

Unexpected Spontaneous Formation of UCl_3 from Metallic Uranium in Molten LiCl-KCl Salt with Stainless Steel Containment Material

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*Keywords : UCl_3 , Corrosion, Stainless Steel, Molten Salt, and Pyroprocessing

1. Introduction

Uranium (III) chloride (UCl_3) is a significant substance utilized in pyroprocessing and molten salt reactors, a class of small nuclear reactors. Its synthesis involves the chemical interaction of metallic U with chlorination agents, like $CdCl_2$ and $PbCl_2$, in a molten chloride salt [1–3]. The present investigation unveils a novel discovery pertaining to the spontaneous formation of UCl_3 from metallic U within a molten LiCl-KCl salt contained within a stainless-steel (SS) crucible, obviating the necessity for an external chlorinating agent. The formation of UCl_3 was substantiated through the observation of a discernible color change (from white to purple) and comprehensive analyses of the salt used for immersing metallic U within the molten LiCl-KCl. Following extensive experimentation aimed at elucidating the source of UCl_3 formation, it was ascertained that the plausible source of UCl_3 formation is attributed to the chemical interaction of metallic U reacting with iron and chromium chlorides originating from the corrosion of the SS crucible by the salt. In contrast, a sustained increase in UCl_3 content was not observed within molten LiCl salt.

2. Experimental

The metallic simfuel containing U prepared through the oxide reduction of the oxide simfuel in our previous study [3] was used. All tests using molten salts were conducted in an Ar-filled glove box. LiCl-KCl eutectic (55.7 mol% LiCl-44.3 mol% KCl) anhydrous salt (99.99% purity, Sigma-Aldrich) was used as received. LiCl salt (99 % purity) was purchased from Alfa Aesar. Thermal dehydration of LiCl was conducted before use. LiCl was heated to 923 K at a linear rate of 3 K/min under reduced pressure (<1 Torr) for melting and maintained for 5 h. The salt was loaded in a SS 304 crucible, heated to reach its target temperature. Then, the temperature was maintained during the test. The fuels were loaded in a cylindrical SS wire mesh basket (ϕ 22.4 mm \times 100 mmH) made of a five-ply layer (30-325-40-20-16 meshes, Poroplate[®]). Then, the SS wire mesh basket containing the metallic simfuel (approximately 80 g) was independently immersed for LiCl and LiCl-KCl salts. The immersion of the fuel per one batch was maintained for 3 h. The salt samples were analyzed with inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 7300 DV, PerkinElmer).

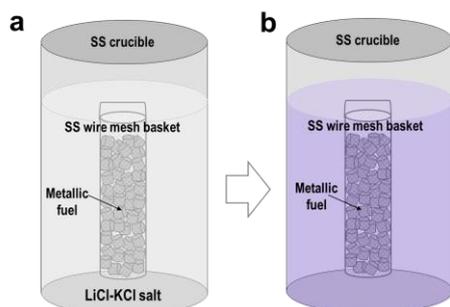
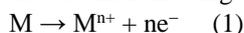


Fig.1. Schematic illustrating of observation made during the immersion of a metallic simfuel loaded in a SS wire mesh basket, into transparent molten LiCl-KCl salt at 773 K contained in a SS crucible (a), resulting in a distinct color change of the previously transparent salt to purple (b).

3. Results and Discussion

The metallic simfuel of approximately 80 g was independently immersed in molten LiCl salt at 923 K and LiCl-KCl at 773 K. Tests of nine batches were conducted for each salt. The SS wire mesh baskets containing the metallic simfuel obtained after the batches are shown in Fig. 2. The U concentrations in the salts sampled during the immersions analyzed through ICP-OES are shown in Table 1. The salt samples from the batches using LiCl-KCl salt at 773 K displayed a notable tendency for U concentrations to increase over time. In contrast, the U concentrations in LiCl salt samples did not show increasing trend in spite of a higher temperature (923 K). The presences of U in the salts cause by the formation of UCl_3 , which indicates the

oxidation of U in the metallic simfuel. It is understood that UCl_3 was produced by the chemical reaction between the metallic U and metal chlorides (MCl_x such as $FeCl_2$, $FeCl_3$, $CrCl_2$, and $CrCl_3$ etc.) as listed in Table 2. The MCl_x were present due to the corrosion of SS crucible as the following oxidation reaction:



