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Development of a Mass Transfer Model and Its Application to the Behavior of the Cs, Sr, Ba, and Oxygen Ions in an Electrolytic Reduction Process for SF

물질 전달 모델 개발과 사용후핵연료 전기환원 공정에서의 세슘, 스트론튬, 바륨 및 산소 이온의 거동에 관한 적용

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Abstract

Isotopes of alkali and alkaline earth metals (AM and AEM) are the main contributors to the heat load and the radiotoxicity of spent fuel (SF). These components are separated from the SF and dissolved in a molten LiCl in an electrolytic reduction process. A mass transfer model is developed to describe the diffusion behavior of Cs, Sr, and Ba in the SF into the molten salt. The model is an analytical solution of Fick's second law of diffusion for a cylinder which is the shape of a cathode in the electrolytic reduction process. And the model is also applied to depict the concentration profile of the oxygen ion which is produced by the electrolysis of Li_2O. The regressed diffusion coefficients of the model correlating the experimentally measured data are evaluated to be greater in the order of Ba, Cs, and Sr for the metal ions and the diffusion of the oxygen ion is slower than the metal ions which implies that different mechanisms govern the diffusion of the metal ions and the oxygen ions in a molten LiCl.

Key Words : Diffusion, Alkali metal, Alkaline Earth Metal, Spent Fuel, Molten Salt

Ⅰ. Introduction

The Advanced Spent Fuel Conditioning Process (ACP) has been under development at the Korea Atomic Energy Research Institute (KAERI) since 1997 to cope with a situation where the number of spent fuels (SFs) inevitably increases and the available space in the inventory built for the SFs decreases with an increased electricity generation. ACP is based on pyroprocessing technology of which the economic potential lies in its relative simplicity and compactness [1-5] when it is compared with the aqueous processes. The aims of ACP are set to reduce the volume and the radiotoxicity as well as the heat load of the oxide spent fuels discharged from the current fleet of commercial PWRs and to create a waste form which is much more stable than the original irradiated fuel.

In the electrolytic reduction process of ACP [6,7], which is a key unit process of the whole conditioning process, an integrated cathode composed of (1) a porous magnesia membrane, (2) the oxide SF which is loaded as a powder form in the membrane, and (3) a solid electricity conductor which is placed in the middle of the oxide powder and unconsumable anodes made of platinum are electrically connected in a Li_2O dissolved LiCl molten salt cell at a high temperature. As the current passes the cell, lithium ions from the dissolved Li_2O are reduced to lithium metals on the cathode and then the lithium metals react with the metal oxides on the cathode producing lithium oxides which travel to the molten salt phase leaving behind the metals reduced from the metal oxides in the cathode. The uranium, plutonium, and TRU oxides in SF are reduced to their corresponding metals while the high heat-generating elements such as Cs_2O and SrO are dissolved in the molten electrolyte and selectively separated from the reduced metal [8,9]. Meantime, oxygen ions are oxidized to gas at the platinum anodes and dissipate into the cell's inert atmosphere. Finally, inert argon gas continuously conveys the oxygen gas out of the reactor to maintain the oxygen partial pressure which affects the anode potential from rising in the cell.

The fine pores of the magnesia filter play an important role as passages for not only the lithium ions which move inward but also the alkali, alkaline earth metal, and oxygen ions penetrating the membrane into the bulk phase of the molten salt. However, the dynamic behaviors of these materials have yet to be investigated thoroughly. In the present work, the mass transfers of the oxygen ions released from the metal oxides and some constituents of an oxide SF which are desirable to be dissolved in a molten salt are studied. An analytic diffusion model is proposed for a cylindrical cathode and the experimental data is correlated with the model. Also the concentration profiles are described by the model with discussions on the characteristics of the diffusion.

Ⅱ. Thermodynamic Analysis

The thermodynamic approach is a very practical method whenever preliminary information on the properties at an equilibrium state are required even though the estimated values are occasionally rough without complex models for considering the non-ideality. And the insight acquired by thermodynamics always helps researchers in setting the experimental boundaries and analyzing the obtained results.

