

Smelting Associated with the Advanced Spent Fuel Conditioning Process

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Abstract: The smelting process associated with the advanced spent fuel conditioning process (ACP) of Korea Atomic Energy Research Institute was studied by using surrogate materials. Considering the vaporization behaviors of input materials, the operation procedure of smelting was set up as 1) removal of residual salts, 2) melting of metal powder, and 3) removal of dross from a metal ingot. The behaviors of porous MgO crucible during smelting were tested and the chemical stability of MgO in the salt –being atmosphere was confirmed.

Keywords: Smelting, spent fuel, ingot, MgO, vaporization

Introduction

The Advanced Spent Fuel Conditioning Process has been under development at KAERI since 1997 to tackle the problems derived from the accumulation of spent fuel [1, 2]. The concept is to convert the spent oxide fuel into a metallic form in a high temperature molten salt. The heat power, volume, and radioactivity of the spent fuel can be decreased by a factor of a quarter via this process. The main objective of the ACP is to treat Pressurized Water Reactor (PWR) spent fuel for a long-term storage and an eventual disposal. Additionally, the ACP can contribute to the GEN-IV system as a key fundamental technology for the preparation method of the metallic fuel. The process consists of 1) the air voloxidation of the oxide fuel pellets, 2) the electrochemical reduction of the oxide fuel powder into a metallic form in a LiCl-Li₂O molten salt, and 3) the smelting of the metallic powder to an ingot (Fig. 1).

The metallic powder from the electrochemical reduction step should be smelted into an ingot to be treated in the post process. Source material for the smelting originated from the electrochemical reduction step. Incidentally, the residual salt can be separated from the metal product during the smelting. The paper will show the experimental results by using surrogate materials, which are of great importance for the successful implementation of the ACP. An inactive test (20 kgU/batch) of the ACP including the smelting will be carried out by using the KAERI hot cell facility (2004-2005). The

completion of this lab scale inactive experiment will shed light on the planned hot test of the ACP in 2006 (20 kgHM/batch) therefore tapping into the commercialization of the ACP.

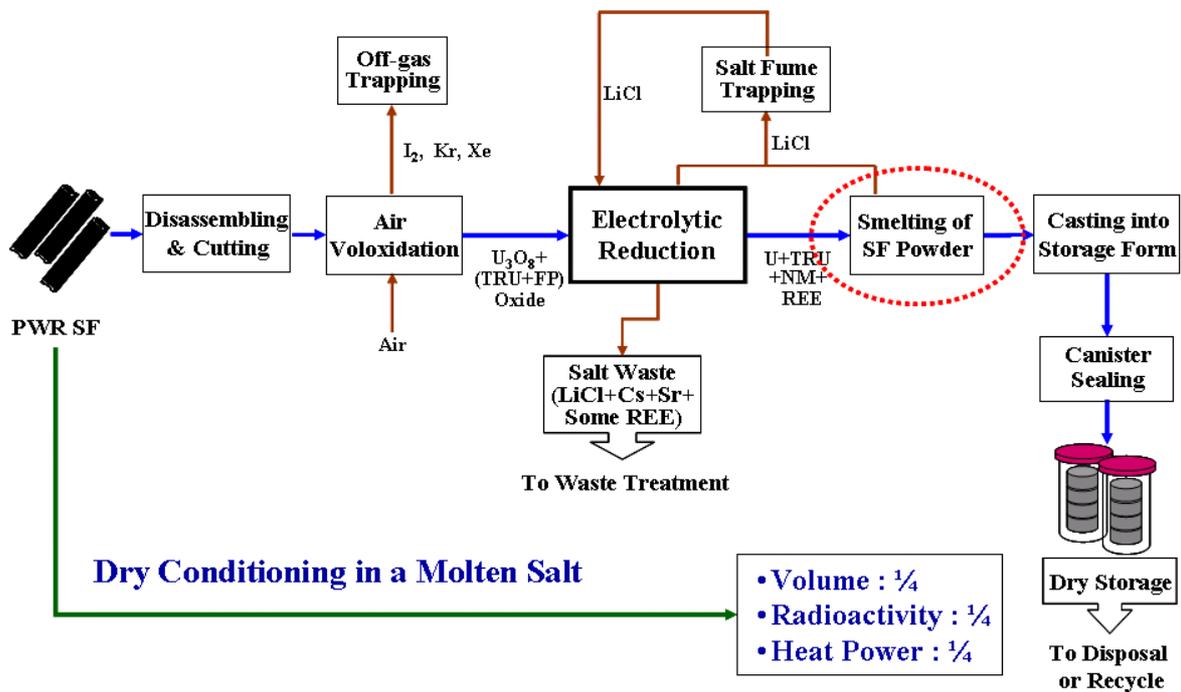


Fig. 1. Flow sheet of the Advanced Spent Fuel Conditioning Process of KAERI.

