KNS

Utilizing Aluminium Chlorides for Oxygen Removal in Molten Fuel Salts

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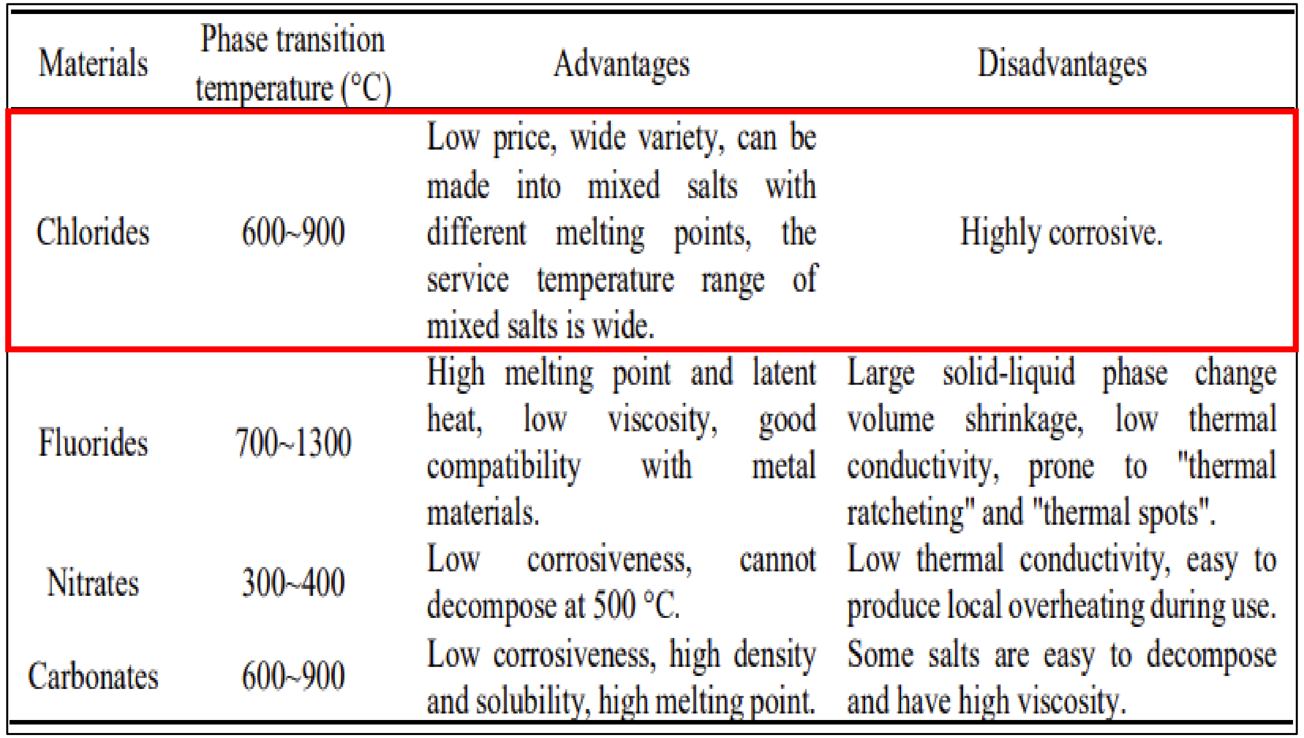
Context

- **Introduction**
  - Redox potential control method
  - Oxygen intrusion in molten salt system and control methods
  - Potential of aluminium chloride usage
- **Experiments**
  - Aluminium chloride thermal stability
  - Oxygen scavenging capacity
  - Redox buffering capability

Chloride-based molten fuel salts

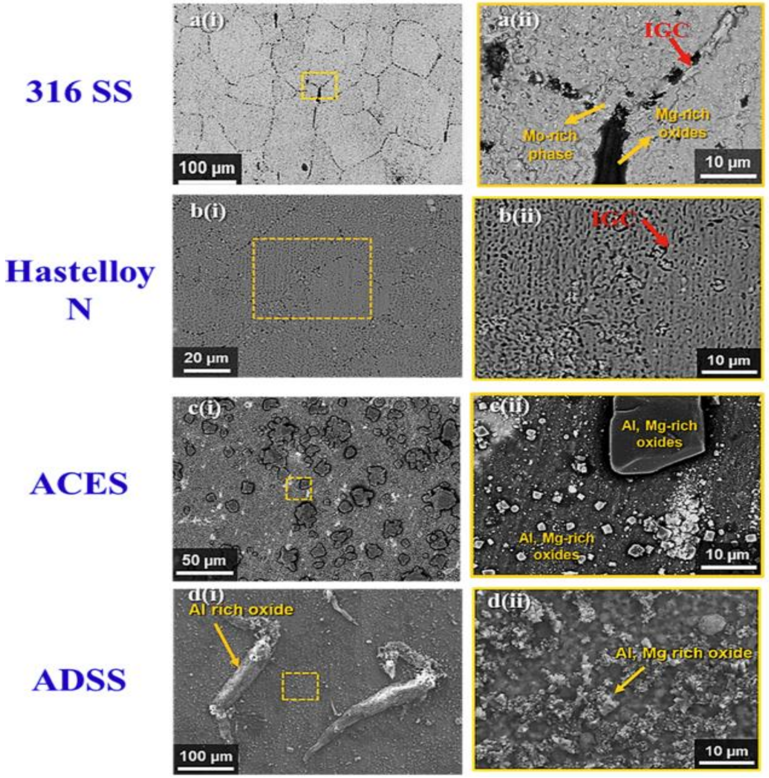
- **Chloride-based molten fuel salts, namely NaCl-UCl_3, KCl-UCl_3, NaCl-KCl-UCl_3, are promising candidates for molten salt small modular reactors.**
- **Chloride-based molten salts are known to be more corrosive compared to other types of molten salts**

