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Distillation and condensation of LiCl–KCl eutectic salts for a separation of pure salts from salt wastes from an electrorefining process

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ABSTRACT

Salt separation and recovery from the salt wastes generated from a pyrochemical process is necessary to minimize the high-level waste volumes and to stabilize a final waste form. In this study, the thermal behavior of the LiCl–KCl eutectic salts containing rare earth oxychlorides or oxides was investigated during a vacuum distillation and condensation process. LiCl was more easily vaporized than the other salts (KCl and LiCl–KCl eutectic salt). Vaporization characteristics of LiCl–KCl eutectic salts were similar to that of KCl. The temperature to obtain the vaporization flux (0.1 g min^{-1} cm^{-2}) was decreased by much as 150 °C by a reduction of the ambient pressure from 5 Torr to 0.5 Torr. Condensation behavior of the salt vapors was different with the ambient pressure. Almost all of the salt vapors were condensed and were formed into salt lumps during a salt distillation at the ambient pressure of 0.5 Torr and they were collected in the condensed salt storage. However, fine salt particles were formed when the salt distillation was performed at 10 Torr and it is difficult for them to be recovered. Therefore, it is thought that a salt vacuum distillation and condensation should be performed to recover almost all of the vaporized salts at a pressure below 0.5 Torr.

1. Introduction

Pyrochemical process has many advantages such as a compactness, economy, radiation stability of the solvent, non-proliferation and produces less secondary wastes [1,2]. This process involves electrochemically partition the fission products from spent nuclear fuels in a molten salt bath [3–5]. In this process, the electrorefining process using LiCl–KCl eutectic salts is a main process and exhausts considerable amounts of salt wastes containing some metal chlorides such as lanthanide chlorides or actinide chlorides [6]. These salt wastes are classified as high-level wastes.

To minimize these salt waste volumes, an oxygen sparging process is being studied in KAERI. It is reported that this process is much more effective when compared to other oxidation precipitation methods for the rare earth chlorides by using an oxidant agent [6]. Almost all of the rare earth chlorides (>99.9 wt%) in the salt wastes are converted into rare earth oxychlorides or oxides and they are precipitated into the bottom of the salts by the oxygen sparging process [6]. About 60–70 wt% of salt is recovered from the salt wastes and about 30–40 wt% of salt as a mixture containing rare earth oxychlorides or oxides is generated through the oxygen sparging process. This mixture consists of 10–15 wt% of rare earth oxychlorides or oxides and 85–90 wt% of LiCl–KCl eutectic salts. Thus, an additional salt separation from this mixture is required to minimize the high-level waste volumes and to stabilize the final waste forms. The mixture can be separated by using a distillation method because the vapor pressure differences between the LiCl–KCl eutectic salts and the rare earth oxychlorides or oxides are very large [7]. A distillation method is more attractive than a chemical method or dissolution process because of much less secondary waste.

In this study, the thermal behavior of the LiCl–KCl eutectic salts containing rare earth oxychlorides or oxides was investigated during a vacuum distillation and condensation process. For this aim, the thermal weight reductions of the salt vacuum distillation were observed by using a salt vacuum distillation and condensation system for a thermo-gravimetric analysis and condensation types of the salts was looked into in this system.

2. Experimental and methods

Salt vacuum distillation and condensation system for a thermo-gravimetric analysis consists of an alumina tube, a load cell, a digital pressure sensor, an electric heater, an alumina crucible, a cooling jacket, a condensed salt storage, a filter, a throttle valve, a vacuum pump and a cooling water circulator as shown in Fig. 1. This system is aspirated continuously to maintain a constant pressure by the vacuum pump. A thermocouple was installed above the alumina crucible to measure the exact salt temperature. The filter was made of stainless steel mesh to capture the fine salt particles not collected in the condensed salt storage. The LiCl–KCl