The alkali metal and alkaline earth metal oxides in SF to be taken into account are Cs, Sr, and Ba of which radioactivity accounts for almost three quarters of the total radioactivity residing in the fission products (FPs). The reactions between the metal oxides and the lithium chloride are expressed as

$$M_xO + 2LiCl \rightarrow 2M_{x/2}Cl + Li_2O \qquad \cdots\cdots\cdots\cdots\cdots (1)$$

The changes of the reaction free energy for some FPs with lithium chloride are calculated from Barin's data collection [10] and the results are presented in Fig. 1. The lines denoted as *a*, *b*, and *c* in Fig. 1 represent the reactions with rare earth (RE) oxides. And the reaction free energies with some of the AM and AEM oxides are given as *d*, *e* and *f* in the figure. The reactions of the RE oxides and lithium chloride could not occur since the oxide form of RE and the chloride form of lithium are more stable than the exchanged forms. However, Cs_2O and BaO are very reactive when they coexist with lithium chloride and the reactions proceed spontaneously at high temperatures. The reaction free energy of SrO with LiCl is positive which means the reaction is not spontaneous but if the relation of the reaction Gibbs free energy (ΔG) with the equilibrium constant (*K*) which represents the composition ratio of the products over the reactants at an equilibrium state is noted the reaction needs to be speculated. The reaction free energy change of SrO with LiCl and the evaluated equilibrium constant at 650℃, for example, are 5.63 (kJ/g-mol O) and 0.48, respectively, which implies that a small amount of the reaction products would be generated.

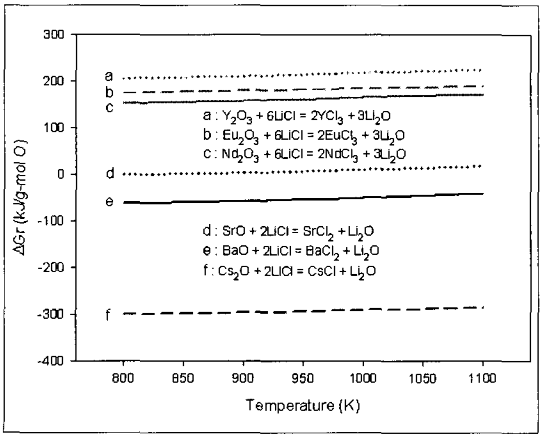


Figure 1. Changes of the Reaction Free Energy with the Temperature.

The reduction of U_3O_8 takes places by the following reactions at a cathode of the electrolytic reduction process [6,7],

$$Li_2O + 2e^- \rightarrow 2Li + O^{2-} \quad \cdots\cdots\cdots\cdots\cdots (2)$$

$$\text{(combination of } Li_2O \rightarrow 2Li^+ + O^{2-} \text{ and } 2Li^+ + 2e^- \rightarrow 2Li\text{)}$$

$$U_3O_8 + 16Li \rightarrow 3U + 8Li_2O \quad \cdots\cdots\cdots (3)$$

The same amount of electrically consumed Li_2O (Eq.(2)) is stoichiometrically produced by a chemical reaction (Eq.(3)). However, the concentration of Li_2O in a bulk phase decreases and that in a cathode - the cathode of the electrolytic process behaves as a three-dimensional electrode and the reactions occur not at the surface of the cathode but in the cathode which contains the wetted U_3O_8 by LiCl which dissolves Li_2O - increases if the mass transfer of Li_2O back to the bulk phase is slower than the reduction of Li^+ (Eq.(2)) and the chemical reaction (Eq.(3)). Thus, the mass transfer of Li_2O - the actual diffusing element is O^{2-} since Li_2O is soluble in the molten LiCl and the Li^+ is the common ion with the medium through which the Li_2O diffuses - takes place during the electrolytic reduction process.

The reduction potentials of Li_2O and LiCl at 650℃ are -2.47V and -3.46V, respectively. And those of CsCl (-3.66V), $BaCl_2$ (-3.69V), and $SrCl_2$ (-3.54V) are beyond the operation condition (-2.47V ~-3.46V) of the electrolytic reduction process [6,7]. Therefore, the chemical reactions of the AM and AEM oxides with LiCl (Eq.(1)) dominate the mass transfer of the alkali and alkaline earth metals.

