

MOLTEN SALT VAPORIZATION DURING ELECTROLYTIC REDUCTION

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The suppression of molten salt vaporization is one of the key technical issues in the electrolytic reduction process developed for recycling spent nuclear fuel from light-water reactors. Since the Hertz-Langmuir relation previously applied to molten salt vaporization is valid only for vaporization into a vacuum, a diffusion model was derived to quantitatively assess the vaporization of LiCl, Li₂O and Li from an electrolytic reducer operating under atmospheric pressure. Vaporization rates as a function of operation variables were calculated and shown to be in reasonable agreement with the experimental data obtained from thermogravimetry.

KEYWORDS : Molten Salt, Spent Fuel, Electrolytic Reduction, Vaporization, Diffusion

1. INTRODUCTION

The R&D program for the advanced fuel cycle in Korea is now focused on recycling spent nuclear fuel from light-water reactors. The Korea Atomic Energy Research Institute (KAERI) regards pyroprocessing as a promising recycling technology considering its enhanced nuclear proliferation resistance and environmental friendliness. Pyroprocessing is characterized by the use of high temperature molten salts as a reaction medium. The pyroprocessing method developed at KAERI consists of electrolytic reduction, electrorefining, electrowinning, and waste salt treatment. One of the main goals of the advanced fuel cycle is to make the spent oxide fuel of light-water reactors suitable as a metal fuel for sodium-cooled fast reactors. In this regard, the electrolytic reduction process, which transforms solid oxide to solid metal with reduction yields of greater than 99%, is a key process connecting the oxide fuel cycle with the metal fuel cycle [1,2].

The electrolytic reduction process developed at KAERI is carried out in a LiCl-Li₂O (1 wt%) molten salt medium at 650°C. The heat, volume, and radioactivity of the spent fuel can be decreased by the functionality of its oxide reduction and the selective dissolution of its high heat-load fission products into a molten salt [1,2]. At the same time, the vaporization of a LiCl-Li₂O molten salt has been observed under normal operating conditions for an electrolytic reduction process. Fig. 1 shows the typical state of an electrolytic reducer where the vaporized molten

salts adhere to the upper wall of the reactor after the electrolytic reduction operation. In the electrolytic reduction process developed at KAERI, Li, generated from *in situ* electrolysis of Li₂O in a LiCl-Li₂O molten salt, reduces the oxide fuel contained in the cathode basket of the electrolytic reducer. The vaporization of Li was also observed during the electrolytic reduction process.

To successfully develop the electrolytic reduction process, it is very important to suppress the vaporization of molten salt, as such vaporization results in salt loss. Of course, the vaporized salt can be recovered and sent out for salt waste treatment or to the electrolytic reducer for reuse. However, any salt vaporization compromises the overall efficiency of the process.

To optimize the electrolytic reduction system, we tried to elucidate the vaporization behavior of molten salt as a function of operation variables. The Los Alamos National Laboratory and Argonne National Laboratory have studied salt vaporization in pyroprocessing treatments of spent nuclear fuel [3-6]. In their studies, only the vacuum evaporation of salts in relation to the Hertz-Langmuir relation was investigated. However, the electrolytic reduction is normally carried out under an inert gas atmosphere. In addition, the residual salts contained in the metal products of the electrolytic reduction process should be separated by vaporization at high temperatures under reduced pressure. Therefore, we derived a diffusion-controlled vaporization equation that can be applied to the vaporization from reduced pressures to atmospheric pressure at high temperatures.

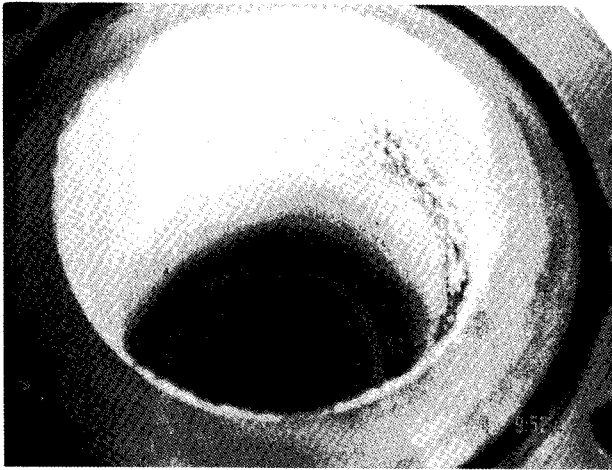


Fig. 1. Inside of an Electrolytic Reducer Covered with Vaporized Salts after Electrolytic Reduction