Advantages and Disadvantages of Different Types of Molten Salts



Materials	Phase transition temperature (°C)	Advantages	Disadvantages
Chlorides	600~900	Low price, wide variety, can be made into mixed salts with different melting points, the service temperature range of mixed salts is wide.	Highly corrosive.
Fluorides	700~1300	High melting point and latent heat, low viscosity, good compatibility with metal materials.	Large solid-liquid phase change volume shrinkage, low thermal conductivity, prone to "thermal ratcheting" and "thermal spots".
Nitrates	300~400	Low corrosiveness, cannot decompose at 500 °C.	Low thermal conductivity, easy to produce local overheating during use.
Carbonates	600~900	Low corrosiveness, high density and solubility, high melting point.	Some salts are easy to decompose and have high viscosity.

Corrosion of Structural Materials in KCl-$MgCl_2$ Salt



[1] Okonkwo, Bright O., et al. "Corrosion behaviour of Al-containing alloys in Cl-based molten salt environment." *Journal of Nuclear Materials* (2024): 155207.
[2] Song, Xiaoyun, et al. "Review on thermophysical properties and corrosion performance of molten salt in high temperature thermal energy storage." IOP Conference Series: Earth and Environmental Science. Vol. 474. No. 5. IOP Publishing, 2020.

Redox potential control method

- **Redox potential is the term used to describe redox condition of molten salt in electrochemical view. It is a measureable voltage that is related to the activities(concentration) of the reduced and oxidized species in the molten salt solution.**
- **Redox potential control is an effective and practical method for maintaining chemical property of salt and mitigating material corrosion in MSR.**

Redox potential control method in fluoride based molten salt

Methods	Equilibrium reactions	Redox potential
Gas phase control (*HF/H$_2$*)	$\frac{1}{2}H_2 + \frac{1}{2}F_2 \leftrightarrow HF$	$E_{HF/H_2} = E^0_{HF/H_2} + \frac{RT}{F}\ln\frac{p_{HF}}{\sqrt{p_{H_2}}}$
Major metal control (*Be^{2+}/Be^0*)	$Be^0 + F_2 \leftrightarrow BeF_2$	$E_{BeF_2/Be^0} = E^0_{BeF_2/Be^0} + \frac{RT}{2F}\ln\frac{a_{BeF_2}}{a_{Be^0}}$
Dissolved salt control (*U^{4+}/U^{3+}*)	$UF_3 + \frac{1}{2}F_2 \leftrightarrow UF_4$	$E_{UF_4/UF_3} = E^0_{UF_4/UF_3} + \frac{RT}{F}\ln\frac{a_{UF_4}}{a_{UF_3}}$

[3] Zhang, Jinsuo, et al. "Redox potential control in molten salt systems for corrosion mitigation." *Corrosion Science* 144 (2018): 44-53.

Redox potential control method

- **The methods developed to control the redox potential of molten salts have focused on using reducing metals and soluble redox couples as redox buffers.**

Redox potential control methods using metals and redox couples

Reducing agent	Salt system	Possible reaction	Zero-state solubility
U metal	$LiF\text{-}CaF_2\text{-}UF_4$ [4] $NaCl\text{-}CaCl_2\text{-}UCl_3$ [5]	$3U(\text{Ⅳ}) + U \rightarrow 4U(\text{Ⅲ})$	Insoluble
Gd liquid metal	$LiF\text{-}CaF_2\text{-}EuF_3$ [4]	$3EuF_3 + Gd \rightarrow 3EuF_2 + GdF_3$	Insoluble
Zr metal	$NaCl\text{-}CaCl_2\text{-}UCl_3$ [5]	$4UCl_4 + Zr \rightarrow 4UCl_3 + ZrCl_4$	Insoluble
Li metal	$LiCl\text{-}KCl\text{-}LnCl_3$ [6] (Ln: La, Ce, Nd)	$Li^0 + Cl_2 \leftrightarrow LiCl_2$ $LnCl_4 + Li \rightarrow Ln + 3LiCl$	Soluble
Be metal	$LiF\text{-}BeF_2\text{-}ZrF_4\text{-}UF_4$ [7]	$Be^0 + F_2 \leftrightarrow BeF_2$ $Be^0 + 2UF_4 \leftrightarrow BeF_2 + 2UF_3$	Soluble
Eu^{2+}/Eu^{3+}	$LiF\text{-}NaF\text{-}KF$ [8]	$Eu^{3+} + e^- \leftrightarrow Eu^{2+}$	-
Sm^{2+}/Sm^{3+}	$NaF\text{-}BeF_2$ [9]	$Sm^{3+} + e^- \leftrightarrow Sm^{2+}$	-