where M represents the metallic element such as Fe, Cr, Ni and Co in the containment material, n is the number of exchanged electrons. M^{n+} can form redox couples with anions (O^{2-} or Cl^-) formed by impurities (O_2 , H_2O , H^+ , OH^- , and Cl_2) in the salt and are either dissolved in the salt as MCl_x and M_xO_y [4–5]. The outcomes of the results show in Table 1 delineate the primary mechanism underlying the UCl_3 formation, as elucidated in Fig. 3. The SS crucible, which interfaced with the molten LiCl-KCl salt prior to the immersion of metallic simfuel into the salt, undergoes corrosion attributable to impurities present in the salt. This corrosion results in the oxidation of metal elements to molten salt (reaction 1), leading to the formation of certain MCl_x . Subsequently, MCl_x can undergo reactions with H_2O within the salt, yielding precipitates (M oxides) and liberating HCl gas (Fig. 3a). Upon immersion of the metallic simfuel into the salt, U reacts with the MCl_x present in the salt, resulting in the production of the metal and UCl_3 (Fig. 3b). In cases where corrosion progresses and the concentration of MCl_x in the salt escalates, the concentration of UCl_3 increases through the reactions listed in Table 2. At this juncture, the metal M generated is susceptible to oxidation, transforming into MCl_x . This MCl_x can subsequently react with the metallic U, generating MCl_x and perpetuating a continual increase in the UCl_3 concentration (Fig. 3c). However, it is postulated that the increase in UCl_3 concentration may decelerate as impurities in the salt, including water, which contribute to corrosion, become depleted.



Fig. 2. Photos of SS wire mesh baskets used for the immersion of the fuel: (a) side view and (b) top view (inset image: cross-section of metallic simfuel).

Table 1. Concentrations of U in the salts sampled during the immersion of metallic simfuel (approximately 80 g per batch) in molten LiCl and LiCl-KCl analyzed by ICP-OES (immersion time

Batch No	U conc. [ppm] after the rinsing	
	In LiCl	In LiCl-KCl
1	14.3	25.3
2	118.0	984.5
3	30.8	670
4	57.3	1074
5	130.2	1973.6
6	26.1	6683
7	16.6	3137.4
8	30.9	3444.9
9	7.7	4175.4

Table 2. The standard state Gibb's free energy of reaction (ΔG°_{rxn}) for reactions

Element	Chemical equation	Temp. [K]	ΔG°_{rxn} [kJ]
Fe	$FeCl_3 + U \rightarrow Fe + UCl_3$	773	-447.8
		923	-435.2
	$1.5FeCl_2 + U \rightarrow 1.5Fe + UCl_3$	773	-333.1
		923	-329.2
Cr	$CrCl_3 + U \rightarrow Cr + UCl_3$	773	-330.83
		923	-332.80
	$1.5CrCl_2 + U \rightarrow 1.5Cr + UCl_3$	773	-261.51
		923	-256.65

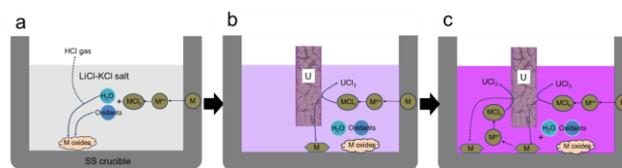


Fig. 3. Schematic drawing of UCl_3 formation mechanism within molten salt contained in SS crucible: (a) reaction of MCl_x produced by corrosion of SS crucible metal (M) elements with impurities in the salt (before the immersion of metallic simfuel in salt), (b) UCl_3 formation by the reaction of U in metallic simfuel with MCl_x in salts after the immersion of the metallic simfuel, and (c) the increase in the UCl_3 concentration.

4. Conclusions

In this study, we observed the spontaneous formation of UCl_3 when metallic U was immersed in LiCl-KCl molten salt within a SS crucible. Our findings indicate that SS corrosion resulted from residual H_2O in the molten salt, leading to the oxidation of Fe and Cr in SS. Consequently, $FeCl_x$ and $CrCl_x$ reacted with metallic U to produce UCl_3 . LiCl-KCl exhibited a more significant tendency for UCl_3 formation compared to LiCl due to enhanced ionization of Fe and Cr, resulting in increased concentrations of $FeCl_x$ and $CrCl_x$.

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