

Development of a Diffusion Model on an Integrated Cathode of an Electrolytic Reduction Process

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1. Introduction

The Advanced Spent Fuel Conditioning Process (ACP) has been developed in KAERI since 1997 to cope with a situation that the number of spent fuels increases with electricity generation. The central purpose of ACP is to reduce the volume, the radiotoxicity, and the heat load of oxide spent fuels from the current fleet of commercial PWRs and create a waste form more stable than the original irradiated fuel for storage and/or reuse. In the concept of ACP, the oxide SF is transformed metal form and high heat-generating elements such as Cs and Sr are selectively separated from the reduced metal.

Metallization by electrolytic reduction of ACP is devised to utilize electrochemical properties of a stable molten salt and eliminate the use of reducing agents such as Li and Ca which are difficult to handle because of their high reactivity. An integrated cathode composed of a porous magnesia membrane in which the oxide SF is loaded as powder form and a solid electricity conductor placed in the middle of the membrane and inconsumable anodes made of platinum are electrically connected in a Li₂O dissolved LiCl molten salt cell. As electric charges pass the cell, the dissolved lithium ions from Li₂O are reduced to lithium metals on the cathode and then the lithium metals react with metal oxides in the cathode producing lithium oxides which travel to the molten salt phase leaving behind the metals reduced from the metal oxides in the cathode. Meantime, oxygen gas is formed at the platinum anodes and dissipates into the cell's inert atmosphere. Finally, inert argon gas continuously conveys the oxygen gas out of the reactor to keep the oxygen partial pressure which affects the anode potential from rising in the cell.

Mass transfers of oxygen ions released from the metal oxides and some constituents of oxide SF desirable to be dissolved in the molten salt are studied in this study. An analytical diffusion model is proposed for a cylindrical cathode and experimental data are correlated with the model. The derived model is based on a physical diffusion theory and expected to expand its applicability readily when including electrochemical considerations.

2. Diffusion Model

On mass transfer by diffusion, Crank [1] obtained many analytical equations over various geometry and numerous boundary and initial conditions. For a long cylinder in which diffusion occurs everywhere radial, the Fick's diffusion equation becomes

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right) \quad (1)$$

If the cylinder is initially at a uniform concentration C_0 , and there is a surface condition expressed as

$$-D \frac{\partial C}{\partial r} = \alpha(C - C_e) \quad (2)$$

where C_e is the concentration required to maintain equilibrium with the surrounding and α is the mass transfer coefficient at the surface.

The analytical solution of Eq.(2) for a cylinder of radius a is obtained as

$$\frac{C - C_0}{C_e - C_0} = 1 - \sum_{n=1}^{\infty} \frac{2LJ_0(r\beta_n/a)}{(\beta_n^2 + L^2)J_0(\beta_n)} \exp\left(\frac{-\beta_n^2 Dt}{a^2}\right) \quad (3)$$

The β_n s are the roots of the following equation.

$$\beta J_1(\beta) - LJ_0(\beta) = 0 \quad (4)$$

where J_0 and J_1 are the Bessel functions of the first kind of order zero and the first order, respectively.

A dimensionless parameter L in Eq.(4) is defined as

$$L = a\alpha / D \quad (5)$$

The total amount of the considering substance at time t , M_t , leaving the cylinder is expressed as a fraction of the amount after infinite time, M_{∞} , by

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{4L^2 \exp(-\beta_n^2 Dt / a^2)}{\beta_n^2 (\beta_n^2 + L^2)} \quad (6)$$

Eq.(6) is a working equation correlating with experimental data.

3. Experiment

A high temperature molten salt reactor consists of a twofold crucible system, the inner magnesia and the outer alumina. An integrated cathode containing metal oxide (Cs₂O/SrO/BaO/Li₂O) and a thermocouple are installed through a lid of the reactor and the temperature and the pressure of the system are monitored and maintained at the system conditions of 650□ and a unit

atmospheric pressure, respectively. An air atmosphere of the reactor is replaced by argon gas before every experiment and the inert atmosphere is kept during experiments. An LiCl salt is melt under the inert condition and the amounts of dissolved substances which are loaded totally in the cathode and dipped in the liquid phase are determined with time by taking samples from the molten salt. The experimental apparatus used in the present experiments is illustrated in Fig. 1.

