

Considerations of Chlorination Process for Molten Chloride Fast Reactor Fuel in View of Material Corrosion by Impurities

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1. Introduction

Recently, there has been a growing interest in the molten chloride fast reactor (MCFR). One of the reasons is its potential for reusing spent nuclear fuel (SNF) and thus minimizing high-level waste.

The conversion of SNF to MCFR fuel involves a chlorination process with multiple process steps, necessary to address the diverse properties of elements within SNF. During chlorination, impurity removal is crucial not only for optimizing reactor physics but also to mitigate material corrosion risks. For instance, certain soluble impurities with high redox potentials can accelerate corrosion reactions [1].

This study focuses on establishing the chlorination process steps of SNF, employing computational analysis using HSC Chemistry 10. Additionally, experimental evaluations were conducted to assess the impact of impurities on the corrosion of SS316. Corrosion experiments with impurities were conducted in NaCl-MgCl₂ salt at 600°C within an Ar-filled glovebox.

2. Methods and Results

2.1. Chlorination process for MCFR fuel

There are two types of nuclear fuel, which are essential for the operation of MCFR: transuranium element (TRU) chlorides for reactor startup and uranium chloride for refueling. Considering the specific nuclear fuel requirements, the established chlorination process for SNF follows the outlined flowsheet in Fig. 1. The initial step involves the voloxidation of SNF to eliminate volatile fission products. Subsequently, the chlorinating agent NH₄Cl is introduced [2]. It selectively converts TRU oxides to TRU chlorides, but cannot transform uranium oxides into uranium chloride. Therefore, the conversion of uranium oxide to uranium chloride is necessary after undergoing a transformation to uranium metal through an electrolytic reduction process. The distinctive chlorination characteristics of NH₄Cl facilitate the segregation of TRU chlorides and uranium chloride.

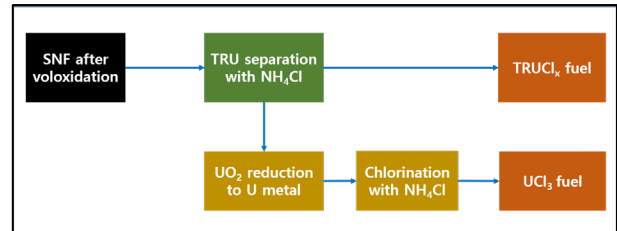


Fig. 1. Flowsheet for spent nuclear fuel chlorination

2.2. Material corrosion of MCFR with impurities

The established flowsheet raises two concerns related to material corrosion: the presence of SmCl₃ and the formation of UCl₄. First, when calculations are based on the SNF compositions of the PNNL report [3], it is determined that 11% of SmCl₃ can coexist in the TRU chlorides. Second, the reaction between uranium metal and NH₄Cl can lead to the formation of UCl₄. Both SmCl₃ and UCl₄ are known to have positive redox potentials, which can expedite material corrosion. Therefore, this study focuses on evaluating the impact of two selected impurities, SmCl₃ and EuCl₃, on material corrosion. EuCl₃ serves as a surrogate of UCl₄ due to the high redox potential of Eu(III)/Eu(II) couples in chloride salts [1].

Table I represents the weight change of SS316 following 100 hours of exposure to different salt compositions at 600°C. It is apparent that the extent of weight loss increases with the addition of SmCl₃ and EuCl₃, indicating that the presence of elements with high redox potential accelerates corrosion.

Table I: Weight change of SS316 after exposure to salts at 600°C for 100hours

Salt composition	Weight change [mg/cm ²]
NaCl-MgCl ₂	-0.41 ± 0.03
NaCl-MgCl ₂ -SmCl ₃ (1.71wt%)	-0.60 ± 0.04
NaCl-MgCl ₂ -EuCl ₃ (1.72wt%)	-1.40 ± 0.08

The analysis of the corroded surface of SS316 was conducted using scanning electron microscopy (SEM), and the results are depicted in Fig. 2. Specimens exposed to NaCl-MgCl₂ and NaCl-MgCl₂-SmCl₃ display localized corrosion, with corroded areas being more widespread in the NaCl-MgCl₂-SmCl₃ salts. In contrast,

specimens corroded with NaCl-MgCl₂-EuCl₃ salts exhibit a predominantly uniform corrosion, affecting the majority of the surface.

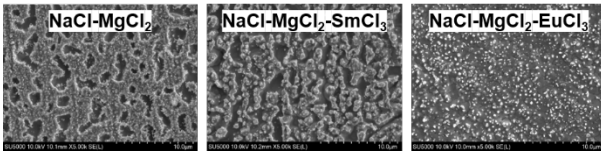


Fig. 2. Surface SEM image of SS316 after exposure to salts at 600°C for 100hours

In summary, soluble impurities characterized by high redox potential possess the ability to accelerate corrosion. Particularly, in the instance of EuCl₃, a heightened redox potential correlates with a more significant corrosion impact.

2.3. Requirements for MCFR fuel chlorination process

In the context of material corrosion, it is crucial to manage the levels of SmCl₃ and UCl₄ throughout the chlorination process. One strategy to minimize both chlorides involves optimizing the quantity of reacted NH₄Cl. As shown in Fig. 3, the quantities of SmCl₃ and UCl₄ decrease with a reduction in the reacted NH₄Cl.

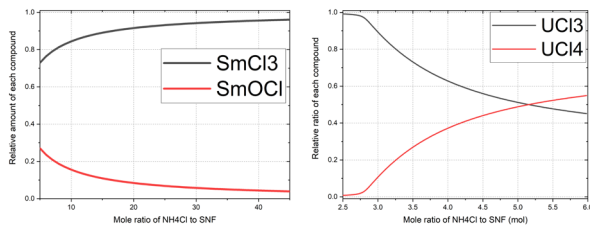


Fig. 3. Remained SmCl₃ and SmOCl ratio depending on the reacted NH₄Cl during reactions between TRU oxides and NH₄Cl (left). UCl₃ and UCl₄ ratio depending on the reacted NH₄Cl during reactions between TRU oxides and NH₄Cl (right).

For SmCl₃ reactions, further optimization is necessary to achieve a high concentration of TRU chlorides. In the case of UCl₄, the use of reducing agents, such as H₂, can be employed to convert UCl₄ to UCl₃.

3. Conclusion

This study proposed a chlorination process for MCFR fuel and investigated the impact of impurities on material corrosion. The chlorination of MCFR fuel involves sequential steps of voloxidation and NH₄Cl reaction steps. Potential by-products, namely SmCl₃ and UCl₄, have the capacity to expedite corrosion owing to their elevated redox potential. Ongoing efforts will focus on further optimizing the chlorination process to ensure the long-term safe and stable operation of MCFR.

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