



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

Hee Chul Eun*, Hee Chul Yang, Han Soo Lee, In Tae Kim

Nuclear Fuel Cycle Process R&D Group, Korea Atomic Energy Research Institute, P.O. Box 150-1 Yuseong, Daejeon 305-353, Republic of Korea

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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 ($0.1 \text{ g min}^{-1} \text{ cm}^{-2}$) 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.

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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

* Corresponding author. Tel.: +82 42 868 2575; fax: +82 42 868 2329.
E-mail address: ehc2004@kaeri.re.kr (H.C. Eun).

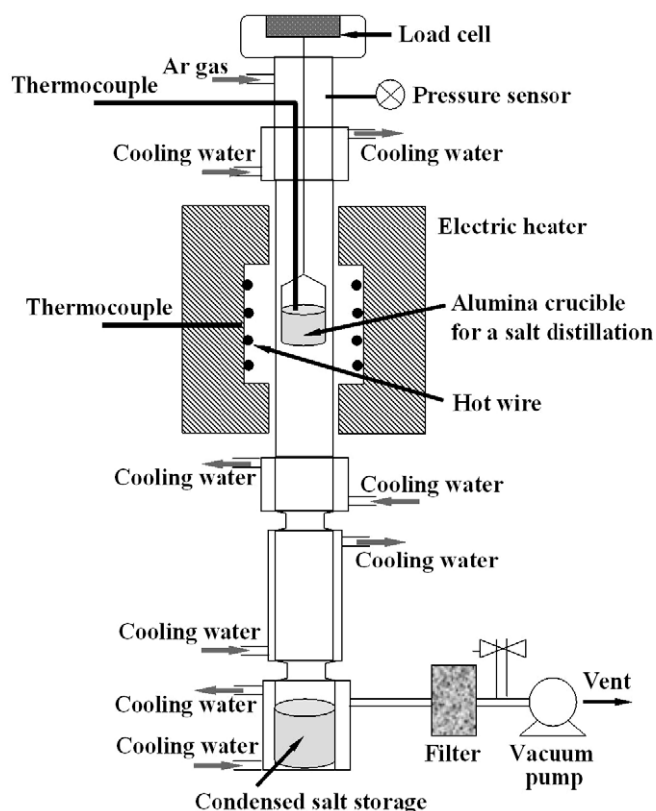


Fig. 1. A schematic diagram of a salt vacuum distillation system for a thermo-gravimetric analysis.

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 consid-

erably 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]:

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

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

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

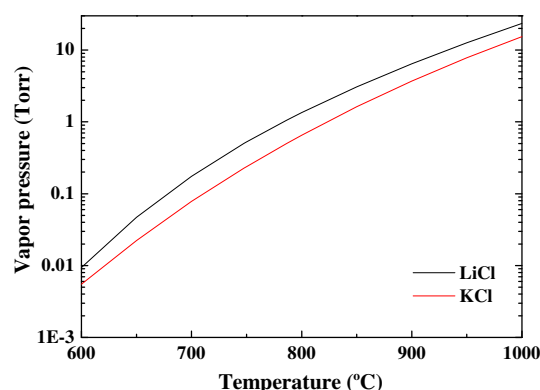


Fig. 2. Vapor pressures of LiCl and KCl with temperatures.

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