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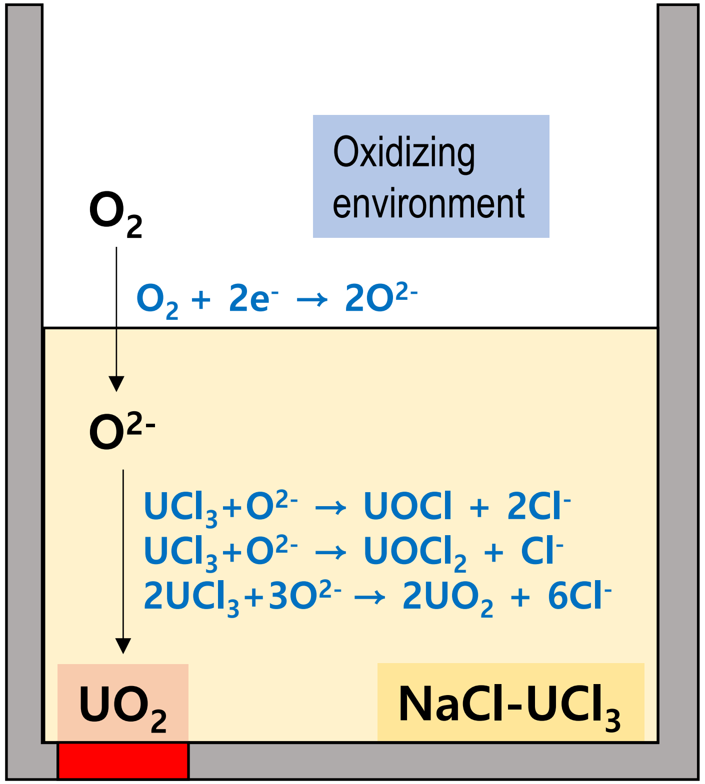
[4] Gibilaro, Mathieu, Laurent Massot, and Pierre Chamelot. "A way to limit the corrosion in the Molten Salt Reactor concept: the salt redox potential control." *Electrochimica Acta* 160 (2015): 209-213.
[5] Newton, Matthew Laughlin, David Ethan Hamilton, and Michael Forrest Simpson. "Methods of redox control and measurement in molten NaCl-CaCl2-UCl3." ECS Transactions 98.10 (2020): 19.
[6] Simpson, Michael F., et al. "Selective reduction of active metal chlorides from molten LiCl-KCl using lithium drawdown." Nuclear engineering and technology 44.7 (2012): 767-772.
[7] Zhang, Jinsuo, et al. "Redox potential control in molten salt systems for corrosion mitigation." *Corrosion Science* 144 (2018): 44-53.
[8] Guo, Shaoqiang, et al. "Measurement of europium (III)/europium (II) couple in fluoride molten salt for redox control in a molten salt reactor concept." Journal of Nuclear Materials 496 (2017): 197-206
[9] Zuo, Yong, et al. "Electrochemical study of the redox buffering behavior of Sm (III)/Sm (II) in NaF-BeF2 melt." Electrochimica Acta 474 (2024): 143564.

Oxygen intrusion in molten salt system

- NaCl or KCl-based fast chloride reactors are expected to control the redox potential by adjusting the U^{4+}/U^{3+} ratio through the introduction of a reducing metal or redox couple.
- Uranium loss in this system can impact not only process efficiency, but also overall system stability.



Oxidizing environment

O_2

$O_2 + 2e^- \rightarrow 2O^{2-}$

O^{2-}

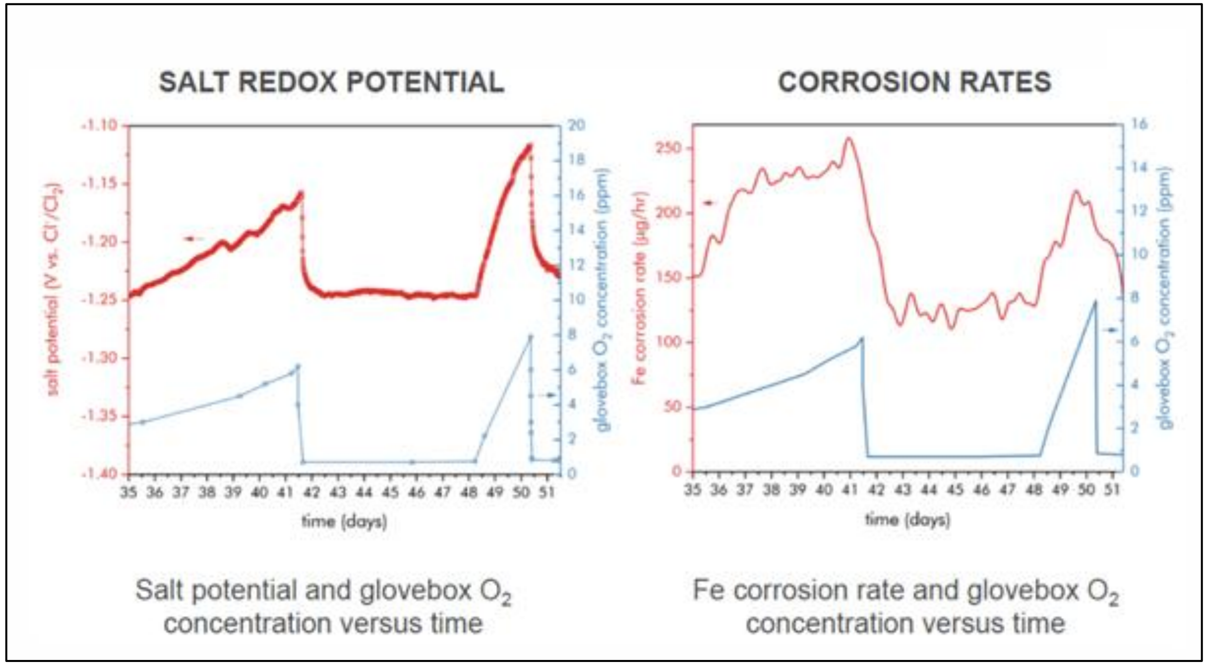
$UCl_3 + O^{2-} \rightarrow UOCl + 2Cl^-$
$UCl_3 + O^{2-} \rightarrow UOCl_2 + Cl^-$
$2UCl_3 + 3O^{2-} \rightarrow 2UO_2 + 6Cl^-$