Ⅲ. Diffusion Model

Diffusion models and equations have been applied to many industries such as the food and pharmaceutical industries [11] for leaching the desired elements from raw materials. On the mass transfer of a diffusion, Crank [12] arranged systematically many analytic solutions derived under various geometries and numerous boundary conditions. In the case that a considered amount of material diffuses everywhere radially and there is no axial diffusion in a long cylinder, the Fick's diffusion equation [13] is derived as

$$\frac{\partial C}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots (4)$$

Solutions of Eq.(4) are obtained in terms of Bessel functions when a method of separating variables is applied to the equation [12]. If the initial concentration, C_0, is uniform inside the whole cylinder and the mass flux at the cylinder surface is equivalent to that of the liquid phase, the initial and boundary conditions become

$$C=C_0, \text{ at } 0 \le r < a \text{ and } t=0 \quad \cdots\cdots (5)$$

$$-D\frac{\partial C}{\partial r}=\alpha(C_s-C_e), \text{ at } r=a \text{ and } t>0 \cdots\cdots (6)$$

where C_s is the concentration just within the cylinder, C_e is the equilibrium concentration where no further diffusion occurs from the cylinder and is the mass transfer coefficient at the cylinder surface. The changes of the concentration profiles are drawn with time in Fig. 2. The concentration of a cylindrical cathode decreases from the surface and the bulk concentration increases, with no concentration gradient of the bulk phase taken into consideration. Actually, the mass transfer at the surface occurs by a concentration difference between the concentrations at the surface and in the bulk (C_s - C_{bulk}). However, the concentration change in the bulk phase is very small when it is compared with that in the cylinder due to its large volume and the constant C_e, thus, is used in Eq.(6) instead of the varying C_{bulk}.

The analytic solution of Eq.(4) for a cylinder of radius with the initial and boundary conditions is obtained as

$$\frac{C-C_0}{C_e-C_0}=1-\sum_{n=1}^{\infty}\frac{2LJ_0(r\beta_n/a)}{(\beta_n^2+L^2)J_0(\beta_n)}\exp\left(\frac{-\beta_n^2 Dt}{a^2}\right) \quad \cdots\cdots (7)$$

The β_ns are the roots of the following equation.

$$\beta J_1(\beta)-LJ_0(\beta)=0 \quad \cdots\cdots\cdots\cdots\cdots (8)$$

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.(7) is defined as

$$L=a\alpha/D \quad \cdots\cdots\cdots\cdots\cdots (9)$$

Although the analytical solution of Eq.(4) is derived as Eq.(7), the concentration of the cylinder inside is difficult to measure and the available data is the concentration change in the bulk phase. In order to correlate the equation with the experimental data, the amount of the dissolving material from the cylinder into the bulk phase is evaluated at the surface by the following equation when A_c is the surface area of the cylinder where the mass transfer is taking place.

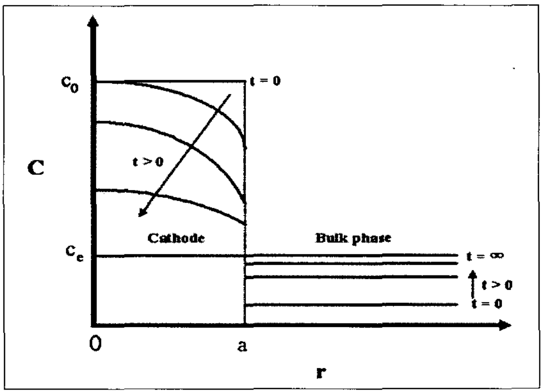


Figure 2. Concentration Profile with Time.

$$M_t = \int_0^t -DA_c\left(\frac{\partial C}{\partial r}\right)_{r=a} dt \qquad \cdots\cdots (10)$$

