Vacuum evaporation of LiCl–BaCl$_2$–SrCl$_2$ system

H.C. Eun*, Y.Z. Cho, H.S. Park, I.T. Kim, H.S. Lee, G.I. Park

Nuclear Fuel Cycle Waste Treatment Research Division, Korea Atomic Energy Research Institute, P.O. Box 150-1 Yuseong, Daejeon 305-353, Republic of Korea

ARTICLE INFO

ABSTRACT

Vacuum evaporation of a LiCl–BaCl$_2$–SrCl$_2$ system was investigated to design a process for waste reduction and salt recycling. Through thermo-gravimetric analysis (TGA) tests of pure LiCl at a reduced pressure, a model equation for LiCl vaporization was established. As results of TGA tests of pure BaCl$_2$ and SrCl$_2$, it was confirmed that they were very stable at 900 °C and 0.5 Torr. At 1 Torr, evaporation of the LiCl–BaCl$_2$–SrCl$_2$ system looked similar to the pure LiCl vaporization results. Co-evaporation of BaCl$_2$ or SrCl$_2$ with LiCl was very slight in this study.

1. Introduction

The pyrochemical process as an alternative technology of spent nuclear fuel (SNF) reprocessing has many advantages such as compactness, radiation resistance, nonproliferation and less secondary waste (Volkovich et al., 2003; Matsumiya and Matsuura, 2005). For these reasons, the pyrochemical process has been widely studied in nuclear advanced countries (Matsumiya and Matsuura, 2005). The Korea Atomic Energy Research Institute (KAERI) has also been developing a pyrochemical process technology for recycling useful resources from SNFs since 1997 (Song et al., 2010). The process includes pretreatment, electroreduction, electrorefining, and electrowinning processes (Song et al., 2010). Among these processes, the electroreduction process plays a role to reduce oxide forms of SNFs to metal forms in molten LiCl salt using an electrochemical method. During this process, LiCl waste salts containing group II nuclides such as strontium and barium are generated. The nuclides must be separated from the salts and immobilized as stable waste forms because they are radioactive, highly heat generative, and soluble in water (Song et al., 2010). The current technology for waste salt disposal is a non-selective total incorporation of the salts in a zeolite matrix, which results in a significant increase of the final waste volume (Simpson et al., 2007). This means that it is necessary to separate the nuclides from the salts selectively for waste reduction and salt recycling. Vaporizing the LiCl salt at a reduced pressure is an effective method for waste reduction and salt recycling owing to

much less secondary waste when compared to a chemical method. There are large vapor pressure differences between LiCl and BaCl$_2$/SrCl$_2$ (Westphal et al., 2008). Thus, it is necessary to investigate the vaporization characteristics of LiCl waste salts containing group II nuclides at a reduced pressure.

In this study, vacuum evaporation of a LiCl–BaCl$_2$–SrCl$_2$ system was investigated to design a process for waste reduction and salt recycling. First, TGA tests of pure LiCl, BaCl$_2$ and SrCl$_2$ were performed in a vacuum furnace system. Based on the results, vacuum evaporation of the LiCl–BaCl$_2$–SrCl$_2$ system was observed.

2. Experimental and methods

2.1. TGA tests of LiCl, BaCl$_2$ and SrCl$_2$ at a reduced pressure

The LiCl, BaCl$_2$, and SrCl$_2$ used in this study have over 99% purity as anhydrous agents. A vacuum furnace system for a TGA test of LiCl, BaCl$_2$, and SrCl$_2$ at a reduced pressure consists of an alumina tube, a load cell, a digital pressure sensor, an electric heater, a type R thermocouple, an alumina crucible, a cooling jacket, a condensed salt storage, a filter, a valve, a vacuum pump, and a cooling water circulator as shown in Fig. 1. This system is continuously evacuated to maintain a constant pressure by a vacuum pump. A thermocouple is installed above the alumina crucible to measure the exact salt temperature. The filter is made of a stainless steel mesh to capture the fine salt particles not collected in the condensed salt storage as shown in Fig. 1. Table 1 shows the experimental conditions for the TGA tests of LiCl. These tests were performed to compute the vaporization rates of LiCl
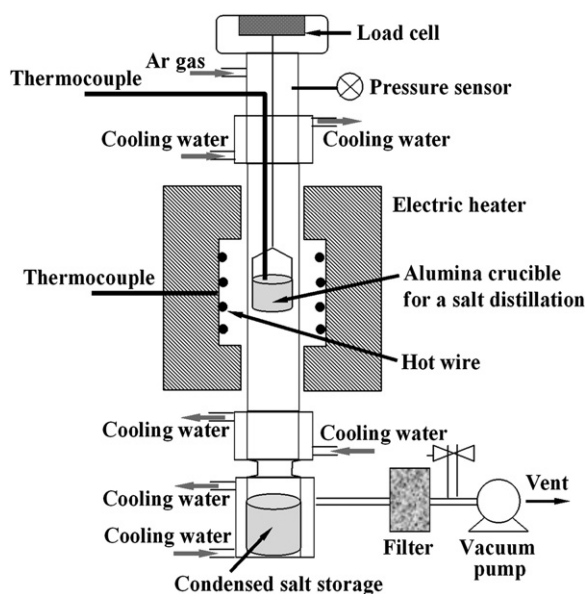
Fig. 1. A schematic diagram of a furnace for a thermo-gravimetric analysis at a reduced pressure.

