and in Europe they include England, France, Spain, Italy, Germany, the Czech Republic and others. Pyroprocessing is now recognized as one of the core methods for treatment of nuclear spent fuels. In addition to enhancement of proliferation resistance, pyroprocessing has other advantages over PUREX (Bychkov, 1999). It is compact, which makes it possible for a processing plant to be collocated with a power plant. This precludes the need to transport the spent fuel from a nuclear power plant to a processing plant. The molten salt has high radiation resistance and does not moderate neutrons, which enables processing of spent fuels with much shorter cooling time and higher actinide concentration solutions, with fewer criticality issues.

Pyroprocessing for the treatment of the spent metallic fuel is shown schematically in Fig. 1. The heart of pyroprocessing is the electrorefiner where U, Pu and minor actinides are separated from fission products. After chopping and de-cladding, the spent fuel is put into anode basket which is immersed into the molten salt. The alkali, alkaline earth and rare earth fission products are thermal-

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Nomenclature

A	surface area or constant		μ	dynamic viscosity
B	constant		ν	kinetic viscosity
C	concentration		ρ	density
D	diffusion coefficient		m	molar weight
E	potential		n	charge number
F	Faraday constant		t	time
I	current		Δt	calculation time step
K	mass transfer coefficient			
M	molar number		*Superscript*	
$\mathbf{N}$	interface normal		0	standard potential
N	total element number		ap	apparent potential for salt/solid electrode
R	gas constant		$ap0$	apparent potential for salt/liquid electrode
Re	Reynolds number		Cd	Cadmium
S	solubility		ed	electrode
$\mathbf{Sc}$	Schmidt number		i	initial value
SF	separation factor		ms	molten salt
T	temperature			
X	concentration in molar fraction		*Subscript*	
V	volume or velocity		N	element
Z	atom number of Cd in MACd$_Z$		a	anode
a	activity		b	bulk
d	hydraulic diameter		c	cathode
f	mass flux		i	element
γ	activity coefficient		j	element
			s	surface

favored oxidized and dissolved into the salt (Nutt et al., 1995). These elements cannot be recovered at the cathode. The minor actinides, U and Pu can be electro- and/or thermal-favored oxidized and dissolved into the salt by applying an electropotential or a current. Laboratory experiments have shown that 99.7% of the actinides in the spent fuel at the anode can be dissolved (Li et al., 2005). The cladding hulls, zirconium and noble fission products are not dissolved into the salt and will stay in the anode basket as wastes (except in some extreme operating conditions). The major actinides, U and Pu can be recovered from the molten salt through electro-deposition at the cathode of the 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, the present study focuses on the liquid Cd cathode) (Nawada and Fukuda, 2005).

Worldwide recent pyroprocessing research activities have been well documented (National Programs in Chemical Partitioning, 2010). These comprise experimental demonstrations of industrial

Fig. 1. Pyroprocessing for spent metallic fuel treatment.

scale applications and the development of plant-level simulation models. The experimental studies not only are very expensive and time-consuming but also cannot simulate all cases that appear in practical operations. A good simulation model can be much cheaper and less time consuming, and an effective tool to aid in the design and evaluation of electrochemical cells. A model based on the equilibrium of the reactions at electrode/salt interface, for example,

$$UCl_3(salt) + Pu(electrode) \leftrightarrow PuCl_3(salt) + U(electrode)$$
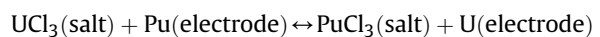
was first developed by Johnson (1988), and improved by Nawada and Bhat (1998). Recently, the model was reanalyzed by Ghosh et al. (2009), who claimed that the simulation model can treat 16 possible conditions of U–Pu alloy electrorefining that could be envisaged with respect to solubility of U and Pu at the liquid anode and cathode. However, the thermodynamic model cannot capture the kinetic features related to the evolution of the variables, for example the partial current of each element.

By applying the Butler–Volmer equation, a model that can study the kinetics of the electrorefining system was developed (Hoover et al., 2010). The authors claimed that the model reduced the guessed parameters to only one. However, the model led to some unreasonable results because the overpotential (Willit, 2011) was not used properly. The model based on diffusion control, which also can study the process kinetics, was first developed by Kobayashi and Tokiwai (1993). This model was improved to include multi-components electrorefining processes (Li, 1999). Comparisons between the modeling results and experimental data showed that the model had high accuracy. However, the model did have some deficiencies. For example, the activity coefficients of all the elements considered in the model were assumed to have a value of 1 (Li, 1999). Further, the model used the same thickness for the mass transfer boundary layer at the salt/electrode interface for all elements and cases. Considering that the thickness will change when the flow conditions of the molten salt and liquid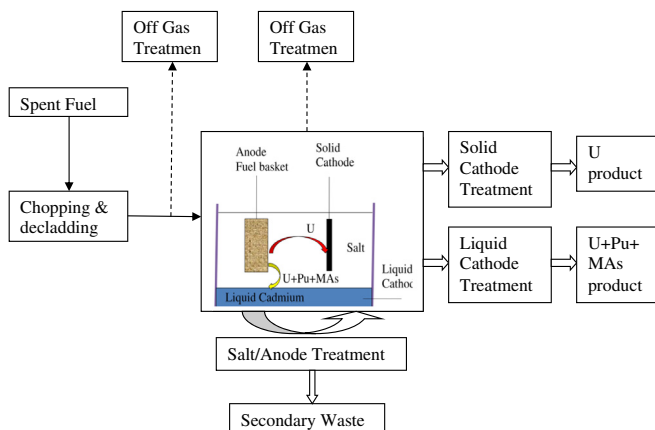 electrodes are changed, this assumption is not reasonable.