Dissolution Behavior of Simulated Spent Nuclear Fuel in LiCl-KCl-UCl$_3$ Molten Salt

Sang-Kwon Lee, Sung-Wook Kim, Jun-Hyuk Jang, Min Ku Jeon, and Eun-Young Choi

Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea

Correspondence should be addressed to Sung-Wook Kim; swkim818@kaeri.re.kr

Received 18 June 2021; Accepted 18 October 2021; Published 2 November 2021

Academic Editor: Guglielmo Lomonaco

Copyright © 2021 Sang-Kwon Lee et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Considering the necessity of the development of methods to reduce the burden of storage and disposal of high-level radioactive waste, in this study, we propose a nuclide separation technique using molten salt immersion. The dissolution behavior of simulated spent nuclear fuels (SSFs) immersed in a LiCl-KCl-UCl$_3$ (LKU) molten salt at 500 °C was investigated using a combination of thermodynamic and experimental studies. Surrogates of transuranic elements (TRUs), that is, rare earth elements (REs), in the SSFs were dissolved into the molten salt without any damage to the UO$_2$ structure of the SSFs. The results suggest that the LKU salt technique can be used to separate REs and, potentially, TRUs from actual spent nuclear fuels (SNFs). It is thought that this technique is advantageous over the conventional TRU recovery techniques because the majority of the SNFs (i.e., UO$_2$) remained stable, thus reducing the process burden. Several SNF treatment process options using this technique were suggested. This study will serve as a guide for future studies on the management of high-level waste discharged from nuclear reactors.

1. Introduction

The management, storage, and disposal of high-level radioactive wastes discharged from nuclear reactors, known as spent nuclear fuels (SNFs), has become a worldwide issue. SNFs contain a variety of radioactive nuclides produced by nuclear fission, such as transuranic elements (TRUs). Underground disposal, especially deep geological disposal, is considered the preferred management option for these wastes [1, 2]. However, underground disposal requires the construction of large repository facilities to provide sufficient protection from the associated radioactivity; consequently, such methods are expected to continue to face a number of social, environmental, and economic challenges [1, 2].

SNFs can be regarded as recyclable resources because they are composed of various valuable elements formed by nuclear fission reactions [3–10]. For instance, although TRUs are the most dangerous nuclides owing to their exceptionally long-lived and strong radioactivity (e.g., half-life of $^{239}$Pu = 24,110 y), they can be utilized as fuels in various nuclear reactors, including Generation IV (Gen IV) reactors such as sodium-cooled fast reactors (SFRs), high temperature reactors (HTRs), and gas-cooled fast reactors (GCFRs) [4–9]. Coupling of back-end fuel cycle of the commercial light water reactors (LWRs) to the fuel cycle of the Gen IV reactors is an attractive option for the management of the LWR SNFs. TRUs generated from the LWRs can be transmuted into stable nuclides in the Gen IV reactors to minimize the amount of the high-level radioactive wastes, which is beneficial on the long-term underground disposal [4–9]. Integrated fuel cycles of LWR-SFR and LWR-HTR-GCFR are promising candidates [4–7]. In addition, SNFs contain valuable rare earth elements (REs) and noble metal elements (NMs). It was recently reported that the recovery of Ru and Rh from SNFs could be expected to yield an amount comparable to a significant portion of total current production [10]. Thus, it is considered that the recovery of useful nuclides from SNFs would be beneficial not only to reduce...
the SNF management burden by decreasing radiotoxicity but also to maximize resource usage.