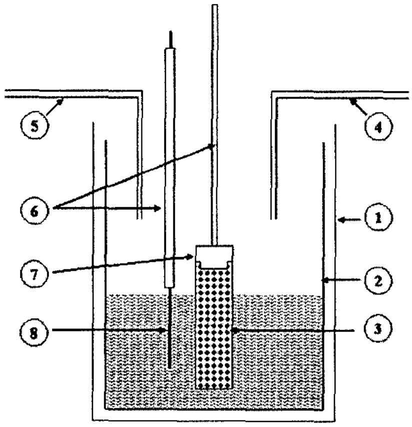
The total amount of the considered substance at time t (M_t) leaving the cylinder is expressed as a fraction of the amount after an infinite time, M_∞, by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4L^2 \exp(-\beta_n^2 Dt/a^2)}{\beta_n^2(\beta_n^2 + L^2)} \qquad \cdots\cdots (11)$$

Eq.(11) is a working equation to be correlated with the experimental data.

Ⅳ. Experiment

A high temperature molten salt reactor consisted of a twofold crucible system, the inner magnesia and the outer alumina as shown in Fig. 3. A porous magnesia filter (OD 16 mm × ID 10mm × L 80 mm, porosity : ~25%, pore diameter : 6~8 μm) was used as a metal oxide container just as in the electrolytic reduction process of ACP. A cylindrical cathode containing metal oxide (Cs_2O/ SrO/ BaO / Li_2O, 5g) and a thermocouple were installed through a lid of the reactor and the temperature and the pressure of the system were monitored and maintained at the required system conditions of 650℃ and the unit atmospheric pressure, respectively. The concentration gradient of oxygen ion takes place by reduction of Li_2O (Eq.(2)) in the actual electrolytic reduction process where Li_2O is added to the molten LiCl phase before an electric current is applied. However, it is experimentally difficult to separate the effects of the concentration gradient and the electric potential gradient on the mass transfer of the oxygen ion. Therefore, Li_2O was loaded into a magnesia filter when the mass transfer of oxygen ion was determined in order to take only the concentration gradient into account. The air atmosphere of the reactor was replaced by argon gas before every experiment and the inert atmosphere was maintained during the experiments. In the electrolytic reduction process of ACP, the SF powder is loaded into a porous magnesia filter and then enshrouded in the LiCl powder pouring into a reaction vessel. Consequently, the alkali and alkaline earth metal oxides of the SF go through the melting of the LiCl. Meanwhile, the concentration gradient of Li_2O occurs when the electric potential is applied after the LiCl melts. Accordingly, in this work, the cathode containing alkali or alkaline earth metal oxide was dipped in LiCl power (125g) before the melting of LiCl and heated to the system condition while the cathode with Li_2O was dipped in a molten LiCl (125g) after the reaction temperature was maintained at 650℃. The LiCl salt was melted under an inert atmosphere and the amounts of the dissolved substances which were initially loaded in the cathode were measured with



①Alumina crucible ②Magnesia crucible ③Porous magnesia filter ④Ar gas inlet ⑤Ar gas outlet ⑥ Alumina sheath ⑦Filter holder ⑧Thermocouple

Figure 3. Experimental Apparatus.

Table 1. Diffusion and Mass Transfer Coefficients.

	Cs^+	Sr^{2+}	Ba^{2+}	O^{2-}
D (㎠/hr)	0.0467	0.0326	0.0486	0.0118
α (㎝/hr)	0.0588	0.0406	0.0611	0.0519

time by analyzing the samples taken from the molten salt phase every five hours. The concentration of the resulting oxides were determined by titrating the samples which were dissolved in distilled water with HCl. AAS (atomic absorption sepctrophotometry) and ICP-AES (inductively coupled plasma-atomic emission spectrometry) were used to analyze the concentrations of the AM and AEM in the samples, respectively.

