

Study on a vacuum distillation of LiCl-KCl eutectic salts containing rare earth oxidative precipitates

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1. Introduction

Of all the unit processes of a pyrochemical process, an electrorefining is a key step[1-2]. This electrorefining process discharges certain amounts of waste salts containing some metal chloride species such as rare-earth chlorides. It is reported that the oxygen sparging method for a recovery of reusable salts from the waste salts is very effective for an economical as well as an environmental aspect[3,4]. However, about 20-30 wt% of the salts is discharged as a mixture of LiCl-KCl eutectic salt and rare-earth oxidative precipitates from the method, and the mixture has about 85-90 wt% of LiCl-KCl eutectic salts. A distillation process can be a promising method for a complete separation of the salts from this mixture[5-7].

In this study, a vacuum distillation of a mixture of LiCl-KCl eutectic salts and rare-earth oxidative precipitates was performed by using the TGA system for a vacuum distillation of the salts. And a distillation flux of the salts was calculated by using the TGA data.

2. Methods and Results

2.1 Distillation modeling of LiCl-KCl eutectic salts

A salt distillation can be modeled by a vaporization theory. Vaporization flux of a salt can be obtained from experimental results as follows;

$$F_{EXP} = \frac{1}{A} \frac{dW}{dt} \quad (1)$$

where, F_{EXP} is the experimental vaporization flux in $\text{mol cm}^{-2} \text{s}^{-1}$, A is the surface area in cm^2 , M is the molecular weight in g mol^{-1} , dW is the weight changes in g and dt is the time changes in s. The vaporization theory is based on Herz-Knudsen's classical kinetic theory[8-9]. If it is assumed that LiCl-KCl eutectic salts are single component, following equation can be used for a calculation of the maximum vaporization flux by M. Trichon and J. Feldman[10-11].

$$F_{MAX} = \frac{P}{(2\pi MRT)^{0.5}} \quad (2)$$

where, F_{MAX} is the theoretical maximum of the vaporization flux in $\text{mol cm}^{-2} \text{s}^{-1}$, P is the vapor pressure in dyne cm^{-2} , R is the ideal gas constant in $8.317 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}$ and T is the absolute temperature of the gas in K. The model equation for a salt distillation can be expressed by the following equation;

$$F_V = \frac{\alpha_{AV} P}{(2\pi MRT)^{0.5}} \quad (3)$$

where, F_V is the vaporization flux in $\text{mol cm}^{-2} \text{s}^{-1}$, α_{AV} is an average of the vaporization coefficient, α , which can be obtained by comparing F_{EXP} in Eq. (1) with F_{THEO} in Eq. (2)[12].

Vaporization tests of pure LiCl-KCl eutectic salt were carried out with an alternating temperature (900 °C – 1100 °C) under atmospheric pressure for 1 hr in an electric furnace. F_{EXP} was calculated by Eq. (1) by using the experimental results. Vapor pressure of the LiCl-KCl eutectic salt was computed with a mixed molar ratio by using the vapor pressure of LiCl and KCl[13]. F_{MAX} was calculated by Eq. (2), and α was determined by the method previously mentioned. The experimental and theoretical results are listed in Table 1. By using the values of α in Table 1, α_{AV} was obtained as 0.00185. Thus, Eq. (3) can be expressed as follows;

$$F_V = 0.00185 \times \frac{P}{(2\pi MRT)^{0.5}} \quad (4)$$

2.2 Vacuum distillation of a mixture under non-isothermal condition

The vapor pressure as a function of the temperature considerably affects a salt distillation [12]. If the vapor pressure of a salt can be increased, the required temperature and time for a salt distillation will be reduced. A reduced pressure by a vacuum pump increases the vapor pressure and elevates the vaporization rate [13]. Therefore, a vacuum distillation can produce efficient results for the separation of LiCl-KCl eutectic salts from a mixture of LiCl-KCl eutectic salts and rare-earth oxidative precipitates. Fig. 2 shows the thermal mass reductions of the mixture by a vacuum distillation. It was shown that the starting temperature and the terminated temperature of the salt vaporization were lowered with a reduction in the pressure.