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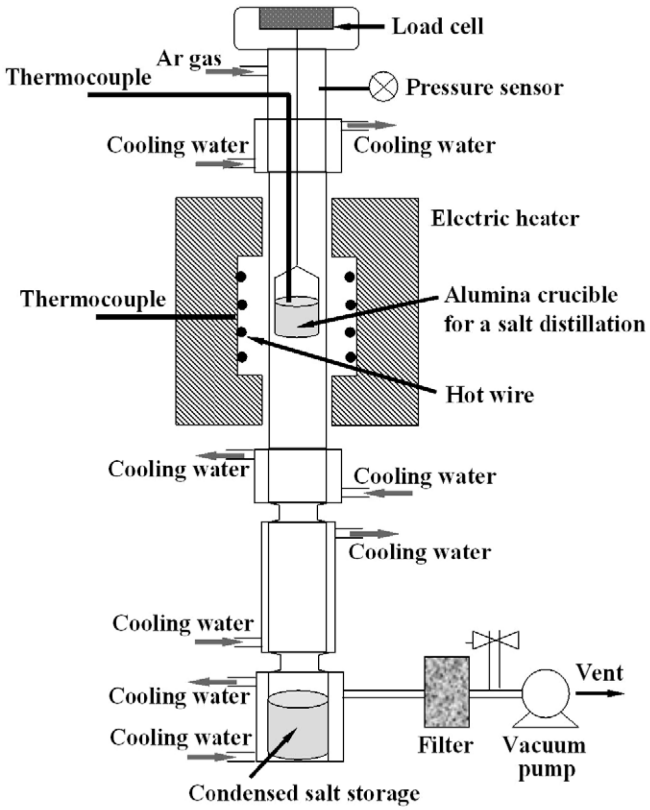


Fig. 1. A schematic diagram of a salt vacuum distillation system for a thermo-gravimetric analysis.

Table 1
Experimental conditions for a thermo-gravimetric analysis during a salt vacuum distillation.

	Non-isothermal	Isothermal
Temperature (°C)	500–1000	
Pressure (Torr)	0.5–10	
Heating rate (°C min^{-1})	5	–
Sample weight (g)	20 ± 0.5	40 ± 0.5
Injection gas	Ar (high purity >99.999%)	

eutectic salts containing rare earth oxychlorides or oxides were obtained from an oxygen sparging process. Table 1 shows the experimental conditions for a thermo-gravimetric analysis during a salt vacuum distillation and condensation. This thermo-gravimetric analysis was performed under non-isothermal and isothermal conditions. Temperatures were varied from 500 °C to 1000 °C. Pressures were reduced by the vacuum pump and were adjusted from 0.5 Torr to 10 Torr by the throttle valve. In the non-isothermal conditions, the heating rate was fixed at a 5 °C/min. Cylindrical type of an alumina crucible containing the LiCl–KCl eutectic salt samples was used to minimize a surface area change according to the crucible height. To maintain an inert condition, high purity (>99.999%) Ar gas was injected into the system.

3. Results and discussion

3.1. Salt behavior during a vacuum distillation process

Vacuum distillation is a method of a distillation whereby the pressure above the liquid mixture to be distilled is reduced to less than its vapor pressure causing an evaporation of the most volatile liquid. The vapor pressure as a function of the temperature considerably affects the vaporization flux [8]. The LiCl–KCl eutectic salt (m.p. 360 °C) used in the electrorefining process is a mixture 44.2 wt% LiCl and 55.8 wt% KCl and there are no vapor pressures for it in existing records. However, the vapor pressures of LiCl and KCl are found in the Handbook of vapor pressure [8]. According to this book, their vapor pressures can be expressed by the following equations [8]:

$$\log_{10}P_{\mathrm{LiCl}} = 1659.2051 - 1.1514 \times 10^5/T - 5.7029 \times 10^2 \log_{10}T + 1.9064 \times 10^{-1}T - 2.4324 \times 10^{-5}T^2 \quad (1)$$

$$\log_{10}P_{\mathrm{KCl}} = -8.0224 - 9.3722 \times 10^3/T + 6.4641 \log_{10}T - 3.1639 \times 10^{-3}T + 3.2745 \times 10^{-7}T^2 \quad (2)$$

where P is the vapor pressure in Torr and T is the absolute temperature in K. The vapor pressures of them were calculated by using these equations, and the results are shown in Fig. 2. As seen in Fig. 2, the vapor pressures of LiCl are approximately double when compared to those of KCl. This indicates that LiCl is more easily vaporized than KCl at the same temperature. The vapor pressure of LiCl–KCl eutectic salt was considered as a value between those of LiCl and KCl. Based on these results, experimental temperatures and pressures were determined.