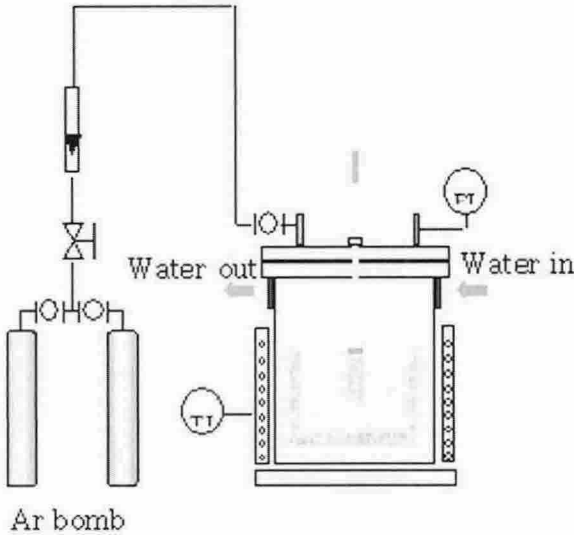


Figure 1. Experimental apparatus

4. Results and Conclusions

With the operating equation of Eq.(6), the experimental results are correlated with satisfaction as shown in Figs. 2 and 3. For calculating convenience and saving calculation times while keeping acceptable precision, the number of β s is bounded to ten.

The diffusion coefficients, D , in the cathode and the mass transfer coefficients, α , at the cathode surface increase in the order of Sr, Cs, and Ba. However, M_{\square} of Sr is greatest among three metals and that of Ba follows as shown in Fig. 2. The diffusion behavior of oxygen ions from Li_2O is sluggish when compared with those of metals. The difference of those behaviors seems to reflect different solvating mechanisms. The metal oxides adopted in these experiments are known to react with LiCl and the reactions boost their diffusion into the molten salt phase along with the concentration gradient. A basic mass transfer model is developed in this study with good accuracy describing some metal ions and oxygen ion diffusions through the integrated cathode of

the metallization process. The proposed diffusion model for a cylinder is expected to be readily applied for the electrolytic reduction process of ACP when it is combined with electrochemical concepts such as ion migration in an imposed electric field.

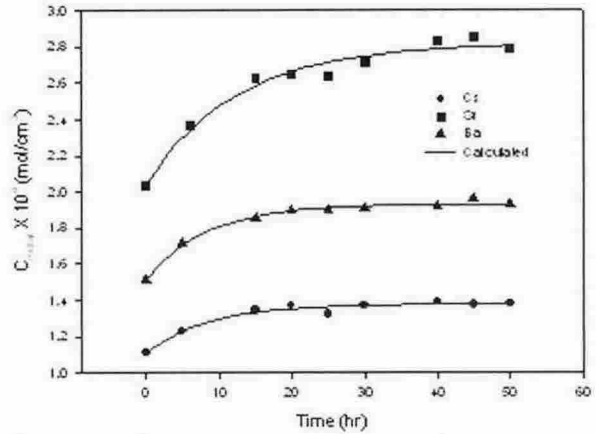


Figure 2. Diffusions of metal ions and calculated results

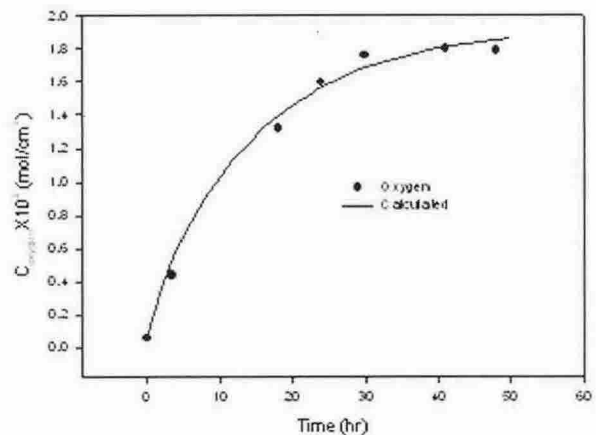


Figure 3. Diffusion of oxygen ion and calculated result

REFERENCES

[1] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, 1975.