Theoretical Analysis for Direct Conversion of U_3O_8 Into UCl_3 as an Alternative to Oxide Reduction Reaction

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1. Introduction

Oxide reduction process is considered as a key link which enables application of the metal fuel based pyroprocessing in PWR (Pressurized Water Reactor) fuels. According to the KAERI's pyroprocessing flow diagram, UO_2 fuel is reduced into its metallic form and then U is selectively recovered through electro-refining. And group recovery of U and TRU (TRansUranic) nuclides performed via electro-winning process [1]. Although these processes show promising results, new approaches should be considered for higher efficiency. In this work, an alternative process, so-called MKZP (Min Ku Zirconium Process) was proposed to convert U_3O_8 into UCl_3 directly to simplify the pyroprocessing.

2. Theoretical calculations

The HSC chemistry code (Reaction Equations module) was employed for the theoretical calculations including changes in Gibbs free energy (ΔG) and equilibrium constants (K). The ΔG value helps to identify direction of the reaction, in other words, right-hand reaction is preferred when ΔG is negative, while reverse reaction is preferred when ΔG is positive.

3. Results and Discussion

3.1 Conversion of U and actinide oxides into chlorides

The key reaction of the MKZP is as follows:

$$U_3O_8 + 7/4Zr + 9/4ZrCl_4(g) \leftrightarrow 3UCl_3 + 4ZrO_2 \quad (1)$$

The calculation results provided ΔG and K values of -258.0 kcal and 8.62 x 10^{72} at 500 °C. These values strongly suggest that the formation of UCl_3 is highly preferred thermodynamically. Sakamura et al. published a similar reaction scheme which was performed using UO_2 instead of U_3O_8 and under a LiCl-KCl molten salt environment [2]. Considering pulverization of UO_2 during the oxidative decladding process to produce fine U_3O_8 powder, and low solubility of $ZrCl_4$ in molten salt (1.3 at% at 500°C), reaction (1) of MKZP is considered to have higher potential for higher reaction rate and scale-up.

Further calculations revealed that the combination of metallic Zr and $ZrCl_4$ can convert other actinide nuclides such as Np, Pu, Am, and Cm into their chloride forms.

3.2 Conversion of other nuclides into chlorides

Other nuclides of major interest in the pyroprocessing are those with high decay heat such as Sr and Cs. It was theoretically identified that these nuclides prefer their chloride forms in the presence of $ZrCl_4$ (metallic Zr is not even necessary).

3.3 Zirconium supply

The biggest concern on the MKZP is that a lot of metallic or chloride form of zirconium is consumed by the process. However, 42 wt% of Zr necessary for the MKZP can be fulfilled by cladding hulls which

consists of more than 95wt% of zirconium. And they are easily converted into $ZrCl_4$ by reacting with chlorine gas.

3.4 Process flow diagram

The overall flow diagram is shown in Fig. 1. The MKZP could eliminate complicate pellet production step between the voloxidation and oxide reduction of the pyroprocessing. It is clear that the MKZP

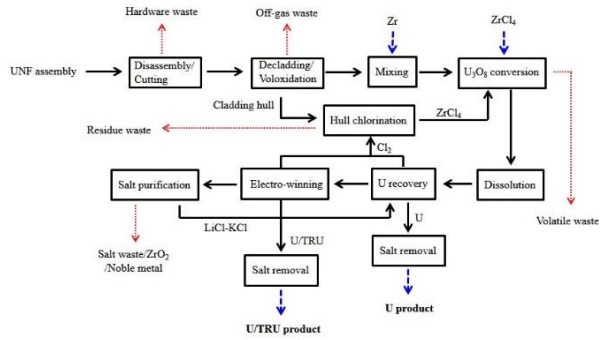

Fig. 1. Process flow diagram of the MKZP.

4. Conclusion

Although experimental study should be performed intensively prior to actual comparison, theoretical calculation results revealed that the MKZP can reduce the number of processes from 16 of pyroprocessing to 11 [3].

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