2. THEORY

From the Hertz-Langmuir relation based on the kinetic theory of gases [4], it can be shown that a vaporization of substance A into a vacuum is

$$J_A = \frac{\alpha P_A}{\sqrt{(2\pi M_A RT)}} \quad (1)$$

where J_A is the gas vaporization rate of substance A, α is the vaporization coefficient, M_A is the molecular weight of A, R is the gas constant, T is the temperature, and P_A is the vapor pressure of A. When the substance vaporizes into a flowing gas stream at finite pressures rather than into a vacuum, the vaporization coefficient α might not be equal to unity. Chatterjee et al. obtained the value of α as 5.8×10^{-5} in the presence of a purge gas [7]. Usually, α is larger than 0.1 [4] and this extremely small quantity was not explained by the Hertz-Langmuir relation [7].

In this paper, the vaporization of LiCl, Li₂O, and Li during the electrolytic reduction process was explained by diffusion-evaporation. For the sake of simplicity, let us consider the steady state mass flux of liquid A contained in a cylindrical tube into a gas B as shown in Fig. 2. Assume that A and B form an ideal gas mixture and that the solubility of gas B in liquid A is negligible. The gas-phase concentration of A at the liquid surface assumes a constant value that equals the equilibrium concentration at the prevailing temperature and pressure. Mass transfer in this system is one-dimensional (z direction) through a stagnant gas layer. The combined flux J_{Az} , the number of moles of A that go through a unit area of a sample interface between the liquid and gas phase in a unit time, is related to the convective flux and the diffusion flux as

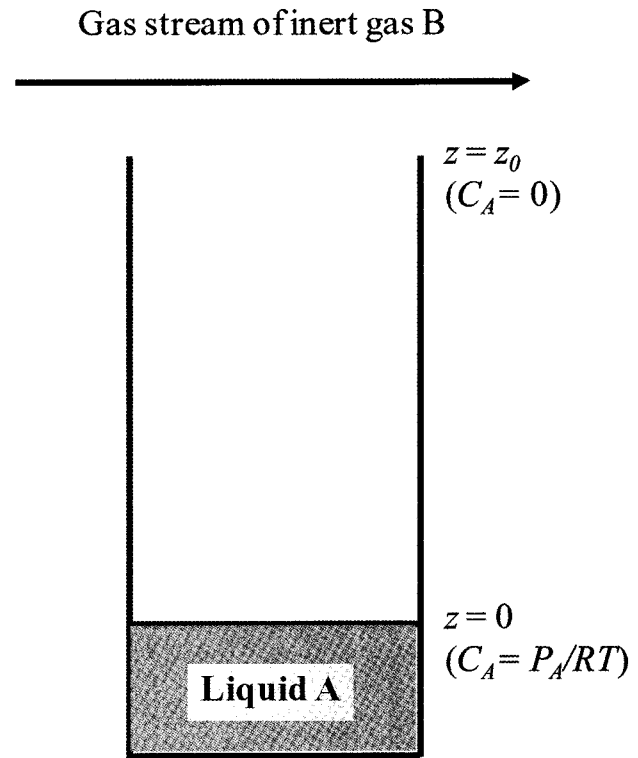


Fig. 2. Steady State Diffusion of A through Stagnant B. Gas A is Swept Away by the Purge Gas B Flowing over the Top when they Emerge from the Tube

$$J_{Az} = x_A(J_{Az} + J_{Bz}) - cD_{AB} \frac{\partial x_A}{\partial z} \quad (2)$$

Where x_A is the mole fraction of A, J_{Bz} is the combined molar flux for B, c is the total molar concentration, D_{AB} is the binary diffusivity for system A-B, and z_0 is the height of the tube occupied by gas in Fig. 2.

When this evaporating system attains a steady state, there is a net motion of A away from the interface and species B is stationary. Hence J_{Bz} is 0. From the boundary conditions

$$x_A = x_{Az} = 0 \quad (\text{at } z = z_0) \quad (3)$$

For an ideal gas mixture the equation of a state is $p = cRT$. Consequently, the evaporation rate of A at the liquid-gas interface can be obtained from Equations (2) and (3) as

$$J_{Az}|_{z=0} = \frac{-cD_{AB}}{1-x_{A_0}} \frac{dx_A}{dz} \Big|_{z=0} = \frac{pD_{AB}}{zRT} \ln \left(\frac{x_{Bz}}{x_{B_0}} \right) \quad (4)$$

