Utilizing Aluminium Chlorides for Oxygen Removal in Molten Fuel Salts

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Keywords : molten fuel salt, aluminium chlorides, oxygen sink, cerium surrogate, uranium chloride

1. Introduction

Chloride-based molten fuel salts, namely NaCl-UCl_3, KCl-UCl_3 and NaCl-KCl-UCl_3, are promising candidates for molten salt small modular reactors due to their excellent thermal properties, high fissile material solubility, low radiation damage, low vapor pressure, and reduced corrosivity [1]. However, during reactor operation, infiltrated oxygen can convert uranium chlorides into uranium oxides, potentially leading to system failure [2]. Specifically, due to their limited solubility, uranium oxides can precipitate as solid phases, altering the physical and chemical properties of the molten fuel salts by reducing the concentration of dissolved uranium. The substantial accumulation of these oxides may also lead to localized overheating and pose a criticality risk [3]. In addition, infiltrated oxygen can shift the redox potential in the positive direction, creating a more oxidizing environment that accelerates the corrosion of structural materials [4,5]. Here, we have explored the application of aluminium chloride in molten salts as an oxygen sink to mitigate this risk of system failure.

2. Methods

2.1 Chemical Preparation

An $AlCl_3$-rich NaCl-KCl salt, hereafter referred to as ASK, was prepared by mixing $AlCl_3$ (sigma-aldrich, 98%), NaCl (sigma-aldrich, 99%), and KCl (sigma-aldrich, 99%) at a molar ratio of 48.2:33.4:18.4, heating the mixture to 143 °C, and subsequently cooling it to room temperature. A NaCl-KCl-$AlCl_3$ salt, referred to as SKA, was prepared by first heating NaCl-KCl (50-50 mol%), referred to as SKE, to 700 ℃ before adding approximately 5 wt% of the ASK salt (Table 1). Immediately after adding the ASK salt, sublimation of $AlCl_3$ was observed for a few minutes and gradually diminished.

Table 1. General composition of salt mixtures.

Salt	Composition
ASK	$AlCl_3$-NaCl-KCl (48.2-33.4-18.4 mol%)
SKE	NaCl-KCl (50-50 mol%)
SKA	NaCl-KCl-$AlCl_3$ (49.4-48.9-1.7 mol%)

Cerium oxide (CeO_2) and cerium oxychloride (CeOCl) were used as surrogates for uranium oxide (UO_2) and uranium oxychloride (UOCl), respectively, to investigate whether aluminum chlorides can function as an oxygen sink in fuel salts containing uranium chlorides. CeO_2 was synthesized by heating $CeCl_3 \cdot 7H_2O$ (sigma-aldrich, 99.9 %) at 600 °C under air [6]. CeOCl was synthesized by heating a pellet composed of CeO_2 and $CeCl_3$ (flourochem ltd.) in a 1:2 molar ratio at 750 °C [7]. Synthesized CeOCl was then washed with water and dried at 70 °C for one day to remove unreacted $CeCl_3$.

2.2 Analysis

Raman (Horiba XploRa Plus) analysis was conducted to identify the chemical forms of aluminium chlorides in the molten salts, using a 532 nm laser, a 2400 gr/mm grating, and a 50 % filter. XRD (PANalytical X'Pert Pro) analysis was conducted to identify the aluminium oxides that formed from the reaction between aluminium chlorides and cerium oxide, using an operating voltage of 40 kV and a current of 40 mA. ICP-OES analysis was conducted to measure the concentration of Na, K, Al in molten salts by dissolving quenched salt samples into 2 % aqueous solution of nitric acid. XRF (Rigaku NEX DE) analysis was conducted to measure the concentration of Ce in molten salts.