UO_2

$NaCl\text{-}UCl_3$

Localized overheating

Influence of Intruding Oxygen on Redox Potential and Corrosion Rates



Salt potential and glovebox O_2 concentration versus time

Fe corrosion rate and glovebox O_2 concentration versus time

[10] ANL, 2019

Developed oxygen control methods

- **The Oak Ridge National Laboratory (ORNL) has proposed bubbling HF/H_2 mixtures into the salt to remove O^{2-} [11].**
    - $O^{2-} + 2HF \leftrightarrow H_2O + 2F^-$
- **ZrF_4 into $LiF\text{-}BeF_2$ molten salt has been proposed to remove O^{2-} [12].**
    - $Zr(\text{IV}) + 2O^{2-} \leftrightarrow ZrO_2$
- **H_2 gas flow and electrochemical/chemical treatment [13].**
    - $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

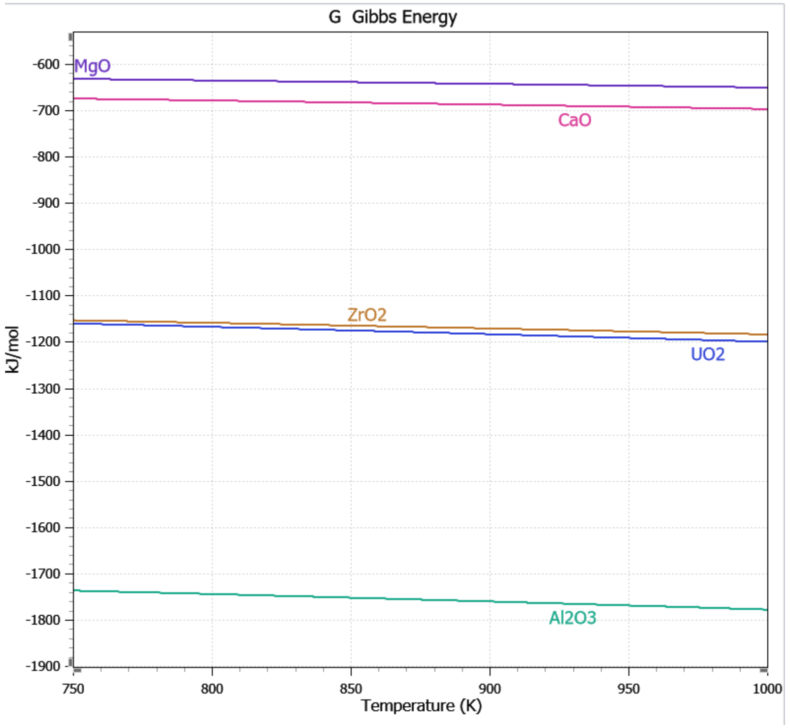
[11] A. L. Mathews and C. F. Baes Jr., Oxide chemistry and thermodynamics of molten lithium fluoride-beryllium fluoride solutions, Inorg. Chem., 1968, 7, 373–382.
[12] Peng, Hao, et al. "Inhibition effect of ZrF 4 on UO 2 precipitation in the LiF–BeF 2 molten salt." *RSC advances* 11.31 (2021): 18708-18716.
[13] Zuo, Yong, et al. "A novel purification method for fluoride or chloride molten salts based on the redox of hydrogen on a nickel electrode." RSC advances 11.56 (2021): 35069-35076.

Possibility of aluminium chloride as oxygen scavanger

- **$AlCl_3$ has been considered as a potential oxygen scavenger to help maintain the redox potential in molten chloride salt systems.**
- **Al_2O_3 can be more thermodynamically stable in a molten salt environment and furthermore convert uranium oxo-species into chlorides.**