V. Results and discussions

The mass transfer coefficient and the diffusion coefficient were regressed from the experimentally measured concentrations with time in the molten salt phase to exhibit minimum deviations from the experimental data and Fig. 4 depicts the numerical procedure. Eq.(8) gives the infinite roots with respect to β but the effect of an additional β on the results becomes insensitive as more and more β s are included in the calculation. The value of the term containing β in Eq.(11) decreases drastically and the summation of each term reaches its maximum when the number of the considered terms exceeds eight as illustrated in Fig. 5. For a calculation convenience and saving on the calculation times while maintaining an acceptable precision, thus, ten βs from β_1 to β_{10} were taken into consideration for

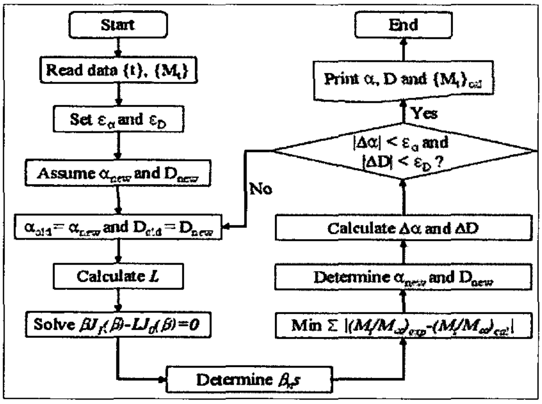


Figure 4. Flow Diagram for Determination of Diffusion and Mass Transfer Coefficients.

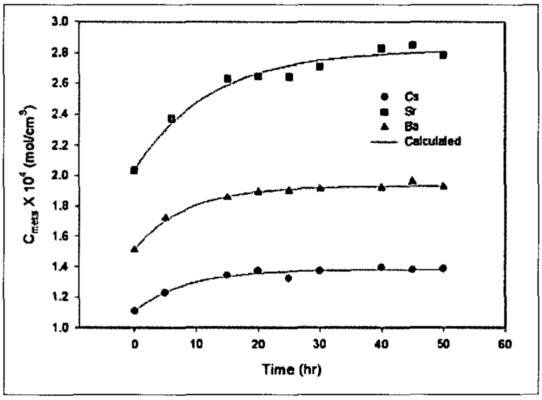


Figure 6. Measured and Calculated Concentration Changes of the Me

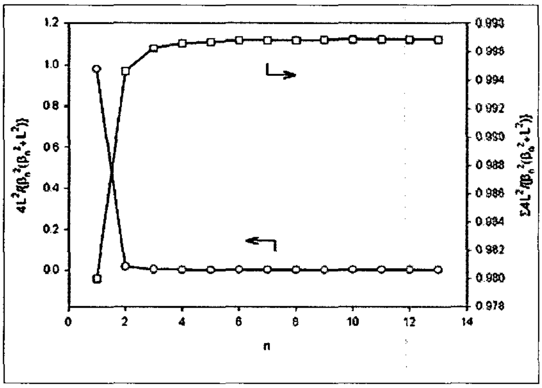


Figure 5. Term by Term and Summation of Eq.(11).

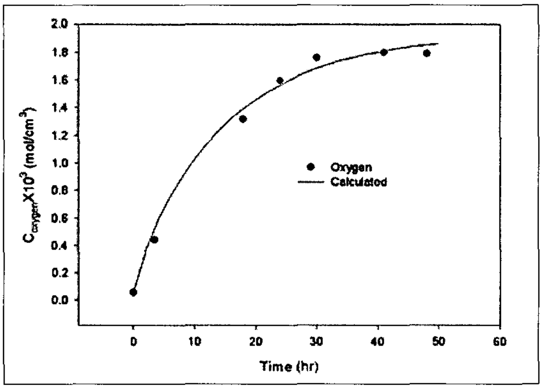


Figure 7. Measured and Calculated Concentration Changes of the Oxygen Ion.

the regression of the parameters in the present work. With the proposed model, the experimental results were correlated with a satisfaction as shown in Figs. 6 and 7. And the regressed parameters are listed in Table 1. Eq.(11) is derived from an assumption that the cylinder is homogeneous. Therefore, the diffusion coefficients in Table 1 were evaluated with an assumption that the cathode which was composed of the metal oxide and the porous magnesia filter was a homogeneous mixture of soluble metal oxide and insoluble magnesia.