3. Results and Discussion

3.1 Chemical Form of Aluminium Chloride in Molten Salt

The SKA molten salt was sampled 1 hour and 5 hours after the addition of ASK, and Raman analysis was conducted to identify the chemical species present in the molten salt (Fig. 1). The 1-hour sample contained both $Al_2Cl_7^-$ and $AlCl_4^-$ [8]; however, only $AlCl_4^-$ was observed in the 5-hour sample. This suggests that the added $AlCl_3$ stabilizes in the form of $AlCl_4^-$ in SKE molten salt.

3.2 Demonstration of Aluminium Chloride as an Oxygen Sink

After the addition of ASK, two batches of SKA molten salts were maintained at 700°C for 5 hours and subsequently cooled down to room temperature under different atmospheres: one under air and the other under argon. Samples were collected from each batch, and ICP analysis was performed to monitor the concentrations of Na, K, and Al over time (Table 2). Assuming that ASK was completely dissolved into the molten salts without any loss, the theoretical Al concentrations were calculated to be 0.72 wt% for the air-exposed batch and 0.63 wt% for the argon-exposed batch. The average ratio of the measured Al concentrations from both batches after 1 hour to their respective theoretical initial concentrations was approximately 90%, indicating an Al yield of about 90%. Considering that $AlCl_3$ exhibits a very high vapor pressure at 700 °C, introducing it in the form of the salt ASK can significantly improve the retention rate by stabilizing $AlCl_3$ as $AlCl_4^-$. Both batches showed that the Na and K concentrations remained constant over time. In contrast, the Al concentration decreased in the air-exposed condition, whereas under an argon atmosphere, it remained constant. This suggests that $AlCl_4^-$ can react with intruded oxygen forming insoluble oxides, Al_2O_3.

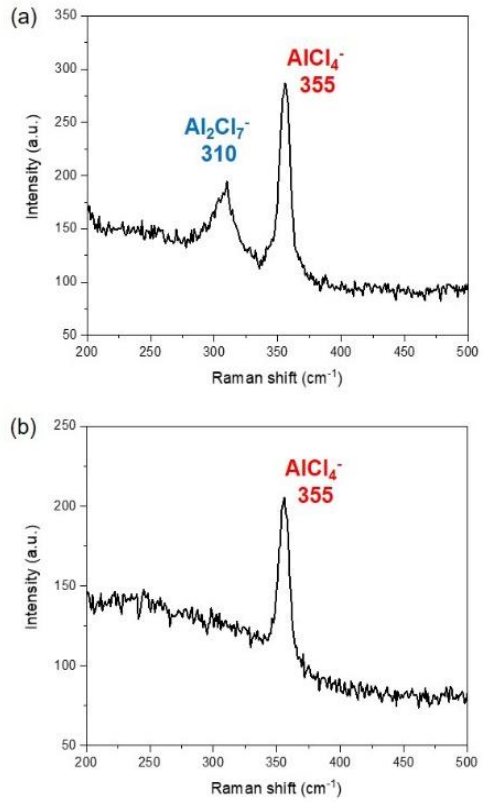

Figure 1. Raman spectra of SKA sampled at (a) 1 hour and (b) 5 hours after the addition of aluminium chloride in the form of the ASK salt.

3.3 Testing with Cerium as a Surrogate of Uranium

Four salt samples were prepared and heated at 700 °C for 48 hours: SKA with CeO_2, SKA with CeOCl, SKE with CeO_2 and SKE with CeOCl. For each sample, 5 g of SKA or SKE was used, and 0.2 g of CeO_2 or CeOCl was used. After cooling down, all salts were immersed in 50 ml of water and then filtered. The concentrations of Ce in the filtrates were analyzed by XRF assuming that all detected cerium originated from $CeCl_3$, given the limited aqueous solubility of CeO_2 and CeOCl, to determine the relative quantity of CeO_2 and CeOCl that reacted to $CeCl_3$ [9]. The concentrations measured from SKA showed higher value than those from SKE (Table 3). Therefore, it is theorized that the added $AlCl_3$ reacts with the cerium oxychloride or oxide, abstracting the oxygen and converting the cerium compounds to $CeCl_3$. To validate this theory, the filtered residue from SKA with CeO_2 was identified consisting of CeO_2 and Al_2O_3 through XRD (Fig. 2). This supports the hypothesis that $AlCl_4^-$ in SKA reacted with CeO_2 and CeOCl, forming $CeCl_3$ and Al_2O_3.