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

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



$LiCl$-KCl-$AlCl_3$-UO_2

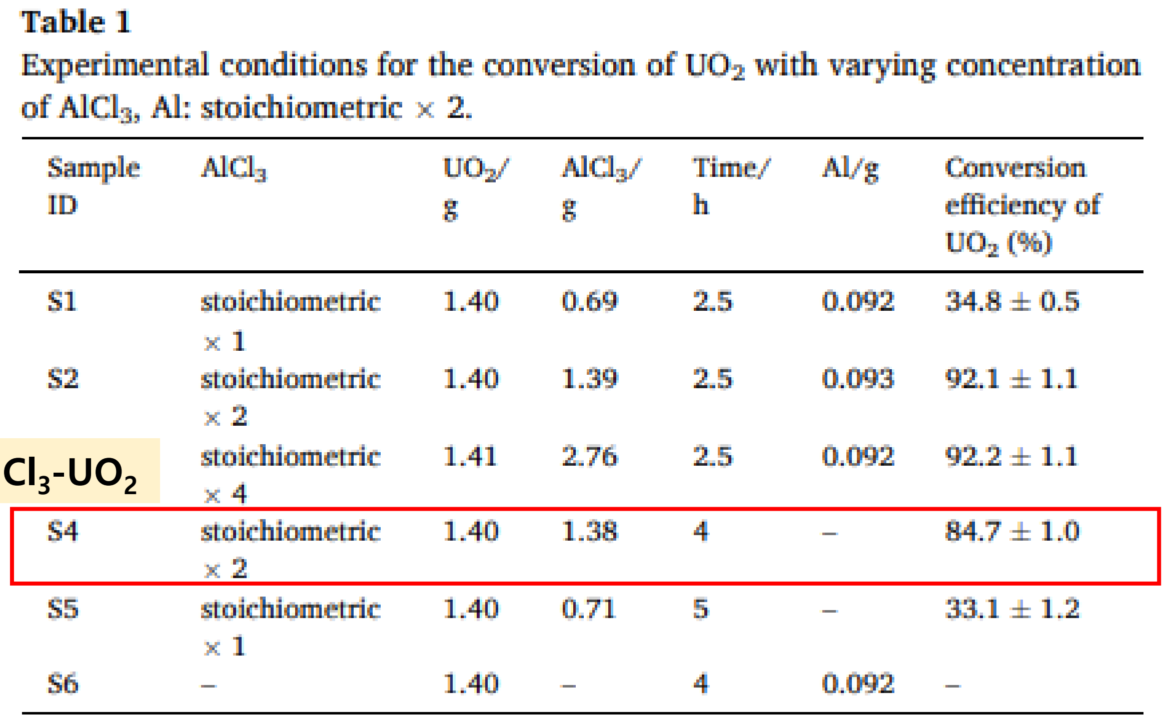


Table 1

Experimental conditions for the conversion of UO_2 with varying concentration of $AlCl_3$, Al: stoichiometric × 2.

Sample ID	$AlCl_3$	UO_2/ g	$AlCl_3$/ g	Time/ h	Al/g	Conversion efficiency of UO_2 (%)
S1	stoichiometric × 1	1.40	0.69	2.5	0.092	34.8 ± 0.5
S2	stoichiometric × 2	1.40	1.39	2.5	0.093	92.1 ± 1.1
	stoichiometric × 4	1.41	2.76	2.5	0.092	92.2 ± 1.1
S4	stoichiometric × 2	1.40	1.38	4	–	84.7 ± 1.0
S5	stoichiometric × 1	1.40	0.71	5	–	33.1 ± 1.2
S6	–	1.40	–	4	0.092	–

[14] Samanta, Nibedita, et al. "Electrochemical and spectroscopic analysis of thermochemical conversion of UO2 to UCl3 using AlCl3 and Al in LiCl–KCl eutectic." *Progress in Nuclear Energy* 153 (2022): 104429

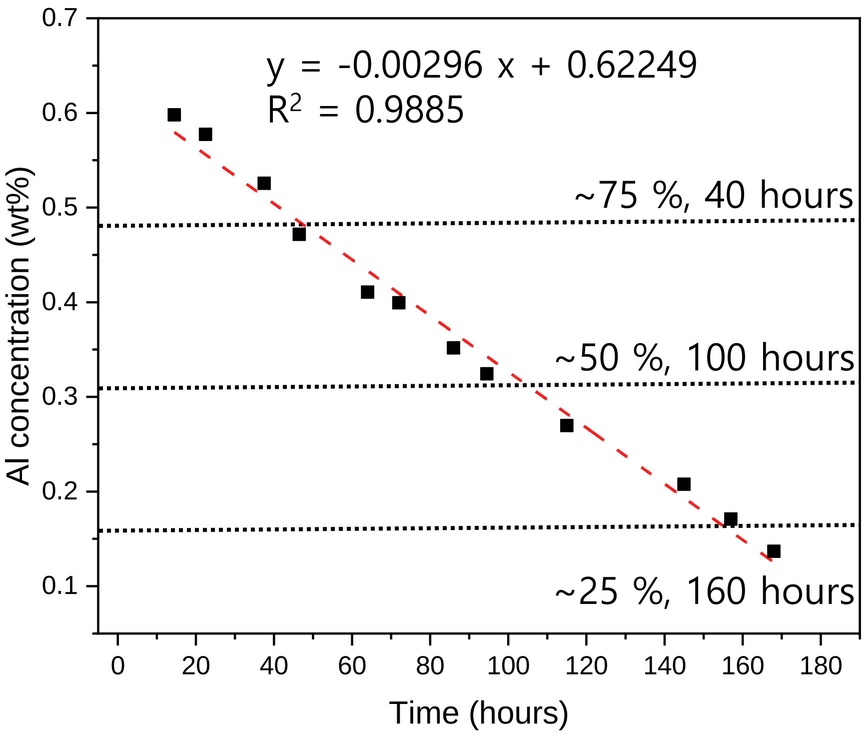
Overview of experiments

- **Objective: Redox potential stabilization and oxygen control in molten fuel salts using aluminium chloride**
- **Basic experiments**
  - Aluminium chloride long-term stability
  - Chemical form of aluminium chloride in molten salt
- **Oxygen removal**
  - Air exposed v.s. Ar exposed atmosphere
  - Oxygen removal efficiency
  - Feasibility in a uranium environment (Ce surrogate usage)
- **Redox potential stabilization**
  - Inducing oxides in Eu^{2+}/Eu^{3+} redox system

