A Simulation Study for Galvanic Reduction of Metal Chloride From LiCl-KCl Eutectic Salt

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1. Introduction

Pyrochemical processing based on molten salt electrolysis is preferred over the conventional wet process for treating spent nuclear fuels in view of several advantages such as its simplicity and less secondary wastes, etc. [1]. This process also includes TRU and rare-earth drawdown steps in order to completely recover the fission products from the LiCl-KCl eutectic salt. The small amount of actinides remaining in the salt used in the electrowinning process is treated by a drawdown step to remove it from the salt before being transferred to the salt purification process.

A residual actinide recovery (RAR) process has been developed by combining the electrolysis and oxidation in the molten salt contacting with immiscible Cd phase [2]. This process is also useful to control TRU/RE ratio for SFR fuel composition.

An alternative drawdown process recently proposed is to employ a galvanic reduction for between the metals which have different redox potentials in the salt. Galvanic reduction is a spontaneous electrochemical process using an active metal as the reductant in the LiCl-KCl eutectic salt.

In this study, a modeling approach for studying an analysis of a galvanic reduction system was used to investigate whether the selective metal reduction is theoretically possible to be an alternative drawdown process.

2. Theory

2.1 Redox reaction

To recover the residual actinides from the salt waste, using chemically active rare earth metal as the reductant directly in the LiCl-KCl eutectic salt is the unique aspect of the galvanic reduction process. The galvanic reduction of actinide chloride ($AcCl_3$) is reduced by contacting the rare earth (RE) metal in the salt phase:

$$RE + AcCl_3 = Ac + RECl_3 \qquad (1)$$

Nernst equation can be employed to calculate the equilibrium potential by the RE/$RECl_3$ redox reaction, in which the reduced species are at unit activity:

$$E_{RE}^{eq} = E_{RE/RECl_3}^{0} + \frac{RT}{nF} ln\left(a_{RECl_3}\right) \qquad (2)$$

For reduction reaction of actinide chloride, an equilibrium equation is given by:

$$E_{Ac}^{eq} = E_{Ac/AcCl_3}^{0} + \frac{RT}{nF} ln\left(a_{AcCl_3}\right) \qquad (3)$$

where E^{eq} is the equilibrium half-cell potential, E^0 is the standard potential, R is the gas constant (8.314 J/K mol), T is the absolute temperature (K), n is the number of electrons transferred, F is the Faraday constant (96,487 coulomb/equiv.), and a is the activity of oxidized or reduced species. The Tafel relationship between reaction rate (i) and overvoltage

(η_a) for activation polarization is:

$$\eta_a = \frac{RT}{nF} ln\left(\frac{i}{i_0}\right) \tag{4}$$

2.2 Numerical model

Binary galvanic reaction (1) depends on the redox potential difference between two redox systems. For a multispecies system, the competing reduction reactions proceed with the potential difference (driving force) for a given oxidation of metal reductant.

For j species in a given reduction system, the variation of the partial and total current density (I) with overpotential are given by:

$$i_j(E^{eq}) = i_j(\eta_a) \tag{5}$$

$$I = \sum i_j \tag{6}$$

A set of these equations is simultaneous nonlinear system and can be solved by iteration process. .

3. Results and discussion

The use of rare earth metals to recover actinide metals has been proposed [3]. In this case, reduced metal accumulated at the bottom of molten salt bath as a precipitate as schematically shown in Fig. 1. The oxidation of the rare earth metal to form ions in the salt phase will proceed at potentials slightly less negative than the equilibrium redox potential for the metal contact with the salt. On the other hand, actinides have a reduction potential more positive than that of the rare earths. Thus, actinides are precipitated as metal from the salt without use of an electrical power supply. In association with this technology possibility, a simulation study was performed to investigate the multispecies reduction behaviors of spontaneous galvanic system.

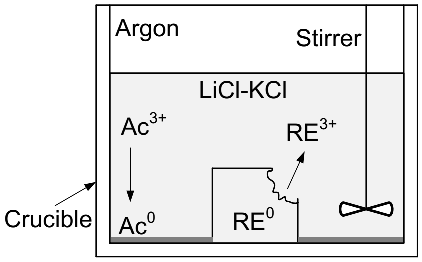

Fig. 1. Conceptual schematic of galvanic reduction system.

4. Conclusion

An analysis of a galvanic reduction system was carried out to investigate whether the selective metal reduction is theoretically possible.

REFERENCES

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