Driven by these considerations, various wet and dry processes have been developed to recover valuable nuclides (especially TRUs) from SNFs [4, 11, 12]. Aqueous solution-based techniques such as plutonium uranium reduction extraction (PUREX) have been well established for the extraction of TRUs, and commercial facilities are operational in many countries [11, 12]. Pyro-processing, a combination of molten salt-based dry processes, has also been studied as an alternative [4]. Pyro-processing has an advantage in terms of non-proliferation because weapons-grade pure Pu cannot be recovered [4]. In pyro-processing, the nuclides in the SNFs are dissolved in chloride molten salts (e.g., an LiCl and LiCl-KCl mixture) to allow them to be chemically and electrochemically recovered [4]. U, the most abundant nuclide in the SNFs (>90% in terms of metals), is less harmful than other nuclides (e.g., TRUs), and it is not seriously considered for underground disposal as it exists in an oxide form, UO2, which is physically and chemically stable. However, during wet and dry recovery processes, the treatment of U from SNFs consumes considerable resources because the SNFs, mostly composed of U, must be destroyed completely into ionic states to be dissolved in the reaction media. Therefore, a significant amount of the dissolved U compounds should be chemically or electrochemically treated in a subsequent extraction stage [4, 11, 12], which contributes substantially to the burden of the entire recovery process. It is conventionally expected that the costs and complexity of such recover processes can be significantly reduced if methods of extracting TRUs without destroying the UO2 matrix in the oxide-phase SNFs are developed.

In this study, we propose a simple nuclide separation technique using a UCl3-containing molten salt, LiCl-KCl-UCl3 (LKU), which does not destroy the UO2 matrix. It is supposed that the oxides of the nuclides comprising SNFs can be transformed into their chlorides. Once the chlorides are formed, they are expected to dissolve in the LKU molten salt out of the UO2 matrix. Meanwhile, UO2 remains stable in the solid phase as the major component. In this study, the dissolution behavior of the oxide-phase simulated spent nuclear fuels (SSFs) in the LKU molten salt at 500°C was investigated to demonstrate the feasibility of the molten salt treatment technique for nuclide separation.

2. Materials and Methods

All experiments were conducted inside Ar-filled glove boxes to minimize exposure to air and moisture. Approximately 0.7% by mass of UCl3 was added into eutectic LiCl-KCl salt inside an Al2O3 crucible to prepare the LKU salt. The SSF pellets (14.46 g) were placed inside a stainless-steel basket with a porous wall (minimum opening = 325 mesh) to be immersed in the LKU molten salt (106.51 g) at 500°C for 20 h. The procedure used to fabricate SSF pellets is detailed in the literature [13], and the composition of the fabricated SSF pellets is specified in Table 1. Importantly, TRUs cannot be included in such experimental SSFs because of strong international and domestic regulations on their handling. In many cases, REs have been utilized as surrogates in place of TRUs in chemical experiments owing to the similarity in their chemical properties [14, 15]. Cs was also not incorporated in the SSF because Cs compounds are easily vaporized under the conditions required for SSF fabrication.

Molten salt samples were collected during the immersion by a dipstick method. Figure 1 shows the experimental procedure used for the immersion test. After immersion, the recovered SSF pellets in the basket were transferred to a vacuum distillation reactor to remove the residual salt phases. Salt distillation was carried out at 900°C under 0.1 Torr for 4 h.

Chemical analysis of the SSF pellets before and after the treatment and of the collected salt was carried out using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Thermodynamic calculations were performed using HSC Chemistry 9 software (Outotec).

3. Results and Discussion

Table 2 shows the calculated change in Gibbs free energy (ΔG) of the chemical reactions between UCl3 and the oxide components of the SNFs at 500°C. The nuclides were categorized into several groups, such as TRUs, alkaline earth elements (AEs), rare earth elements (REs), and others. The oxides of TRUs and AEs were predicted to be converted to their chlorides in the presence of UCl3. Among the REs, only Y2O3 had a positive ΔG value, while the others had negative values. However, considering that the ΔG value of the Y2O3 reaction was quite low (+7.316 kJ), the chlorination of Y2O3 to YCl3 is thought to occur under practical operating conditions (UCl3-rich). For instance, with a composition of UCl3:Y2O3 = 10:1, the equilibrium composition of UCl3: Y2O3:YCl3:UO2:U was calculated as 155.6:1:36.4:27.3:9.1 at 500°C, suggesting that most Y2O3 (Y2O3:YCl3=1:36.4) can be converted to YCl3 under these conditions. ZrO2 was calculated to be stable, and MoO2 and Rh2O3 were thought to be dissolved in the molten salt.