Aluminium chloride long-term stability

- **Aluminium concentration gradually decreases over time.**
  - 0.493 g of $AlCl_3$-NaCl-KCl (ASK, 48.2-33.4-18.4 mol%) was added into 10 g of NaCl-KCl (SKE, 50-50 mol%) at 700 ℃.
  - The loss of aluminium when introducing ASK into SKE was negligible (Input amount : 0.63 wt% *v.s.* regression: 0.62 wt%).

Al concentration in molten salt over time



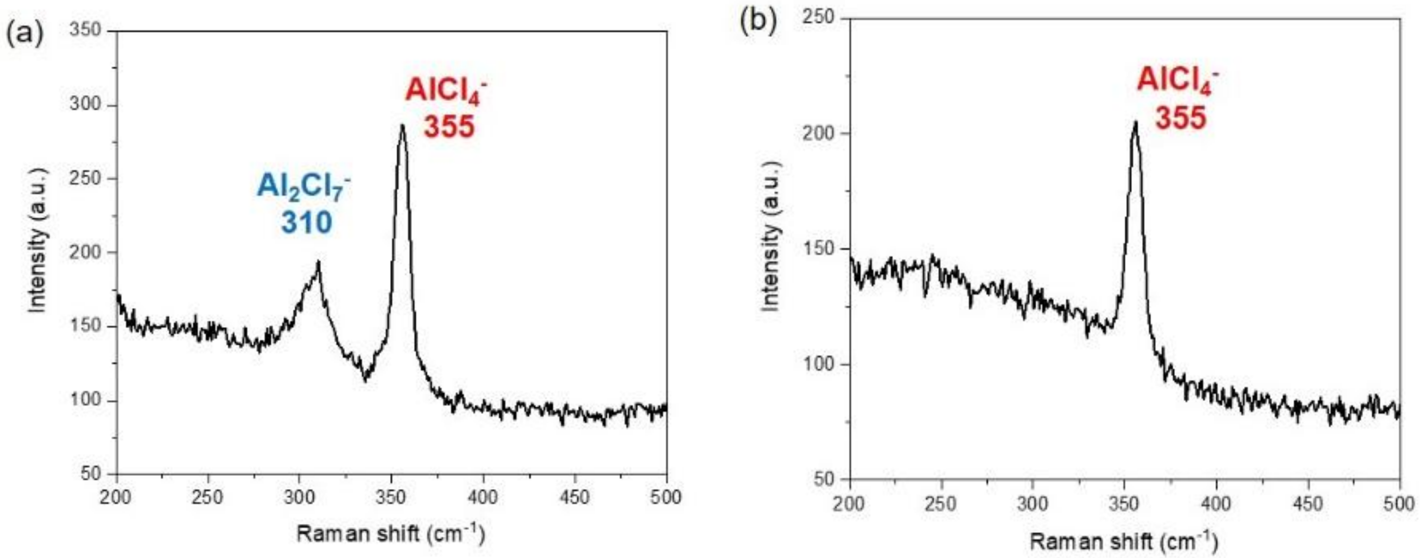
$AlCl_3$- NaCl-KCl salt mixture

Open quartz cell

Chemical form of aluminium chloride in molten salt

- **$AlCl_3$ initially stabilizes as both $Al_2Cl_7^-$ and $AlCl_4^-$. As time passes, the aluminium concentration became uniform over molten salt, and only $AlCl_4^-$ was observed.**
  - 2.8456 g of $AlCl_3$-NaCl-KCl (ASK, 48.2-33.4-18.4 mol%) was added into 50 g of NaCl-KCl (SKE, 50-50 mol%) at 700 ℃.
  - Powder Raman analysis was performed at six different points on each sample. All samples were prepared by quenching molten salt. After 3 hours, only $AlCl_4^-$ peak was observed, and its intensity became uniform across all measured points.

