

# Residual Salts Separation from Metal Reduced Electrolytically in a LiCl-Li<sub>2</sub>O Molten Salt

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## 1. Introduction

The PWR spent oxide fuel can be reduced electrolytically in a hot molten salt for the conditioning and the preparation of a metallic fuel. Then the metal product is smelted into an ingot to be treated in the post process. Incidentally, the residual salt which originated from the molten salt and spent fuel elements should be separated from the metal product during the smelting. In this work, we constructed a surrogate material system to simulate the salt separation from the reduced spent fuel and studied the vaporization behaviors of the salts.

## 2. Methods and Results

The components of the spent oxide fuel can be categorized into four groups according to their chemical behavior: (a) uranium and transuranics (TRU), (b) alkali(AM), alkaline earths(AEM), (c) rare earth elements (RE), and (d) noble metal elements (NM). After the electrolytic reduction in a LiCl-Li<sub>2</sub>O molten salt at 650 °C, the metallized spent fuel consists of uranium, TRU, and NM in a powder form [1, 2]. The high heat load alkali and alkali earth oxides change chemically to corresponding chlorides during the electrolytic reaction and can be separated from the reduced spent fuel. Consequently, the heat load and radioactivity of the reduced spent fuel can be significantly decreased. Most rare earth elements accompany the reduced spent fuel in the oxide form due to their low solubility in a LiCl molten salt.

The vapor pressure variation of the chloride compounds with the temperature was calculated by using thermodynamic data. In the case of LiCl and CsCl, the main components of the residual salts, a drastic increase of the vapor pressure was observed above 900 °C. Considering the vaporization behaviors of the chloride compounds, the removal of the residual salts at 950 °C was set up for the 1<sup>st</sup> step of a smelting. The metal elements in the targets of the smelting have a relatively low vapor pressure when compared to the chloride compounds. Actually, the vaporization of U and Pu is negligible during the smelting process. However, Am is a very peculiar element which has a very stable gas phase ground state and accordingly shows a high vapor pressure. To prevent the vaporization of Am, the heating condition should be carefully controlled. Mn shows a similar vaporization behavior to Am. Therefore, Mn was used as a surrogate material for Am in this study. For the melting of a metal powder, the melting temperature should be higher than the melting point of the uranium metal, 1132 °C. The

oxide compounds will not be melted in the normal melting condition and can be collected as dross after the smelting process. Y<sub>2</sub>O<sub>3</sub> was selected as a surrogate material to represent the behavior of the rare earth elements during the separation of residual salts.

Table 1. Surrogate material system

Actual	TRU	AM, AEM	RE	Salts
Surrogate	Mn	CsCl, SrCl <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	LiCl-Li <sub>2</sub> O

Removal of volatile materials will be facilitated in a vacuum condition by an enhanced diffusion rate. Fig. 1 shows the vaporization behaviors of the surrogate materials during the inactive experiments. The final temperature was held for 5 hours in a vacuum condition of  $\sim 10^{-2}$  torr.

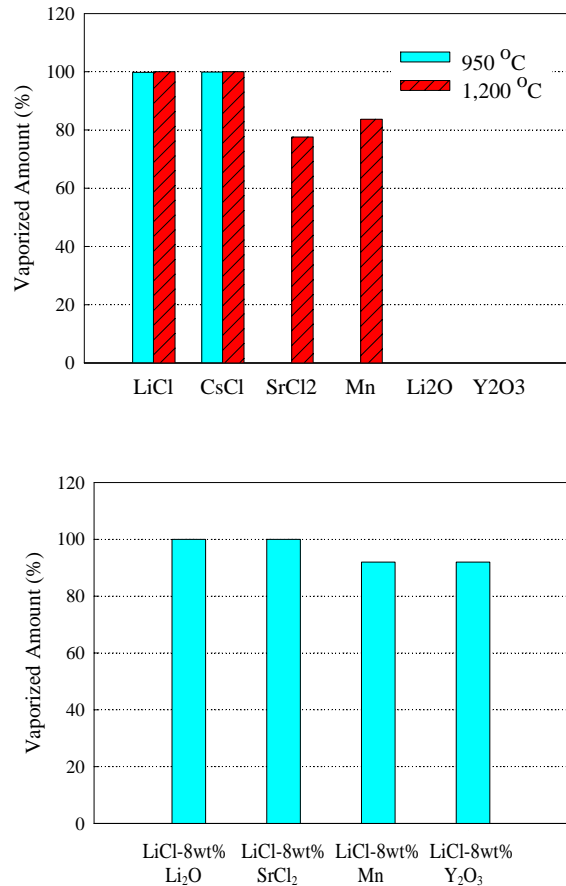


Fig. 1. Vaporization of the surrogate materials during a smelting.

In the case of the mono-component vaporization experiments, the chloride compounds except for SrCl<sub>2</sub> were completely removed from the metal products at

950 °C. Mn, the surrogate of Am, and SrCl<sub>2</sub> were partially vaporized at 1,200 °C in our experimental condition. The separation of Am from the metal product is not desirable. On the other hand, SrCl<sub>2</sub>, a high heat load fission product, should be separated from the metal product. For the selective vaporization of SrCl<sub>2</sub>, we studied the mixing effect of the salts. 8 wt% Li<sub>2</sub>O and 8 wt% SrCl<sub>2</sub> are soluble in LiCl at 650 °C, respectively, and the DSC (differential thermal calorimetry) experiment using a closed pen showed the strong interaction of Li<sub>2</sub>O and SrCl<sub>2</sub> with LiCl. The lowering of the vaporization temperature of Li<sub>2</sub>O and SrCl<sub>2</sub> in a bi-component sample was explained accordingly. Mn and Y<sub>2</sub>O<sub>3</sub> are actually not soluble in a LiCl molten salt in the tested temperature range and the DSC experiments did not show any interaction of them with LiCl. Consequently, the mixing effect was not observed in the case of Mn and Y<sub>2</sub>O<sub>3</sub>.

### 3. Conclusion

The separation of residual salts has been studied by using surrogate materials. The residual chloride salts were selectively separated from the metal product while suppressing the vaporization of Mn, the surrogate of Am. Y<sub>2</sub>O<sub>3</sub>, the representative surrogate of the rare earth elements, can be recovered as dross after a smelting. Considering the vaporization behaviors, salt vaporization at 950 °C was set up for the 1<sup>st</sup> step of the spent fuel smelting.

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### REFERENCES

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