Fig. 3 shows the thermal weight reductions of LiCl, KCl and LiCl–KCl eutectic salt during a distillation at 0.5 Torr. According to Fig. 3, LiCl, which has higher vapor pressures than KCl, was vaporized rapidly at a higher temperature than about 725 °C and the LiCl vaporization was completed at about 785 °C. Thermal weight reductions of the LiCl–KCl eutectic salt were similar to those of KCl. These salts were vaporized rapidly at about 760 °C and their vaporization was completed at about 825 °C. The starting temperatures for a rapid vaporization were lower than the temperatures for a vapor pressure of 0.5 Torr. This means that the vaporization rate is increased exponentially when the ambient pressure approaches the vapor pressure. The slopes of the thermal weight reductions were increased gradually with an increase in the temperatures. This agreed well with an increase in the vapor pressures in Fig. 2.

As shown in the prior section, the ambient pressure considerably affects the vaporization flux and the required time and temperature for a salt distillation can be decreased by a reduction of the ambient pressure. A TGA test for a salt distillation was performed under an isothermal condition at 0.5 Torr and 5 Torr. During a distillation of the LiCl–KCl eutectic salts, the rare earth oxychlorides or oxides had little influence on the salt distillation. It is thought that this tendency was caused because the salts adhered to the rare earth particles were easily evacuated and were vaporized by continuously aspirating to maintain a constant pressure with using the vacuum pump in the distillation test. The rare

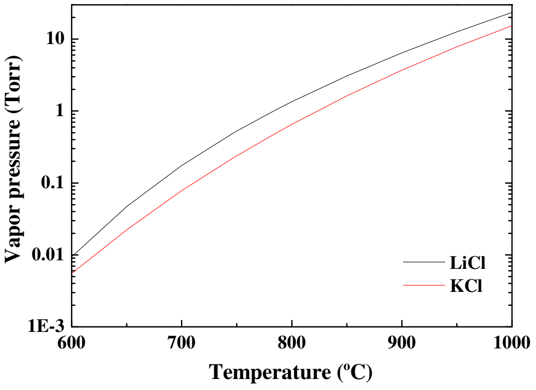


Fig. 2. Vapor pressures of LiCl and KCl with temperatures.

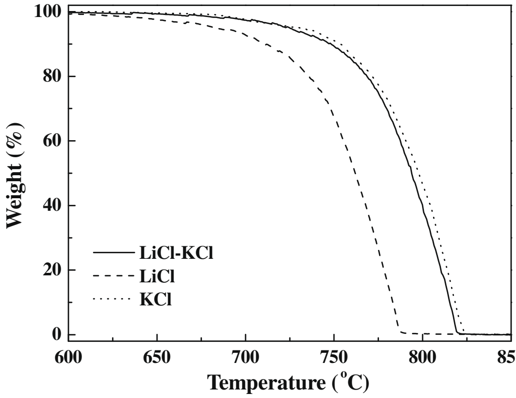


Fig. 3. Thermal weight reductions of LiCl, KCl and LiCl–KCl eutectic salt during the distillation at 0.5 Torr (non-isothermal, 5 °C min^{-1}).

