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Study on the distillation rates of LiCl–KCl eutectic salt under different vacuum conditions

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ABSTRACT

A study on the distillation rate of LiCl–KCl eutectic salt under different vacuums from 0.5 to 50 Torr was performed by using thermogravimetric (TG) method. A distillation rate of the order of 10^{-4}–10^{-5} mol cm^{-2} s^{-1} was obtainable at temperatures of 1200–1300 K and vacuums of 5–50 Torr. Based on the non-isothermal TG data, model distillation flux equations could be derived as a function of temperature. Pure gas-phase and gas–liquid interfacial resistances at different vacuum conditions were evaluated from the comparison of experimental vaporization fluxes with the maximum flux obtained from the kinetic theory of gas. The difference between interfacial mass transfer coefficients and gas-phase ones increases with the temperature. Gas-phase resistance is much greater than that of the phase transition between condensed and gas phases at tested vacuum conditions of 0.5–50 Torr.

1. Introduction

At present, a commercial scale reprocessing of a spent nuclear fuel is carried out using a hydrometallurgical process. A pyrochemical process has been evaluated as a promising alternative because of its compactness, radiation resistance and nonproliferation as well as economics [1–5]. An electrorefining, a key unit of a pyrochemical process, generates waste eutectic salts containing some radioactive metal chlorides. The most effective method is to separate the radioactive metals from the non-radioactive salts. A promising approach is to precipitate radioactive metals by converting them into salt-insoluble metal compounds by an oxygen sparging. Following this, a vacuum distillation process for the removal of LiCl–KCl eutectic salt is available to effectively separate the precipitated particulate metal oxides from the eutectic salt [6–8].

This study investigated the distillation rates of LiCl–KCl eutectic salt under different vacuum conditions. A fundamental study on the distillation rates of pure eutectic salt was performed by using a vacuum thermogravimetric (TG) furnace. The objective of this study was to get to understand the salt distillation rates under different vacuums.

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2. Experimental methods

A schematic of the vacuum thermogravimetric (TG) furnace system used in this study is shown in Fig. 1. This vacuum TG furnace system mainly consisted of a long cylindrical alumina tube, a load cell, an electric heater, an alumina crucible and a vacuum control unit. This TG furnace system is capable of controlling the temperature to 1400 K and a vacuum of less than 0.1 Torr. Distillation rates of a pure LiCl–KCl eutectic salt under different vacuums were observed using this TG furnace system. Both non-isothermal and isothermal TG analyses of a LiCl–KCl eutectic salt mixture loaded in the cylindrical crucible (30 mm ID × 70 mm *H*) were performed under various conditions as shown in Table 1.

3. Results and discussion

3.1. Salt distillation rate under different vacuums

Changes in the sample weight under different vacuums as a function of the time are plotted in Fig. 2. About 10% of the salt remained at the crucible surface to form non-volatile complex compounds such as $Li_2Al_2O_4$, $K_2Al_2O_4$, Li_2SiO_3 and K_2SiO_3. Assuming that the vaporizing surface area in the cylindrical crucible does not change with time, the distillation rate per unit vaporizing surface area is determined from the weight loss obtained from the TG analysis. This is expressed as follows:

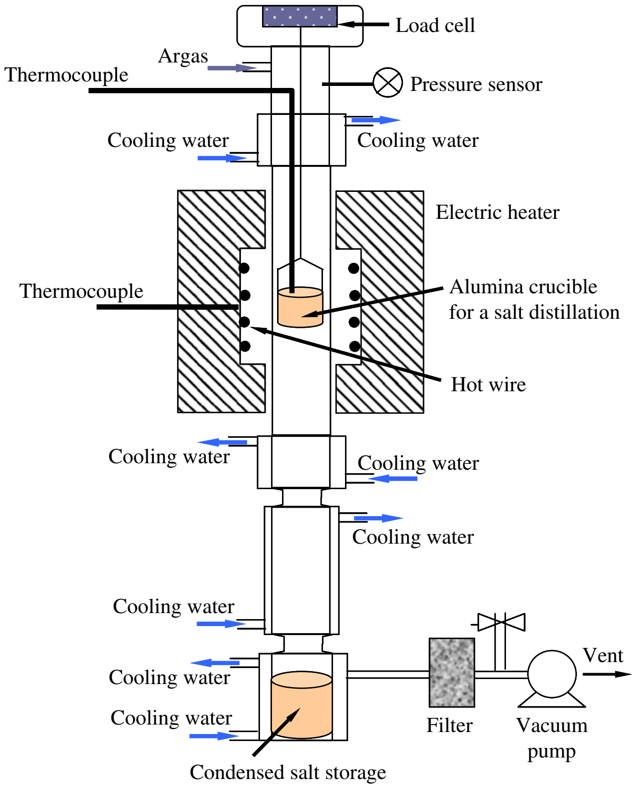

Fig. 1. A schematic of the thermogravimetric vacuum furnace system.

$$N_{exp} = -\frac{1}{AM}(dw/dt) \quad (1)$$

where A is the inner cross-sectional area of the cylindrical crucible (cm^2), M is the molecular weight (g/mol), and dw/dt is the weight changes (g) with a time difference (s). In non-isothermal condition with a fixed heating rate of B (K/min), dt in Eq. (1) can be rewritten as dT/B. Therefore the distillation rate can be written as follows [9]:

$$N_{exp} = -\frac{1}{AM}B(dw/dT) \quad (2)$$

Using Eq. (2), experimentally obtained distillation rates were calculated from the weight changes with the temperature, as shown in Fig. 3. A distillation rate of 10^{-4}–10^{-5} mol cm^{-2} s^{-1} is obtainable at temperatures of 1200–1300 K and a vacuum of 5–50 Torr.