Results and Discussion

The components of spent oxide fuel can be categorized into four groups according to their chemical behavior: (a) uranium and transuranics (TRU), (b) alkali, alkaline earths, Eu, Se, and Te, (c) rare earth elements (REE), and (d) noble metal elements (NM). The laboratory scale inactive tests (5 kgU/batch) carried out by KAERI show that more than 99% of the uranium oxides can be reduced to metal by the electrochemical method [3, 4]. The high heat load alkali and alkali earth oxides change chemically to a chloride form during the electrolytic reaction and 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 due to their low solubility in a LiCl molten salt. Fig. 2 shows the mass and radioactivity of spent fuels calculated by using ORIGEN II code. The metal product transferred from electrochemical reduction step as a powder form is mostly composed of U metal. Therefore, the melting of uranium dominates the entire heating process.

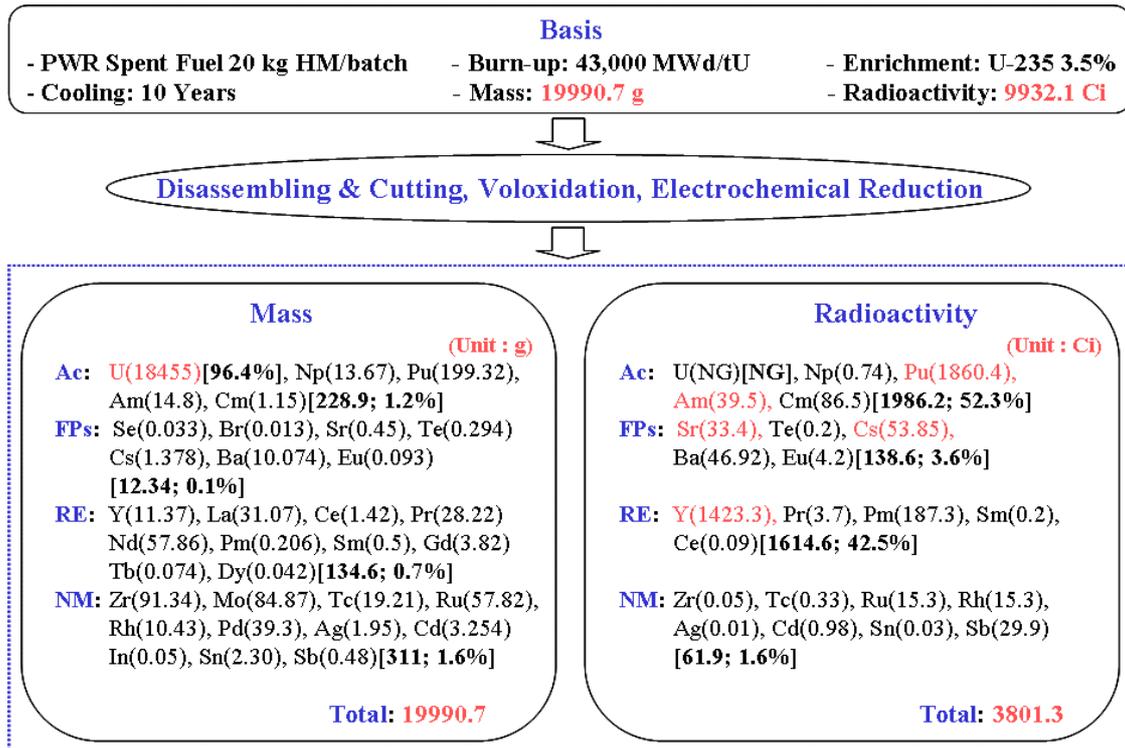


Fig. 2. Mass and radioactivity of spent fuels for the smelting process.

The physical properties of target materials for the design of the smelter was investigated and shown in Table 1. For the melting of 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. The electrochemical reduction process is normally carried out in a 3wt% Li₂O-LiCl molten salt. Therefore LiCl and Li₂O are originated from the electrochemical reduction process and the amount will vary according to the preconditioning step in order to reduce residual salts in a metal product. The chloride compounds such as LiCl, SrCl and CsCl have relatively low melting and boiling points and expected to vaporize during the smelting process.