To use Equation (4), D_{AB} is obtained from the Chapman-

Enskog theory as follows [8]:

$$D_{AB} = \frac{3}{16} \sqrt{\frac{2(RT)^3}{\pi} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \frac{1}{N_A p \sigma_{AB}^2 \Omega_{D,AB}} \quad (5)$$

The collision integral $\Omega_{D,AB}$ for diffusion and the Lennard-Jones parameter σ_{AB} used in Equation (5) are found in the literature [8,9]. N_A in Equation (5) is Avogadro's number. The mole fraction of B is 1 at ($z = z_0$) and $1 - p_A/p$ at ($z = 0$), respectively. For p_A , the vapor pressure variations with

the temperatures were investigated using thermodynamic data [10,11] and they are shown for LiCl, Li₂O, and Li in Fig. 3. Now, the mass loss rate of A (m_A) measured in the electrolytic reduction process and the thermogravimetry experiments can be related to the experimental parameters such as the total gas pressure (p), the evaporation surface area (S), and the evaporation distance (z) as follows:

$$\frac{dm_A}{dt} = S \frac{p D_{AB}}{z R T} \ln \left(\frac{x_{B_i}}{x_{B_0}} \right) = S \frac{p D_{AB}}{z R T} \ln \left(\frac{p}{p - p_A} \right) \quad (6)$$

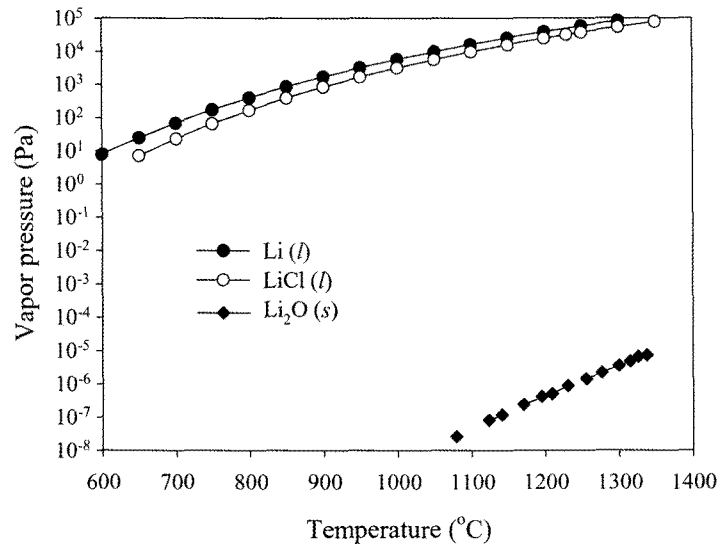


Fig. 3. Vapor Pressure Changes of LiCl, Li₂O, and Li at Various Temperatures

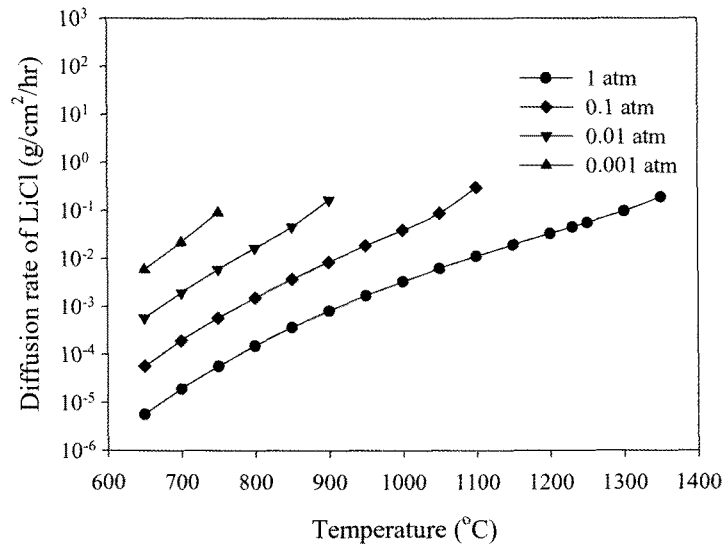


Fig. 4. Effects of Pressure on the Diffusion Rate of LiCl (z : 20 cm, Purge Gas: Ar)