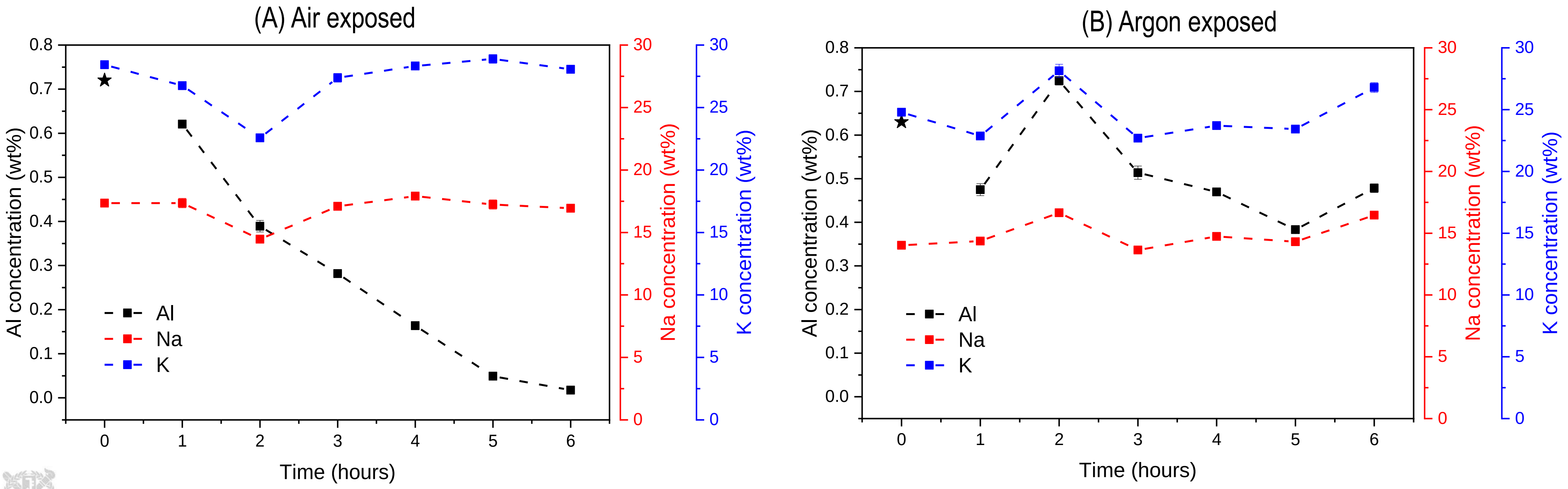
Raman spectra sampled at (a) 1 hour and (b) 5 hours after the addition of ASK



Air *v.s.* Ar exposed atmosphere

- **Aluminum chloride can help maintain the concentration of base salts (Na, K) when exposed to air.**
  - 2.8456 g and 4.98 g of ASK was respectively added into 50 g and 100 g of SKE at 700 ℃.
  - When exposed to air, the concentrations of Na and K remained stable, whereas the Al concentration decreased significantly.
  - It seems that aluminium oxide forms when aluminium chloride reacts with oxygen (directly O_2 form or intruded O_2^- form)
    - $2\,Al^{3+} + 3\,O^{2-} \longrightarrow Al_2O_3$

Concentration of Al, Na, K over time after adding ASK into SKE in (a) air atmosphere and (b) argon atmosphere



Apparatus

Oxygen removal efficiency

- **All intruded oxide ions can be removed in molten salts containing aluminium chloride.**
    - 0.504 g of ASK was added into 10 g of SKE at 700 ℃. Na_2O was then added gradually.
    - After each addition, the molten salt was stirred for 5 minutes and analyzed every 20 minutes thereafter.
    - Oxygen removal efficiency (%) = [Removed O (mol)/ O input (mol)]*100.

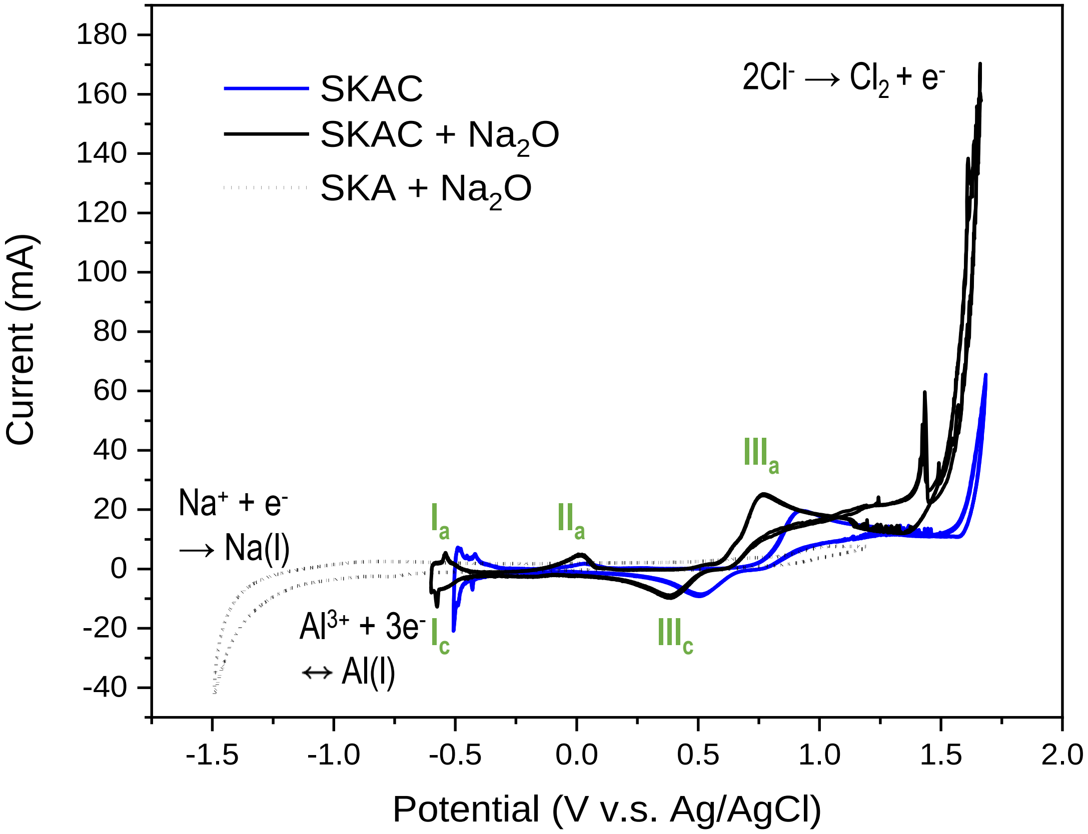
Concentration of Al and calculated O removal efficiency in $NaCl-KCl-AlCl_3$ molten salt at 700 ℃

