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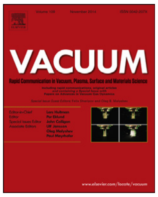

# Measurement of LiCl removal behavior from porous solids by vacuum evaporation

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ABSTRACT

Molten salt processes have been developed in various fields of engineering. In such a process, its efficiency and the quality of products would be enhanced when the used molten salt is effectively separated from the product and recycled into the process. Vacuum evaporation has been applied to recover molten salts due to the low vapor pressure and the high melting point. However, most of researches have been focused on the bulk salts evaporation. In this work, LiCl salt evaporation behavior from a porous solid was investigated to develop a post-treatment process of an electrolytic reduction process which uses LiCl as an electrolyte and produces porous solid products. The electrolytic reduction process is one of the main components of pyroprocessing to treat spent nuclear fuel and produce metallic uranium. Instead of using radioactive material, we prepared porous MgO chips and rods to determine the conditions and measure the behavior with different physical characteristics of the rods. The temperature and pressure were set to 700 °C and 20 mTorr, respectively, and more than 70% of salt was removed within 5 h.

## 1. Introduction

Molten salt or fused salt refers to a salt material in a liquid phase due to elevated temperature, which is in a solid state at ambient condition. It is an ionic and stable substance in a wide range of temperature and exhibits a lot of interesting features such as an ability to conduct heat and electricity. Molten salts have been adopted as reacting or inert media in various technologies such as fuel cell, coal gasification, and pyroprocessing of non-ferrous metals.

Recently, the molten salt has been used in pyroprocessing of spent nuclear fuels, which has been developed as a promising alternative to aqueous processes because of its compactness, radiation resistance, and enhanced proliferation resistance features [1–3]. Therefore, many countries including Japan, United States, and France have developed the pyroprocessing as a technical option among various nuclear fuel cycle technologies to accomplish their own future nuclear energy plans as well as to cope with their spent nuclear fuel management issues [4].

In Korea, Korea Atomic Energy Research Institute (KAERI) has led national R&Ds on fuel cycle technologies and established a basic concept of pyroprocessing for the purpose of treating spent fuels from light water reactors (LWRs) [5]. Based on electro-metallurgical principles, three core unit processes were actively developed as connected in series to convert the oxide fuels into metallic form and, then, collect uranium to be disposed of or recycled in a fuel cycle for the future fast reactors; they are referred to as electrolytic reduction, electrorefining, and electrowinning, respectively.

Pyroprocessing for spent fuels has focused on treating the metallic fuels [1] of which chemical components are readily ionized into their corresponding ionic species in a high temperature molten salt medium and selectively recovered with respect to their reduction potentials by an electrochemical means. This process is known as the electrorefining. However, the commercial LWRs burn nuclear fuels in the form of oxide and, as a consequence, spent fuels are discharged as oxides. The oxide spent fuels are stable in the molten salt medium of the electrorefining process and not allowed to be directly introduced into an electrorefining bath without a pretreatment step. Converting the oxides into a metallic form could resolve the technical difficulty on accepting the oxide spent fuels in the molten-salt-based process.

A metallothermic technology was adopted as a reduction method from 1990s [6–8]. It utilized a reducing ability of Li metal and produced $Li_2O$ with the reduced metal product in a molten LiCl salt. The Li reduction process required an additional process for collecting Li metal from the used molten salt after the reduction

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process so that Li metal could be recycled within the processes. Recently, the two steps in the reduction process were combined into a single step under an electrochemical concept and referred to as an electrolytic reduction process [9–12]. The electrolytic reduction adopting LiCl could be summarized by the following equation.

$$M_xO_y + 2y\text{Li}(\text{in LiCl}) \rightarrow x\text{M} + y\text{Li}_2\text{O (in LiCl)} \quad (1)$$

In the electrolytic reduction cell, oxide ($M_xO_y$) to be reduced is used as an electrode where oxygen elements in the solid oxide are electrochemically dissolved into a molten salt. The shape of the loaded oxide (powder, pellet and so on) is maintained throughout a reduction operation and the reduced metal becomes sparse due to the loss of oxygen elements. The molten salt gradually fills the pores of the reduced metal product, which are formed by the loss of oxygen as the reaction proceeds. Therefore, the entangled LiCl salt is pulled out with the porous metal product after the oxide reduction. The percolated salt should be removed from the metal before being transferred to the following electrorefiner, otherwise the accompanied LiCl salt will shift the salt composition of the electrorefiner where LiCl–KCl eutectic salt is used, resulting in the alteration of the physico-chemical properties of the salt medium.