If the TRUs, the most critical nuclides for underground disposal, can be separated from the SNFs by the UCl3 treatment, as shown in Table 2, the radiotoxicity of the SNFs can be greatly reduced. Figure 2 shows promising scenarios.

| Table 1: ICP-AES analysis of the SSF pellets before and after the immersion in the LKU molten salt. |
| --- | --- | --- | --- |
| Category | Elements | As-fabricated (wt.%) | Salt-immersed (wt.%) |
| U | U | 83.6 | 84.5 |
| RE | La | 0.16 | 0.08 |
| | Ce | 0.31 | 0.20 |
| | Pr | 0.15 | 0.08 |
| | Nd | 0.53 | 0.28 |
| | Sm | 0.10 | 0.03 |
| | Eu | 0.02 | 0.02 |
| | Gd | 0.04 | 0.02 |
| | Y | 0.06 | 0.02 |
| Others | Zr | 0.63 | 0.60 |
| | Rh | 0.02 | 0.02 |
| | Mo | 0.02 | 0.01 |

Figure 2 shows promising scenarios
**Table 2:** Thermodynamic calculation results of chemical reactions between UCl₃ and oxide components of SNFs at 500°C.

| Category | Oxides | Reactions | ΔG (kJ) |
|----------|--------|-----------|---------|
| TRU      | PuO₂   | UCl₃ + PuO₂ = PuCl₃ + UO₂  | −131.16 |
|          | Pu₂O₃  | UCl₃ + 0.5Pu₂O₃ = PuCl₃ + 0.75UO₂ + 0.25U | −71.75 |
|          | AmO₂   | UCl₃ + AmO₂ = AmCl₃ + UO₂  | −251.31 |
|          | Am₂O₃  | UCl₃ + 0.5Am₂O₃ = AmCl₃ + 0.75UO₂ + 0.25U | −73.07 |
|          | CmO₂   | UCl₃ + CmO₂ = CmCl₃ + UO₂   | −252.69 |
|          | Cm₂O₃  | UCl₃ + 0.5Cm₂O₃ = CmCl₃ + 0.75UO₂ + 0.25U | −66.34 |
| AE       | SrO    | UCl₃ + 1.5SrO = 1.5SrCl₂ + 0.75UO₂ + 0.25U | −310.51 |
|          | SrZrO₃ | UCl₃ + 1.5SrZrO₃ = 1.5SrCl₂ + 1.5ZrO₂ + 0.75UO₂ + 0.25U | −186.78 |
|          | BaO    | UCl₃ + 1.5BaO = 1.5BaCl₂ + 0.75UO₂ + 0.25U | −391.99 |
|          | BaZrO₃ | UCl₃ + 1.5BaZrO₃ = 1.5BaCl₂ + 1.5ZrO₂ + 0.75UO₂ + 0.25U | −206.83 |
| RE       | La₂O₃  | UCl₃ + 0.5La₂O₃ = LaCl₃ + 0.75UO₂ + 0.25U | −111.12 |
|          | CeO₂   | UCl₃ + CeO₂ = CeCl₃ + UO₂   | −193.09 |
|          | Pr₂O₃  | UCl₃ + 0.5Pr₂O₃ = PrCl₃ + 0.75UO₂ + 0.25U | −89.66 |
|          | Nd₂O₃  | UCl₃ + 0.5Nd₂O₃ = NdCl₃ + 0.75UO₂ + 0.25U | −73.18 |
|          | Sm₂O₃  | UCl₃ + 0.5Sm₂O₃ = SmCl₃ + 0.75UO₂ + 0.25U | −50.84 |
|          | Eu₂O₃  | UCl₃ + 0.5Eu₂O₃ = EuCl₃ + 0.75UO₂ + 0.25U | −40.69 |
|          | Gd₂O₃  | UCl₃ + 0.5Gd₂O₃ = GdCl₃ + 0.75UO₂ + 0.25U | −43.06 |
|          | Y₂O₃   | UCl₃ + 0.5Y₂O₃ = YCl₃ + 0.75UO₂ + 0.25U | −7.31 |
| Others   | ZrO₂   | UCl₃ + 0.75ZrO₂ = 0.75ZrCl₄ + 0.75UO₂ + 0.25U | +134.21 |
|          | MoO₂   | UCl₃ + MoO₂ = MoCl₃ + UO₂   | −82.43 |
|          | Rh₂O₃  | UCl₃ + 0.5Rh₂O₃ = RhCl₃ + 0.75UO₂ + 0.25U | −36.10 |