2.3 Vacuum distillation of a mixture under isothermal condition

To obtain a distillation flux of LiCl-KCl eutectic salts, a vacuum distillation of a mixture was performed at a fixed pressure (5 Torr) under isothermal condition, and the results were shown in Fig. 2. In comparison with an experimental distillation flux in Table 1, a distillation flux of the salts under the vacuum condition was largely increased. It is considered that the distillation fluxes in Fig. 2 can be utilized to establish a model equation for a vacuum distillation of the salts.

Table 1 Experimental and theoretical vaporization flux of LiCl-KCl eutectic salt

Temperature, (°C)	900	950	100	1050	1100
Vaporization rate*, (%)	2.45	6.02	7.40	11.85	20.46
dW/dt , (g s ⁻¹)	2.03×10^{-5}	4.90×10^{-5}	6.47×10^{-5}	1.07×10^{-4}	1.81×10^{-4}
F_{EXP} , (mol cm ⁻² s ⁻¹)	7.42×10^{-8}	1.79×10^{-7}	2.37×10^{-7}	3.91×10^{-7}	6.63×10^{-7}
P , (dyne cm ⁻²)	24.62	47.74	87.36	152.1	253.5
F_{MAX} , (mol cm ⁻² s ⁻¹)	4.05×10^{-4}	7.69×10^{-4}	1.38×10^{-3}	2.35×10^{-3}	3.85×10^{-3}
α	1.83×10^{-3}	2.33×10^{-3}	1.72×10^{-3}	1.66×10^{-3}	1.72×10^{-3}

*vaporization rate is calculated by $\frac{W_i - W_f}{W_i} \times 100$, where W_i and W_f are

the weights of the pure salt at the initial, and distilled time.

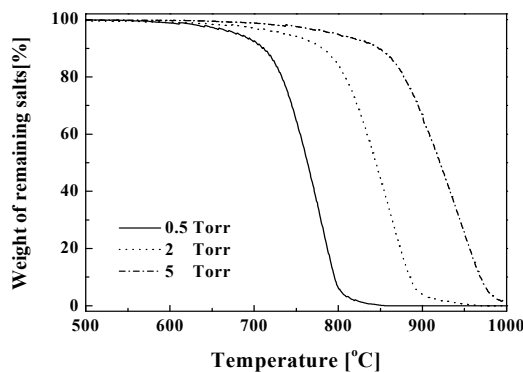


Figure 1 Thermal mass reductions of a mixture of the LiCl-KCl eutectic salts and the rare-earth oxidative precipitates with a pressure reduction.

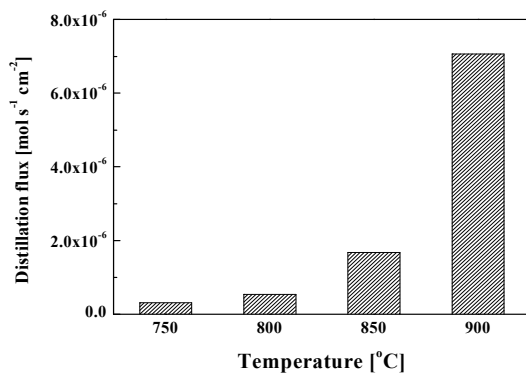


Figure 2 Distillation fluxes of LiCl-KCl eutectic salts containing oxidative precipitates at a fixed pressure (5 Torr) with temperatures.

3. Conclusion

A distillation of LiCl-KCl eutectic salts was performed under an atmospheric pressure and vacuum condition. It was found that the distillation flux of the salts was considerably increased by a reduction in the pressure. And it is thought that the distillation fluxes can be utilized to establish a model equation for a vacuum distillation of these salts.

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