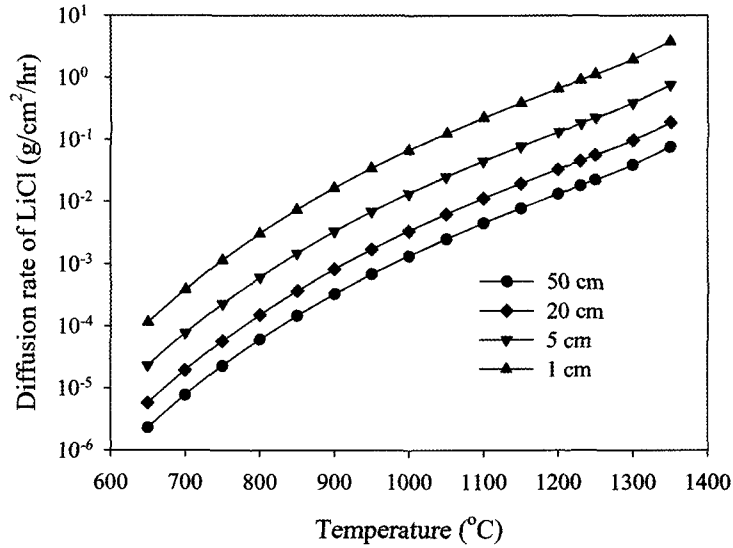


Fig. 5. Effects of Evaporation Distance on the Diffusion Rate of LiCl (p : 1 atm, Purge Gas: Ar)

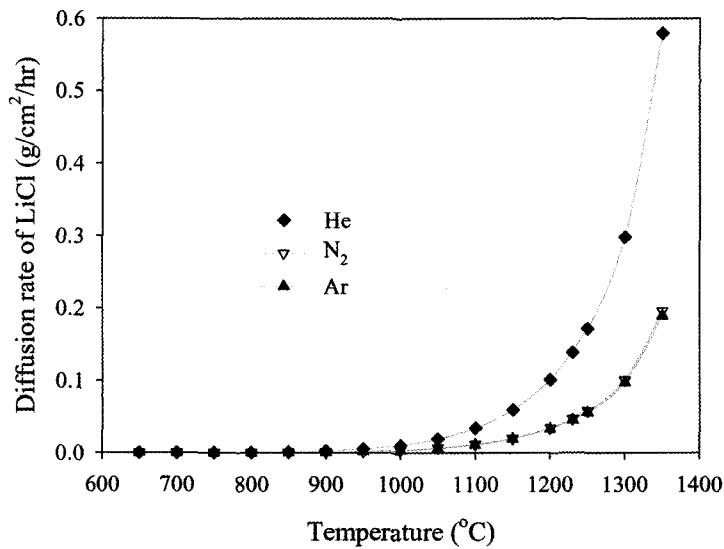


Fig. 6. Effects of Various Inert Gases on the Diffusion Rate of LiCl (z : 20 cm, p : 1 atm)

3. RESULTS AND DISCUSSION

According to Equations (4) and (6), the diffusion rates of LiCl, Li₂O, and Li were calculated to enhance understanding of the salt vaporization quantitatively. Figs. 4-5 show the diffusion rate of LiCl as a function of p and z , respectively. For Fig. 4, z is 20 cm. And in the case of Fig. 5, p is fixed at 1 atm. The diffusion evaporation rate increases with a decreasing p and z . The effect of a purge gas was also investigated. Fig. 6 shows that among the investigated inert gases, He gas is the poorest at preventing salt vaporization. When N₂ gas is used, uranium nitride formation is expected during the electrolytic

reduction of uranium oxides. In addition, Ar gas is slightly better than N₂ for decreasing the diffusion rate of LiCl. Therefore, we selected Ar as a purge gas. The diffusion rates of LiCl, Li₂O, and Li were compared in Fig. 7. Li has a higher vapor pressure and D_{AB} than LiCl. However Li has a smaller molecular weight than LiCl and so the Li diffusion rate calculated in g/cm²/hr is slightly higher than LiCl at 650°C. The melting point of Li₂O is 1,570°C and it has a very low vapor pressure as shown in Fig. 3. Hence it sublimates negligibly in the temperature range investigated.