**Figure 1:** Photographs of the experimental procedure of the immersion test.

**Figure 2:** Flowchart of the back-end fuel cycle processes with the LKU salt treatment technique in a case when TRUs are separated from the SNFs.
of back-end fuel cycles with the assumption that the TRUs can be extracted from the SNFs with high efficiency through UC\(_3\) treatment. After the UC\(_3\) treatment, the SNFs, which are mainly composed of UO\(_2\) with reduced radiotoxicity (less TRU amounts), can more easily be disposed of in underground repositories. The TRUs and REs are supposed to be dissolved into the salt to be further treated electrochemically or chemically for recovery. The recovered TRU/RE products can be disposed of underground, separately from the treated SNFs (mainly UO\(_2\)), after proper immobilization process (option 1). Because no further treatment of the complex TRU/RE mixture is required after immobilization, this option is preferable in terms of nuclear nonproliferation and process simplicity. Alternatively (option 2), the TRUs can be recycled in SFRs after RE removal via pyroprocessing [4, 16, 17]. The RE content in the SFR fuels should be maintained low because the REs are neutron absorbers which disturb nuclear fission reactions [18]; thus, the RE removal process should be performed prior to fuel fabrication. If possible, TRU recycling is attractive in terms of the minimization of high-level radioactive waste. For both options, the whole process burden on the SNF treatment is suspected to be significantly reduced because the recovery of U, which is present in the majority of the SNFs, does not need to be considered.

The thermodynamic calculations in Table 2 were performed with single or binary oxides, but these chemical states are more complicated in actual SNFs [19, 20]. There should be some difference between the calculation results and the actual system; hence, a dissolution test of the SSFs in the LKU molten salt was conducted at 500°C. Table 1 compares the composition analysis results of the SSF pellets before and after immersion in the LKU molten salt. Prior to the ICP analysis, salt distillation of the salt-immersed SSF pellets was performed to remove the residual salt. The SSF pellets retained their original shape after the immersion, as shown in Figure 1. The composition of U in the immersed pellets was comparable to that of the pristine pellets. These results reveal the physical and chemical stability of the UO\(_2\) matrix of the SSF during LKU salt treatment. It was found that Ba and most of the REs were partially dissolved in the LKU salt after immersion. Eu was the only RE that had no compositional change after immersion. Sr was predicted to be dissolvable, as seen from Table 2, but it remained almost stable in the SSFs. Zr was almost not dissolled in the molten salt, consistent with the calculation results. The composition of Rh before and after LKU treatment was identical, which did not agree with the calculation. Mo was partially dissolved.

The composition change of the LKU molten salt was tracked, as shown in Table 3. The U concentration in the LKU molten salt decreased gradually with the immersion time and, at the same time, the accumulation of dissolved elements, such as Ba and several REs, was identified. Because of the low nuclide content in the SSFs, only those with relatively high concentrations were detected by the chemical analysis. These results demonstrate that UC\(_3\) consumption and nuclide dissolution occurred simultaneously. The U concentration did not saturate with time, as shown in Table 3, suggesting that a longer immersion time could enhance the dissolution efficiency.