Table. 1. Physical Properties of the Key Target Materials

Element	U	Am	CsCl	SrCl ₂	LiCl	Li ₂ O	Y ₂ O ₃
m.p. (°C)	1132	1173	646	868	613	1570	~2410
b.p. (°C)	3930	2600	1303	2056	1360	-	-
d (g/cm ³)	19.07	13.67	3.99	3.052	2.07	2.013	5.03

The vapor pressure variation of chloride compounds with temperature is shown in Fig. 3. The significant increase of vapor pressure is found above 900 °C. Considering the vaporization behaviors of chloride compounds, the removal of residual salts at 950 °C was set up for the 1st step of smelting. The metal elements in the targets of smelting have relatively low vapor pressure compared to 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 high vapor pressure. To prevent the vaporization of Am, the heating condition should be carefully controlled. Mn shows similar vaporization behavior of Am. Therefore, Mn was used as a surrogate material for Am in this study.

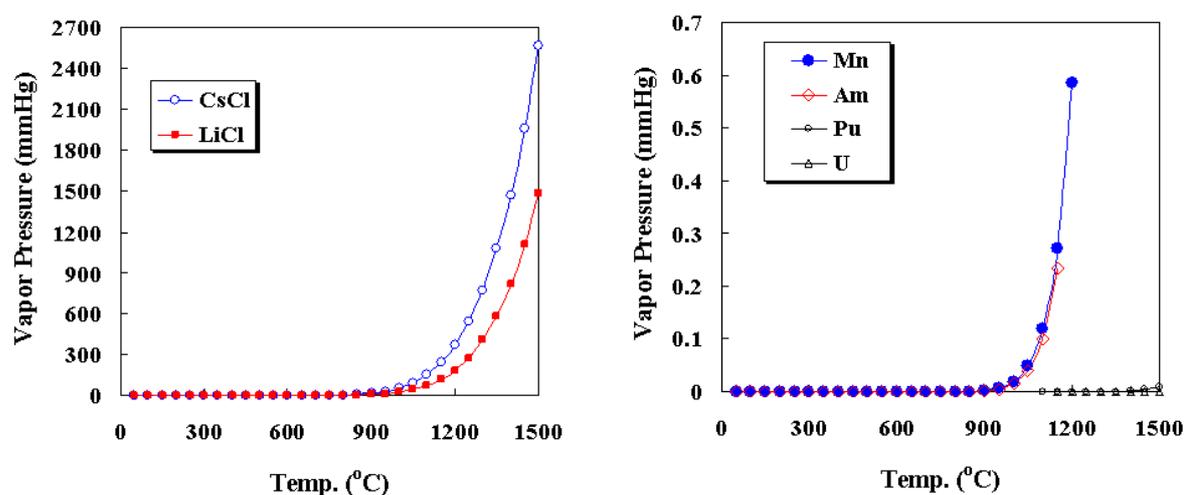


Fig. 3. Vapor pressure changes of the target materials of the smelting with temperature.

The surface of metal powder can easily be attacked by oxygen in the oxidative condition and the resultant oxide layer will inhibit the melting of metal powder. Therefore, the smelting should be carried out at much higher temperature than the melting point of U. Removal of volatile materials will be facilitated in vacuum condition by enhanced diffusion rate. Fig. 4 shows the vaporization behaviors of some characteristic materials during inactive experiments conducted by using induction furnace. The final temperature was kept for 5 hours in the vacuum condition of $\sim 10^{-2}$ torr. Chloride compounds except SrCl_2 were completely removed from metal product during the 1st step of smelting at 950 °C. The vaporized chlorides will be transferred to the salt waste treatment process. Mn, the surrogate of Am, and SrCl_2 were partially vaporized at 1,500 °C. The separation of Am from the metal ingot is not desirable. The lowering of the smelting temperature or decrease of the vaporization rate by increasing the pressure inside the smelter can be an effective method for the prevention of Am vaporization. The further study to get quantitative data on the vaporization behaviors of Am and SrCl_2 will be carried out to optimize the operation of the smelter.