Table 1
Experimental conditions for a thermo-gravimetric analysis test of LiCl.

Temperature (°C)	Pressure (Torr)	Sample weight (g)	Injection gas	Vaporization time at a given temperature (min)
600–1100	0.5, 5, 760	40 ± 0.5	Ar (> 99.999%)	10–30

under isothermal conditions. Temperatures were varied from 600 °C to 1100 °C. Pressures were reduced by the vacuum pump and adjusted from 0.5 Torr to 760 Torr by the valve (throttle valve). TGA tests of $BaCl_2$ and $SrCl_2$ were performed under a non-isothermal condition. The temperatures were changed from 50 °C to 900 °C and the pressure was fixed at about 0.5 Torr. In these TGA tests, a cylindrical type of alumina crucible containing the samples was used to minimize the surface area change according to the crucible height.

2.2. Vaporization rate equation

Vaporization rate of an inorganic material can be modeled using a vaporization theory. The vaporization rate can be obtained from the experimental results as follows:

$$V_{EXP} = \frac{1}{AM}\frac{dW}{dt} \tag{1}$$

where V_{EXP} is the experimental vaporization rate 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 change in g, and dt is the time change in s. The vaporization theory is based on Hertz–Knudsen's classical kinetic theory (Lamoreaux and Hildenbrand, 1984,1987). The following equation is used for calculation of the maximum vaporization rate by Feldman and Trichon, (1987a, 1987b).

$$V_{MAX} = \frac{P_V}{(2\pi MRT)^{0.5}} \tag{2}$$

where V_{MAX} is the theoretical maximum of the vaporization rate in mol cm^{-2} s^{-1}, P_V is the vapor pressure in dyne cm^{-2}, R is the ideal gas constant in 8.314 J mol^{-1} K^{-1} and T is the absolute temperature

of the gas in K. The model equation for the salt vaporization rate can be expressed using:

$$V_P = \frac{\alpha P_V}{(2\pi MRT)^{0.5}} \tag{3}$$

where V_P is the modeled vaporization rate in mol cm^{-2} s^{-1} at an ambient pressure of P, α is a vaporization coefficient that can be obtained by comparing V_{EXP} in Eq. (1) with V_{MAX} in Eq. (2) (Yang et al., 1994).

2.3. Vacuum evaporation of LiCl–BaCl₂–SrCl₂ system

The LiCl–BaCl₂–SrCl₂ system was prepared as follows. First, about 20 g of LiCl and about 3.2 g of $BaCl_2$ (1.6 g) and $SrCl_2$ (1.6 g) were mixed in an alumina crucible. The crucible was treated at about 610 °C and cooled to room temperature to manufacture a LiCl–BaCl₂–SrCl₂ ingot as a similar form of LiCl waste as in the pyrochemical process.

Based on the TGA results of the LiCl, $BaCl_2$ and $SrCl_2$, vacuum evaporation of the LiCl–BaCl₂–SrCl₂ system was carried out in the vacuum furnace system. Temperatures were heated from room temperature to a given temperature and were then fixed at the given temperature for 3 h. The given temperature was varied from 750 °C to 900 °C at an interval of 50 °C. The pressure was fixed at about 1 Torr.

3. Results and discussion

3.1. Vaporization rate of LiCl at a reduced pressure

TGA tests of pure LiCl were performed to evaluate the vaporization characteristics of LiCl. The results were utilized to calculate the vaporization rate of LiCl. To obtain a higher vaporization rate at a relatively low temperature, the ambient pressure was adjusted from 760 Torr to 0.5 Torr.

The vaporization rates of the LiCl were calculated using the thermal mass reduction results obtained from the TGA tests and Eq. (1). They are expressed in Table 2. The vapor pressure as a function of temperature considerably affects the vaporization rate (Yaws, 1995). The vaporization rate is increased when the ambient pressure is reduced and approaches the vapor pressure. In this study, these tendencies were confirmed. As shown in Table 2, the vaporization rate was increased considerably with a reduction of the ambient pressure. At 750 °C and 0.5 Torr, 2.91×10^{-5} mol cm^{-2} s^{-1} as the vaporization rate of LiCl could be obtained. To evaluate the vaporization rates as objective values, the vaporization coefficients were computed using Eq. (3), and their average values are expressed in Table 3. These values indicate that the vaporization rate was increased by about 1000 times by reducing the pressure from 760 Torr to 0.5 Torr, and this tendency was agreed well with LiCl–KCl vaporization results (Eun et al., 2009). The model equation of the LiCl vaporization rate can be established by inserting the vaporization coefficient in Eq. (3). To verify the model equation, the results calculated by using the model equation were compared with the experimental results, which are expressed in Fig. 2. As shown in Fig. 2, the model calculations agree reasonably well with the experimental results. Thus, it was considered that the model equations can be utilized to design a vacuum evaporation process and to determine the operating conditions.

3.2. Thermal stability of BaCl₂ and SrCl₂ at a reduced pressure

Before vacuum evaporation of the LiCl–BaCl₂–SrCl₂ system, the thermal behaviors of $BaCl_2$ and $SrCl_2$ were investigated at a