The experimental results shown in Tables 1 and 3 are not completely identical to the calculation results in Table 2. In SNFs, the nuclides form a solid-solution phase with a UO\(_2\) matrix (e.g., TRUs, REs, and AEs), oxide precipitates (e.g., Zr, Mo, and AEs), or metallic precipitates (e.g., noble metals) depending on their chemical properties [19–22]. Thus, it is speculated that the chemical state difference of the nuclides between the simple single or binary oxides listed in Table 1 and the fabricated SSFs induced the difference between the predicted and experimental results. For instance, Sr is known to possess both a solid solution ((U, Sr)O\(_2\)) and an oxide precipitate with a complicated (Ca, Sr, Ba) (U, Zr, Mo) O\(_3\) perovskite structure [21, 22]. Only simple SrO and SrZrO\(_3\) were considered in the calculation (Table 2); thus, the behavior of Sr may not have been accurately predicted. Similarly, the chemical behavior of Sr in the SNFs and SSFs remains unknown in the oxide reduction step of pyroprocessing, where LiCl molten salt is used as an electrolyte [23–25]. Sr was supposed to be dissolved into the LiCl salt during the oxide reduction reaction, but the experimental results revealed unexpectedly low Sr accumulation in the salt after the reaction [23, 24]. The poor dissolution behavior of SrZrO\(_3\) in the LiCl molten salt was identified in comparison to the highly dissolvable BaZrO\(_3\), emphasizing the importance of the chemical states of Sr in the molten salt system [25]. On the other hand, SrO is highly soluble in the LiCl molten salt by forming Sr\(_4\)OCl\(_6\) phase [26]. This implies difficulty of predicting the Sr behavior in the molten salt process. In addition, no evidence of the dissolution of Eu or Rh was identified through the experiment. Eu in SNFs has been regarded as a LiCl-soluble nuclide during oxide reduction [23, 24]. Similar to the Sr case, the dissolution behavior of Eu has not been clearly revealed [23, 24], and it is thought that the chemical states of Eu in the SNFs might affect the unexpected behavior. Rh tends to form metallic precipitates in SNFs [19]. Rh metal was calculated not to react with UC\(_3\) (UC\(_3\) + Rh = RhCl\(_3\) + U, \(\Delta G = +605.794\) kJ at 500°C).

Notably, a significant portion of the nuclides in the SSFs was removed by the LKU salt treatment without the destruction of the UO\(_2\) matrix; this behavior is applicable to SNFs as well. This study has a limitation in terms of the unrevealed dissolution behaviors of TRUs in the experiment. It is thought that they might behave like REs owing to their similar chemical properties, but at present, this remains unclear. Nonetheless, it is considered that the LKU salt treatment technique can be beneficial in SNF treatment processes, regardless of whether the TRUs are dissolvable. As shown in Figure 3(a), it is thought that this salt treatment technique would be viable in combination with molten salt-based pyroprocessing, even if the TRUs cannot be separated into the salt. As described earlier, the reduction of the RE contents in the SFR fuels is important; thus, additional RE removal processes should accompany the recovery process (Figure 3(b)), which increases the process burden of pyroprocessing [3, 16, 17]. By applying the LKU treatment technique, the REs can be removed before the
The electrochemical recovery process (more specifically, before the OR) to improve the quality of the metal products and reduce the process load (Figure 3(a)). While it may be observed that the RE removal process (Figure 3(b)) is simply replaced with the LKU salt treatment (Figure 3(a)), the process difficulty of the LKU treatment (simple immersion) is much easier than RE removal (complicated chemical/electrochemical processes). While the RE dissolution efficiency achieved in this experiment was limited, it can be improved by using a longer immersion time and higher UCl₃ concentration in the salt to make this scenario more promising.