As shown in Fig. 4, the logarithmic values of distillation rates appear to be increasing linearly with temperature. Therefore, the distillation rate equation could be determined as a function of the temperature by linear regressions of the logarithmic value of experimental rates versus temperature. Obtained distillation rates as a function of temperature are shown in Table 2. The slope (B)

Table 1
Non-isothermal and isothermal vacuum TG test conditions.

	Non-isothermal test	Isothermal test	
Temperature (K)	800–1300	873, 923, 973, 1023, 1073	923, 973, 1023, 1073, 1123, 1273, 1323
Pressure (Torr)	0.5, 5, 50	0.5	5
Distillation time (min)	125	20–30	
Heating rate (K/min)	4	–	
Sample weight (g)	20 ± 0.5	40 ± 0.5	

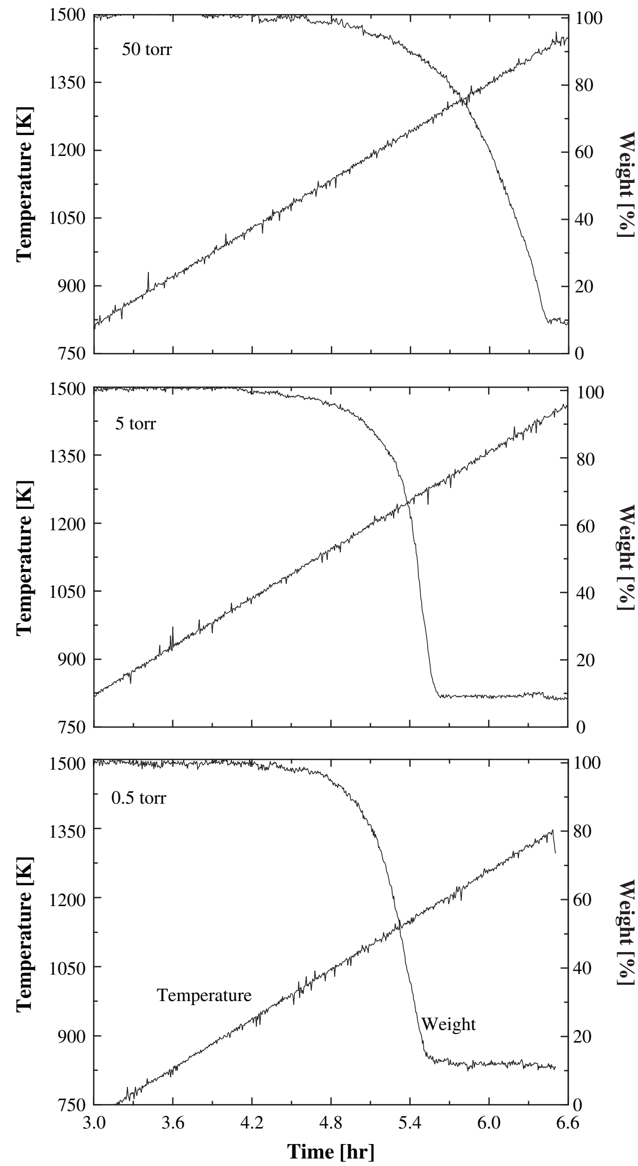

Fig. 2. Weight loss of the eutectic salt in the TG furnace by a heating up to 1500 K with a ramping rate of 4 K min^{-1} under three different vacuums (0.5, 5 and 50 torr).

increases as the vacuum increases. This indicates that the effect of temperature on the distillation rate becomes greater as the vacuum increases. In Fig. 4, the distillation rates obtained from the isothermal TG tests under 0.5 and 5 Torr were compared with the rates by the rate equation in Table 2. Distillation rates determined from the isothermal TG data are generally in agreement with the calculated ones from the model equations obtained by the non-isothermal TG tests.

3.2. Vaporization model

The condensation and vaporization model for the evaluation of gas-phase resistance to vaporization of metal compounds without any chemical reaction is described in Fig. 5, in which, T_i and T_s are temperatures at gas–liquid interface and that at liquid surface, respectively. In equilibrium condition, vapor pressure at liquid–gas interface, P_i, is equal to vapor pressure at liquid surface, P_s. There is no net transfer from one phase to another phase in such condition. However, the gas molecules are moving at a high speed. Some of