Vacuum evaporation method has been applied to pyro-processes as a post-treatment step for separating a molten salt [13] or a liquid metal [14,15] from metal products or precipitates [16–18]. In principle, the method could be readily applied to LiCl salt removal from the metal products obtained after the electrolytic reduction process because the effective removal of LiCl salt included in the porous metal product of the electrolytic reduction process can be achieved by applying the high vacuum evaporation technique due to the low vapor pressures even at high temperatures. Experimental data are required in designing a large-scale evaporator and calculating material balances throughout the pyro-processes. However, the evaporation condition and the behavior of LiCl salt evaporation from a porous medium under high vacuum have not been investigated. In this work, we addressed thermodynamic considerations on the LiCl evaporation, examined the LiCl removal conditions by changing process variables such as temperature and pressure, and measured the evaporation rates from different porous solids to investigate the effect of porosity and shape of the solid. The porosity and shape of uranium oxide to be electro-reduced can be controlled by adjusting the conditions of the voloxidation process [5] which feeds materials to the electrolytic reduction process. Therefore, the study of the effect of porous solid characteristics on the evaporation rate is of significance to integrating the two processes.

The electrolytic reduction process using spent fuels produces radioactive metals which should not be handled in a typical chemical laboratory. Thus, in this work, a porous inert solid material was adopted to observe the behaviors of the LiCl evaporation with respect to solid characteristics prior to the use of the radioactive materials.

## 2. Thermodynamic considerations

Thermodynamic analysis on a considered process is of essence in determining the limit of the process and setting the process conditions. As for the vacuum evaporation of LiCl, solid LiCl would be evaporated after being fused to a liquid phase when an imposed temperature is higher than its triple point. Otherwise, solid LiCl would be changed directly into a vapor phase. The triple point of LiCl is not known. On a pressure–temperature (P–T) diagram of a pure substance, a sublimation line meets a melting line at the triple point. Therefore, the triple point can be estimated by P–T behavior on the solid–liquid phase change line expressed as the following Clapeyron equation.

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{sl}}{T\Delta V^{sl}} \quad (2)$$

In general, the volume change by the solid–liquid phase transition $\Delta V^{sl}$ is nearly negligible for a number of substances, which implies that the solid–liquid transition temperature is nearly independent of the saturated pressure and the triple point is very close to the melting point. Therefore, a higher temperature than the melting point of LiCl (610 °C) on a system would evaporate LiCl from a liquid phase even under an extremely reduced pressure.

The vapor pressure of the salt can be calculated using a correlated equation for phase changes of pure salt vapor. The equation and the temperature parameters for the vapor pressures of liquid LiCl were found from tables of a metallurgical thermochemistry book [19]. The equation including coefficients for LiCl is expressed as follows with units of mmHg and $K$ for pressure and temperature, respectively.

$$\log p = -10760/T - 4.02 \log T + 22.3 \quad (3)$$

If we reduce the pressure on an evaporation system, the temperature difference between the boiling and the melting point gets closer and the liquid region narrows as expected from Fig. 1 which is drawn by using Eq. (3). The temperature range of the stable liquid phase is not so significant for the evaporation. However, it becomes an important factor to be considered when recovering the evaporated salt for recycling. If the liquid phase range is wide, the evaporated salt would be condensed as a liquid phase in a receiver and then solidified to be a crystalline form which is tightly adhered on the receiver. Meanwhile, an instant cooling rapidly crossing the liquid range could change the salt vapor directly into a solid. In such a case the powder could be formed due to the reduced pressure and the sparsity of salt molecules in the vapor phase, which could be readily collected and recovered from a receiver. Consequently, the high vacuum should be imposed on the evaporation system taking the salt recovery into consideration along with the rate of evaporation.

Chemical stability of the substances in the evaporation system is also an important aspect in deciding the temperature condition. After the electrolytic reduction, the reduced metal of which major component is uranium contains the LiCl salt including $Li_2O$ which is

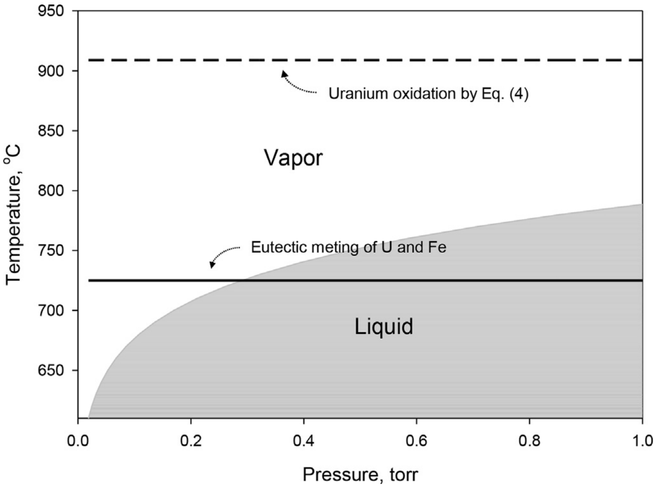

**Fig. 1.** Pressure–temperature diagram of LiCl and temperature limits of LiCl evaporation.