4. Conclusions

In this study, the dissolution behavior of SSFs in an LKU molten salt was investigated to identify the feasibility of such processes in back-end fuel cycles for managing the SNFs by thermodynamic calculations and experimental studies using SSFs. It was found that various elements including the REs as a surrogate of the TRUs were dissolved into the LKU molten salt, and there was no noticeable damage to the SSF pellets after immersion. This means that the nuclides in SNFs can be separated by the proposed salt treatment without degradation of the UO₂ matrix. This simple technique can be applied to the treatment of SNFs prior to underground disposal. In the best case, the SNFs with TRUs removed can be disposed more safely in underground facilities to mitigate the social and economic issues surrounding their disposal. Practically, this technique can be combined with pyroprocessing to enhance product quality and reduce the cost and complexity of the process. However, experimental data on the dissolution behaviors of TRUs remain unclear, and thus further investigation with TRUs (or SNFs) should be conducted to determine the feasibility of this technique. The present study will serve as a guide for the management of high-level radioactive waste at nuclear facilities.

Data Availability

The data used to support the findings of the study are available from the corresponding author upon request.
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This study was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean Government (MSIT) (2021M2E3A1040059).

References

[1] N. Chapman and A. Hooper, “The disposal of radioactive wastes underground,” *Proceedings of the Geologists’ Association*, vol. 123, no. 1, pp. 46–63, 2012.

[2] M. Kojo, M. Kari, and T. Liltmanen, “The socio-economic and communication challenges of spent nuclear fuel management in Finland,” *Progress in Nuclear Energy*, vol. 52, no. 2, pp. 168–176, 2010.

[3] Y. S. Cho and S. G. Hong, “Physics analysis of new TRU recycling options using FCM and MOX fueled PWR assemblies,” *Nuclear Engineering and Technology*, vol. 52, no. 4, pp. 689–699, 2020.

[4] H. Lee, G.-I. Park, J.-W. Lee et al., “Current status of pyro-processing development at KAERI,” *Science and Technology of Nuclear Installations*, vol. 2013, Article ID 343492, 11 pages, 2013.

[5] F. Gao and W. I. Ko, “Dynamic analysis of a pyroprocessing coupled SFR fuel recycling,” *Science and Technology of Nuclear Installations*, vol. 2012, Article ID 390758, 10 pages, 2012.

[6] M. M. Khan, J. M. Lee, J. H. Cheong, and J. H. Whang, “Feasibility studies on Pyro-SFR closed fuel cycle and direct disposal of spent nuclear fuel in line with the lasted national policy and strategy of Korea,” *Science and Technology of Nuclear Installations*, vol. 2017, Article ID 1953256, 17 pages, 2017.

[7] E. Bomboni, N. Cerullo, and G. Lomonaco, “Assessment of LWR-HTR-GCFR integrated cycle,” *Science and Technology of Nuclear Installations*, vol. 2009, Article ID 193594, 14 pages, 2009.

[8] E. Bomboni, N. Cerullo, G. Lomonaco, and V. Romanello, “A critical review of the recent improvements in minimizing nuclear waste by innovative gas cooled reactors,” *Science and Technology of Nuclear Installations*, vol. 2008, Article ID 265430, 18 pages, 2008.

[9] B. Vezzoni, N. Cerullo, G. Forasassi et al., “Preliminary evaluation of a nuclear scenario involving innovative gas cooled reactors,” *Science and Technology of Nuclear Installations*, vol. 2009, Article ID 940286, 16 pages, 2009.

[10] S. Bourg and C. Poinssot, “Could spent nuclear fuel be considered as a non-conventional mine of critical raw materials?” *Progress in Nuclear Energy*, vol. 94, pp. 222–228, 2017.

[11] F. Baumgärtner and D. Ertel, “The modern purex process and its analytical requirements,” *Journal of Radioanalytical and Nuclear Chemistry*, vol. 58, pp. 11–28, 1980.

[12] J. P. Duckworth and L. R. Michels, “New neptunium recovery facility at the Hanford purex plant,” *Industrial and Engineering Chemistry Process Design and Development*, vol. 3, no. 4, pp. 302–306, 1964.

[13] S.-C. Jeon, J.-W. Lee, J.-Y. Yoon, and Y.-Z. Cho, “Scaling up fabrication of UO2 porous pellet with a simulated spent fuel composition,” *Journal of the Nuclear Fuel Cycle and Waste Technology (JNFCWT)*, vol. 15, no. 4, pp. 343–353, 2017.