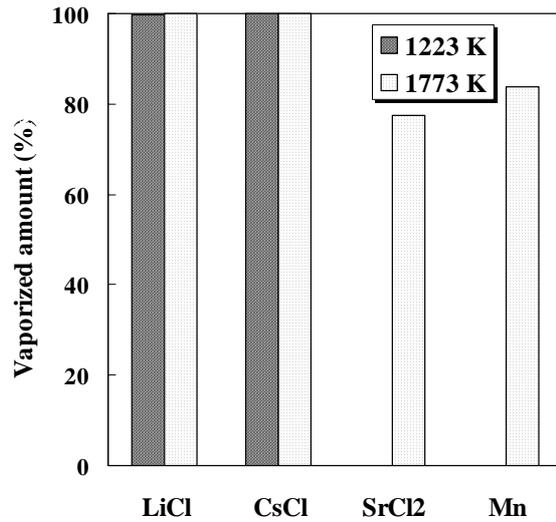


Fig. 4. Vaporization of the volatile materials during smelting.

A porous MgO crucible was used in the electrochemical reduction process as a part of cathode system. The MgO crucible containing metal powder and residual salts should be transferred from the electrochemical reduction process to the smelter for the smelting. Consequently, it will be exposed to the salt-being atmosphere at 1,500°C. Therefore, it is important to verify the stability of MgO in a smelting process to ensure its applicability to the smelter as an inner container.

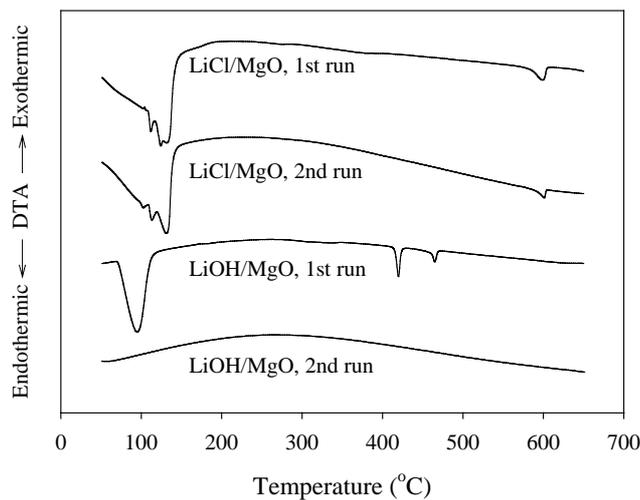


Fig. 5. DTA curves obtained under air atmosphere for LiCl/MgO and LiOH/MgO.

LiCl was mechanically mixed with MgO to make 10 mol% LiCl/MgO and a DTA experiment was carried out to 650 °C (Fig. 5, LiCl/MgO, 1st run). Since LiCl is a very hygroscopic material, the peaks in the lower temperature region were attributed to the desorption of physisorbed H₂O. The relatively

small peak around 600 °C was due to the melting of the LiCl. The sample was cooled down to room temperature and the second *in-situ* DTA experiment was performed to 650 °C (Fig. 5, LiCl/MgO, 2nd run) resulting in peaks similar to that of the 1st run and suggesting that the interaction between MgO and LiCl is negligible. Li₂O readily absorbs H₂O and transforms to LiOH. 10 mol% LiOH (kokusan, EP)/MgO was made and a DTA experiment was performed according to the same procedure applied to the 10 mol% LiCl/MgO. The three peaks (Fig. 5, LiOH/MgO, the 1st run) were identified as the desorption of physisorbed H₂O, phase transformation of LiOH, and melting of the LiOH, respectively. However, no peak was obtained during the 2nd run. The reason was attributed to the transformation of LiOH to Li₂O during the 1st run. So, we believe that Li₂O is stabilized on the surface of MgO at 650 °C. After smelting test at 1,500 °C, MgO crucible was analyzed by XRD to elucidate the interaction of MgO with the chloride compounds and only the MgO structure was detected.

In the following process, the smelted ingot may be cast into rods for storage. After an optimization of the crucible (Si₃N₄ mold) design to decrease the temperature gradient, a successful casting of a uranium metal rod of 2500 mm in length with a withdrawal speed from 25 mm/min to 80 mm/min was achieved without any remains of the charged raw material.

Conclusions

The smelting of metallic powder from the electrochemical reduction process has been tested by using surrogate materials and induction furnace. LiCl and CsCl were removed from a metal product by evacuation at 950 °C and Mn, a surrogate for Am, was partially vaporized at 1,500 °C. Considering the vaporization behaviors of input materials, the operation procedure of smelting was set up as 1) removal of residual salts, 2) melting of metal powder, and 3) removal of dross from a metal ingot. The behaviors of porous MgO crucible used as a container of metal powder and residual salts were analyzed and the chemical stability of MgO in the salt-being atmosphere was confirmed.

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