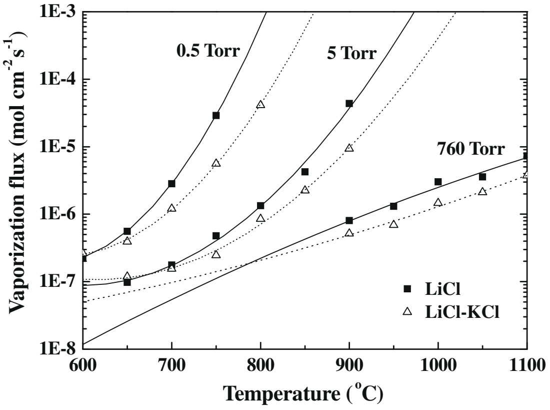


Fig. 4. Vaporization fluxes of LiCl and LiCl–KCl eutectic salt with pressures and temperatures.

earth particles were residual in the alumina crucible as a very thin layer of powder form after the distillation and they were easily dusted off from the crucible. Fig. 4 shows the vaporization fluxes of LiCl and LiCl–KCl eutectic salt with the pressures and temperatures. These vaporization fluxes were reduced by using the isothermal TGA results and Herz–Knudsen classical kinetic theory as follows [9,10]:

$$F = \frac{1}{AM}\frac{dW}{dt} \tag{3}$$

where F is the vaporization flux in mol cm^{-2} 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. According to Fig. 4, the vaporization flux of LiCl was higher than that of LiCl–KCl eutectic salt and this agreed well with the results in Fig. 3. However, the vaporization flux of LiCl–KCl eutectic salt was higher than that of LiCl at 5 Torr and a temperature below 680 °C, and at 0.5 Torr and a temperature below 620 °C. It is thought that this tendency was brought about because the melting point of LiCl–KCl eutectic salt is lower than that of LiCl (m.p.: 610 °C). To utilize the vaporization fluxes of the LiCl–KCl eutectic salt in a salt vacuum distillation system, they were reduced to a unit such as g min^{-1} cm^{-2}, and the results are presented in Table 2. As shown in Table 2, the vaporization flux was about 0.1 g min^{-1} cm^{-2} at 5 Torr and 950 °C. However, this flux could be obtained at 0.5 Torr and 800 °C. In other words, 150 °C in the distillation temperature to obtain the vaporization flux, 0.1 g min^{-1} cm^{-2}, was decreased by a reduction of the ambient pressure from 5 Torr to 0.5 Torr. This decrease in the distillation temperature is an important factor to separate a pure salt from a LiCl–KCl eutectic salt containing lanthanide oxychlorides or oxides.

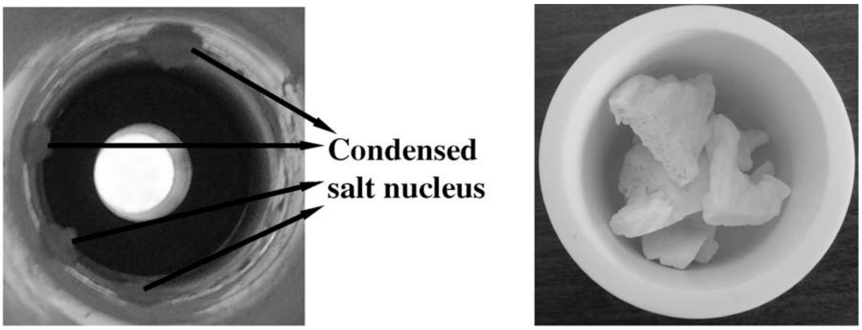
Table 2
Vaporization fluxes of the LiCl–KCl eutectic salt with pressures and temperatures (g cm^{-2} min^{-1}).

Temperature	Pressure	
	0.5 Torr	5 Torr
600	6.65×10^{-4}	–
650	9.98×10^{-4}	3.02×10^{-4}
700	3.05×10^{-3}	3.94×10^{-4}
750	1.42×10^{-2}	6.24×10^{-4}
800	1.04×10^{-1}	2.16×10^{-3}
850	–	5.68×10^{-3}
900	–	2.38×10^{-2}
950	–	9.61×10^{-2}

3.2. Salt condensation behavior

As well as a salt separation from the salt wastes, a salt recovery is very important to reduce the high-level waste volumes and to guarantee an economic feasibility for the electrorefining process. To elevate a salt recovery efficiency, it is necessary to understand the salt condensation behavior.