Table 2. Concentrations of Al, Na, and K in SKA molten salts over time under (a) air and (b) argon atmospheres.

(a) Air atmosphere

Sampling time	Al (wt%)	Na (wt%)	K (wt%)
Before addition	ND	17.35±0.1	28.42±0.1
1 hour	0.67±0.01	17.35±0.4	26.75±0.1
3 hour	0.32±0.004	17.09±0.2	27.38±0.4
5 hour	0.20±0.001	17.91±0.1	28.32±0.1
After cooling	0.04±0.001	16.94±0.1	28.06±0.1

(b) Ar atmosphere

Sampling time	Al (wt%)	Na (wt%)	K (wt%)
Before addition	ND	14.02±0.3	24.79±0.2
1 hour	0.55±0.006	14.36±0.02	22.86±0.2
3 hour	0.51±0.004	13.64±0.2	22.69±0.1
5 hour	0.51±0.007	14.74±0.3	23.71±0.1
After cooling	0.52±0.005	16.46±0.1	26.79±0.4

Table 3. Determined quantities of Ce-oxo species reacted in Al containing saltss.

Salt sample	Reacted CeOCl/CeO_2 ratio (%)
SKA with CeOCl	30.7
SKA with CeO_2	15.3
SKE with CeOCl	1.3
SKE with CeO_2	0.8

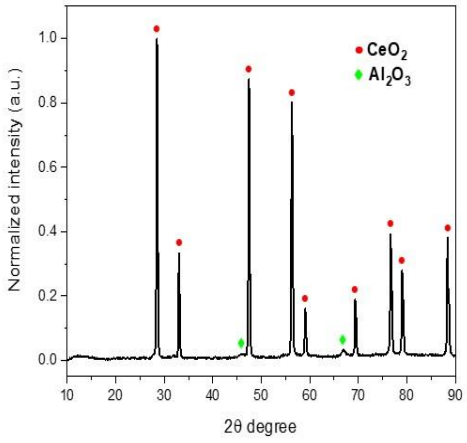

Figure 2. XRD analysis of the remaining residue of SKA with CeO_2 after aqueous dissolution.

3.4 Validation in Uranium Containing Molten Salts

The following equations represent the Gibbs free energy change for the reaction of UO_2 and UOCl with $AlCl_3$, forming uranium chlorides and Al_2O_3 [10]. Although aluminium chlorides exist as $AlCl_4^-$ in molten salts, the values from the following reactions further support the role of aluminium chloride as an oxygen sink.

$$3UOCl + 2AlCl_3 \rightarrow 3UCl_3 + Al_2O_3,\ \Delta G^0_{973K} = -275\ \frac{kJ}{mol} \quad (1)$$

$$3UO_2 + 4AlCl_3 \rightarrow 3UCl_4 + 2Al_2O_3,\ \Delta G^0_{973K} = -185\ \frac{kJ}{mol} \quad (2)$$

4. Conclusions and Future work

In molten salts, aluminium chlorides primarily exist as $AlCl_4^-$ ions, which can act as effective oxygen sinks, thereby protecting fissile materials from oxidation. Preliminary experiments using cerium as a surrogate for uranium demonstrated that $AlCl_4^-$ effectively scavenges oxygen and inhibits the formation of cerium oxides.

As future work, we plan to validate the oxygen scavenging capability of aluminium chloride in molten fuel salts by conducting experiments with UCl_4. Specifically, SKE and SKA salts will be mixed with UCl_4 and Na_2O, and the concentrations of aluminium and uranium will be monitored over time to evaluate the efficiency of $AlCl_4^-$ as an oxygen sink.

Acknowledgements

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. RS-2024-00401407).

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