The initial concentrations of Cs, Sr, and Ba in the molten salt phase were not zero which meant the metal oxides had gradually dissolved into the molten salt phase from the time when the solid LiCl began to melt in part and before the time when the system temperature was maintained at the experimental condition. However, the removal of metal oxides from the cathode could not be completed during the melting of LiCl and the effective saturation values were reached around 45 hours after the diffusion had occurred.

The diffusion coefficients and the mass transfer coefficients, at the cathode surface increase in the order of Sr, Cs, and Ba. However, the M_∞ of Sr is the greatest among the three metals and that of Ba follows as shown in Fig. 6. The dissolution of SrO could not be understood by the chemical reaction since the reaction free energy is positive as shown in Fig. 1 while the dissolving amount is greatest among the three metal oxides. In order to explain the phenomenon, the processes of dissolution of metal oxides in a molten LiCl are divided into the following steps [14].

$$MO(s) \leftrightarrow MO(l) \qquad \cdots\cdots (12)$$

$$MO(l) \leftrightarrow M^{2+} + O^{2-} \qquad \cdots\cdots (13)$$

$$M^{2+} + 2Cl^- \leftrightarrow MCl_2 \qquad \cdots\cdots (14)$$

$$O^{2-} + 2Li^+ \leftrightarrow Li_2O \qquad \cdots\cdots (15)$$

Eq.(12) describes the solvation of a metal oxide in which the metal oxide molecule of a solid state ($MO(s)$) is surrounded by solvents and then solvated as a molecular state ($MO(l)$) not an ionic state. The ionization (Eq.(13)) follows the solvation and finally the cross-interactions between the ionized solute and the molten salt take place. The thermodynamic analysis based on the free energy change considers the whole process from the solvation to the cross-interactions. However, in the case of SrO the solvation described as Eq.(12) prevails according to the study of Cherginets and Khailova [15], which means SrO is soluble but incompletely dissociated. The dissolved amount of SrO, thus, reflects the characteristics of the interaction between SrO molecules and the molten salt.

The diffusion behavior of the oxygen ions from Li_2O was sluggish when compared with those of the AM and AEM. The difference of these behaviors seems to demonstrate that there are different solvating mechanisms operating. The metal oxides adopted in these experiments are known to react with LiCl and the reaction boosts their diffusion into the molten salt phase along with the concentration gradient. According to the IR spectroscopic data which were referred to in Barbin and Nekrasov's work [16], however, the oxide ions introduced into the molten halogenides of the alkali metals by an oxidation of the melt with a molecular oxygen, form bridge complex groups including cations with high magnetic moments and chloride anions. Lithium oxides, which are gradually dissolved in the molten lithium chloride, are thus expected to form bridge complex groups and the diffusion of the oxygen ions is supposed to be retarded by the stabilized complex in the molten salt.

Ⅵ. Conclusion

An analytic mass transfer model was developed based on the Fick's second law of diffusion for a cylindrical electrode of the electrolytic reduction process in ACP. The model was applied to describe the behavior of the high heat-generating cesium, strontium and barium oxide components of SF, which dissolved in a molten LiCl and the oxygen ions which were produced as a result of the breakage of the bonds between the metals and oxygens of spent oxide nuclear fuel by the reduced Li in the actual electrolytic reduction process. The concentration changes of Cs, Ba, and Sr in the molten LiCl phase were experimentally determined by using the corresponding metal oxides in a porous magnesia filter. And the mass transfer of the oxygen ion was measured by dissolving Li_2O which has the same cation to that of LiCl to account for only the concentration gradient unlike the electrolytic reduction process where both the concentration and the electric gradients affect the mass transfer of oxygen ion.

The model was proved to be suitable for depicting the experimental data with a good accuracy. The diffusion coefficients in the cathode are greater in the order of Ba, Cs, and Sr while the amounts of dissolution are in the order of SrO, BaO, and Cs_2O which means the solvation prevails in the case of SrO which is difficult to react with LiCl according to the thermodynamic analysis. The proposed diffusion model for a cylindrical cathode is expected to be readily applicable to the electrolytic reduction process of ACP when it is combined with electrochemical concepts such as an ion migration in an imposed electric field regarding the mass transfer of the oxygen ions.

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