The applicability of the diffusion evaporation model to an electrolytic reduction process was verified by

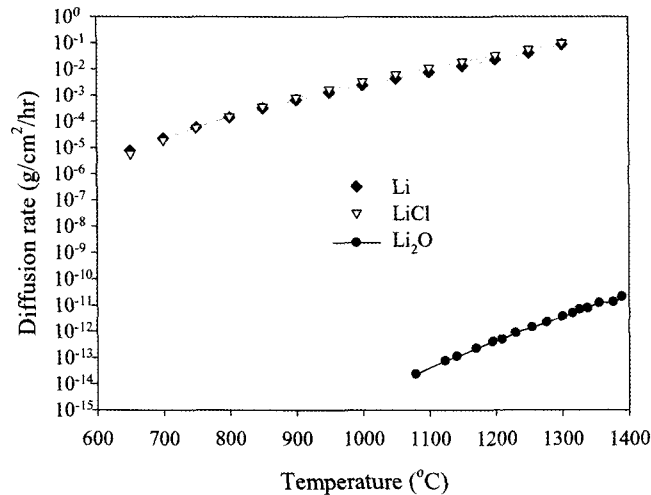


Fig. 7. Comparison of Diffusion Rates for LiCl, Li₂O, and Li (z : 20 cm, Purge Gas: Ar, p : 1 atm).

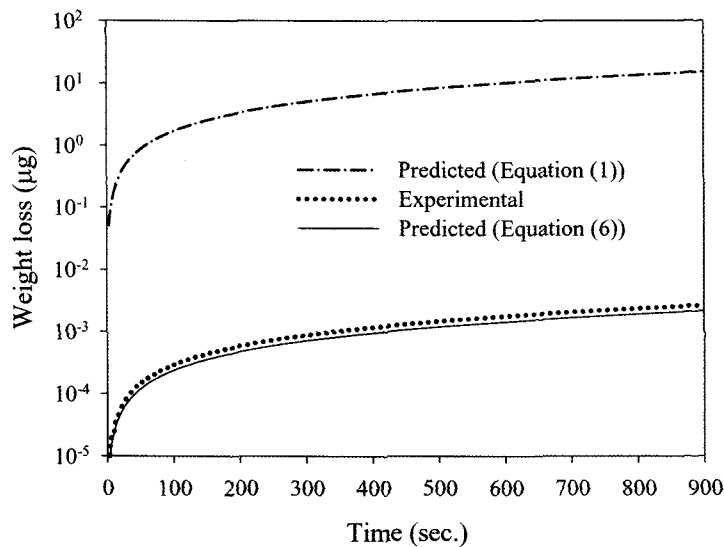


Fig. 8. Comparison of Experimentally Determined and Theoretically Predicted (Equations (1) and (6)) Evaporation Rates for LiCl

thermogravimetric analysis. Setaram 92-18 TG with a protected rod and an alumina pan was used for the analysis. A temperature scan at a rate of 20°C/min. was carried out to reach 950°C and the TG pan was then kept at that temperature under an Ar gas atmosphere. In this case, z is the TG pan height occupied by the gas.

Fig. 8 shows the results of the isothermal evaporation of LiCl (Alpha, 99.95%) after 5 minutes of stabilization at 950°C. The predictions of the diffusion evaporation model (Equation (6)) are much better than that of the Hertz-Langmuir model (Equation (1)). However, the diffusion model underestimates the experimental results by about 23%. This may be largely attributed to the fact that we did not consider two-dimensional diffusion and the enhancement of vaporization by a flowing gas. We

also investigated the vaporization of Li₂O (Cerac, 99.5%) by the thermogravimetric method. The vaporization of Li₂O was not observed and the reason can be easily deduced from the vapor pressure of Li₂O, which is almost zero at the experimental temperature, 950°C. The isothermal vaporization experiment for Li was not carried out because Li is too chemically reactive to be applied to a thermogravimetric experiment. However, it is at least clear from Fig. 7 that like LiCl, Li will vaporize during the electrolytic reduction process.

4. CONCLUSION

To reduce salt loss in the electrolytic reduction process,

the vaporization behavior of $\text{LiCl-Li}_2\text{O-Li}$ was studied. The Hertz-Langmuir relation is not appropriate when the electrolytic reduction process is carried out under a purge gas stream. Hence the diffusion-controlled evaporation model was derived and the effects of the process parameters, such as the purge gas, ambient pressure and evaporation distance, on the diffusion rates were investigated for a quantitative analysis of salt vaporization during the electrolytic reduction process. The diffusion evaporation rate increased with decreasing pressure and evaporation distance. Ar gas was more beneficial for preventing vaporization than He and N_2 . Thermogravimetric experiments showed that the derived diffusion model can provide very reasonable predictions under a purge gas stream. It is concluded that the electrolytic reduction process, which was carried out under an inert gas atmosphere, should be carried out considering the diffusion-controlled vaporization rather than the Hertz-Langmuir relation.

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