As shown in Fig. 1, the TGA system for a salt vacuum distillation and condensation was operated at a constant pressure by a continuous aspiration. In this test, almost all of the salt vapors were condensed in the cooling jacket and were collected in the condensed salt storage. The fine particles not collected in the condensed salt storage were captured in the stainless steel mesh filter. In the test for a salt vacuum distillation and condensation, a fluid stream type greatly affected the condensation behavior of the salt vapor. The ambient pressure considerably affected the fluid stream type. For such this reason, the condensation behavior of the salt vapor depended on the ambient pressure in the TGA system. When the ambient pressure was 0.5 Torr, condensed salt nucleus were observed above the cooling jacket. Fig. 5a shows the condensed salt nucleus deposited above the cooling jacket. Almost all of the salt vapors were condensed around the salt nucleus. When the salts condensed around the salt nucleus become lumps, the condensed salts fell down to the condensed salt storage as shown in Fig. 5b. The amount of salt collected in the mesh filter was very low. However, a large amount of the salt vapors was deposited above the condensed salt storage and around the outlet of the condensed salt storage as shown in Fig. 5c during the salt distillation at 10 Torr. The amount of salt captured in the filter was much more when compared to the salt distillation at 0.5 Torr. When aerosol particles come into contact and coalesce or adhere to one another, the process is called coagulation [11]. This coagulation depends on a particle collision and is generated well in a turbulent flow with a lateral mixing [12]. Also, it considerably affects the condensed particle size [11,12]. The more it is increased, the lager a condensed particle size becomes. In this study, the lumps of the condensed salts were formed when the salt distillation was performed at 0.5 Torr. This means that a turbulent flow was constituted and coagulation effectively occurred around the salt nuclei deposited above the cooling jacket in this condition. However, fine salt particles were formed when the salt distillation was processed at 10 Torr. And the particle sizes were similar. This indicates that only a laminar flow occurred in this condition and the salt vapors were condensed without a particle collision and they were formed into fine particles. As shown in Fig. 5c, the fine salt particles deposited at the operating pressure of 10 Torr have a difficulty to be recovered completely. Thus, it is considered that the ambient pressure should be lower than 0.5 Torr to elevate a salt distillation and



(a) Condensed salt nucleus (b) Salt collected in the salt storage

(c) Fine salt particles deposited above the salt storage

Fig. 5. Photos of salts condensed or collected in the TGA system for a salt vacuum distillation.

recovery efficiency in a salt vacuum distillation and condensation system aspirated continuously to maintain a constant pressure by a vacuum pump.

4. Conclusion

Thermal behavior of LiCl–KCl eutectic salts containing rare earth oxychlorides or oxides was investigated during a vacuum distillation and condensation process in this study. LiCl was more easily vaporized than the other salts (KCl and LiCl–KCl eutectic salt). Vaporization characteristics of LiCl–KCl eutectic salts were similar to that of KCl. It was confirmed that the required temperature and time were decreased by a reduction of the ambient pressure, and the temperature to obtain the vaporization flux ($0.1\ \mathrm{g\ min^{-1}\ cm^{-2}}$) was decreased by much as 150 °C by a reduction of the ambient pressure from 5 Torr to 0.5 Torr. Condensation behaviors of the salt vapors were different with the ambient pressure. The salt vapors were almost changed into salt lumps by the thermal coagulations existing in the turbulent flow during at the ambient pressure of 0.5 Torr and they were collected in the condensed salt storage. However, fine salt particles were formed when the salt distillation was processed at 10 Torr and it is difficult for them to be recovered. Thus, it is thought that a salt vacuum distillation and condensation should be performed at an ambient pressure below 0.5 Torr to elevate a salt distillation and recovery efficiency in a salt vacuum distillation and condensation system aspirated continuously by a vacuum pump to maintain a constant pressure.

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