Na_2O input (mg)	O input (mol)	Al conc (wt%)	Reacted Al (estimation, mol)	Reacted Al (experiment, mol)	Removed O (mol)	O removal efficiency (%)
0	0	0.67273	-	-	-	-
71.1	0.00128	0.44501	8.53333E-4	8.8748E-4	0.00133	104.0
151.4	0.00273	0.22227	0.00182	0.00175	0.00263	96.4
181.7	0.00328	0.104	0.00219	0.00222	0.00332	101.3
201.9	0.00364	0.04357	0.00243	0.00245	0.00368	101.0
222.7	0.00402	0.00586	0.00268	0.0026	0.0039	96.9

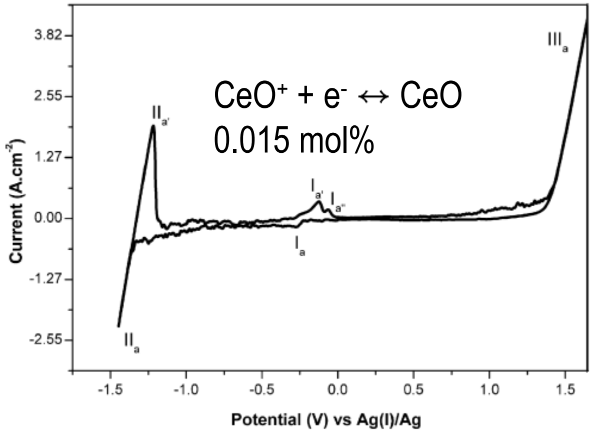
Ce study as a uranium surrogate

- **Oxychlorides are unstable in molten salt at 700 ℃.**
  - ~ 0.018 g of Na_2O was added into 10.05 g of NaCl-KCl-$CeCl_3$ (SKA, 0.135 mol% of $CeCl_3$) and 10.55 g of NaCl-KCl-$AlCl_3$-$CeCl_3$ (SKAC, 1.59 mol% of $AlCl_3$ and 0.13 mol% of $CeCl_3$).
  - CeOCl redox peak wasn't observed suggesting that CeOCl thermally decomposed into CeO_2 rapidly.

CV of SKA and SKAC with/without addition of Na_2O



CeOCl redox peak in NaCl-KCl-$MgCl_2$ at 550℃

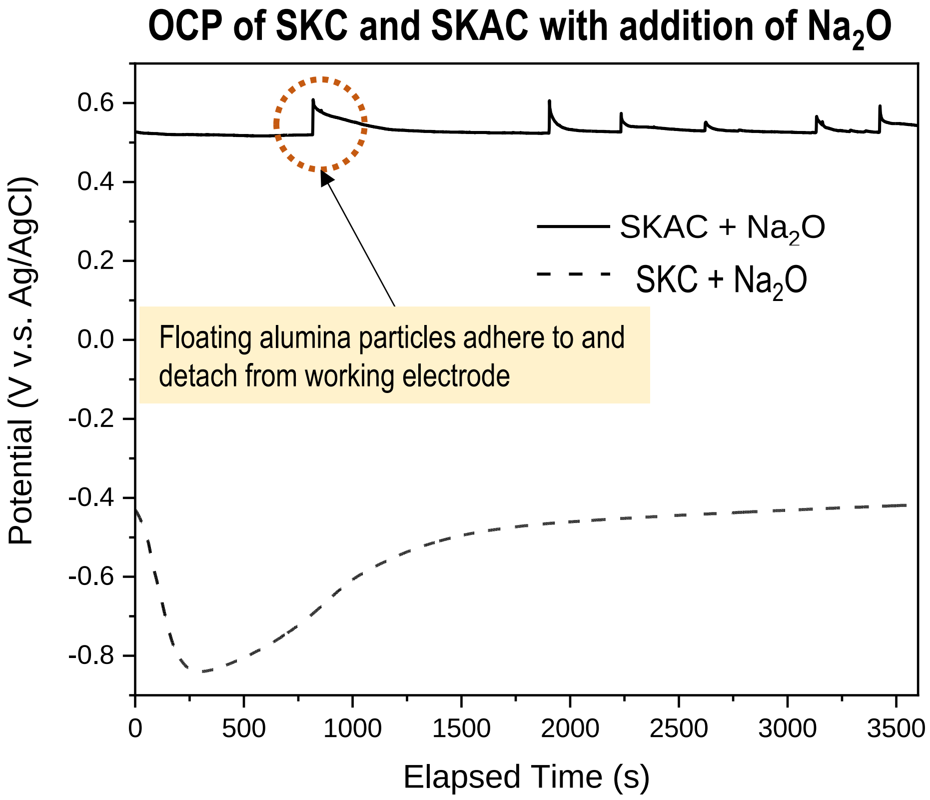


Redox reactions

Redox peak	Reaction
I_a, I_c	Al-Ce redox couple
II_a	$Ag \rightarrow Ag^+ + e^-$
III_a ,III_c	$AlCl_4^-$ associated

Ce study as a uranium surrogate

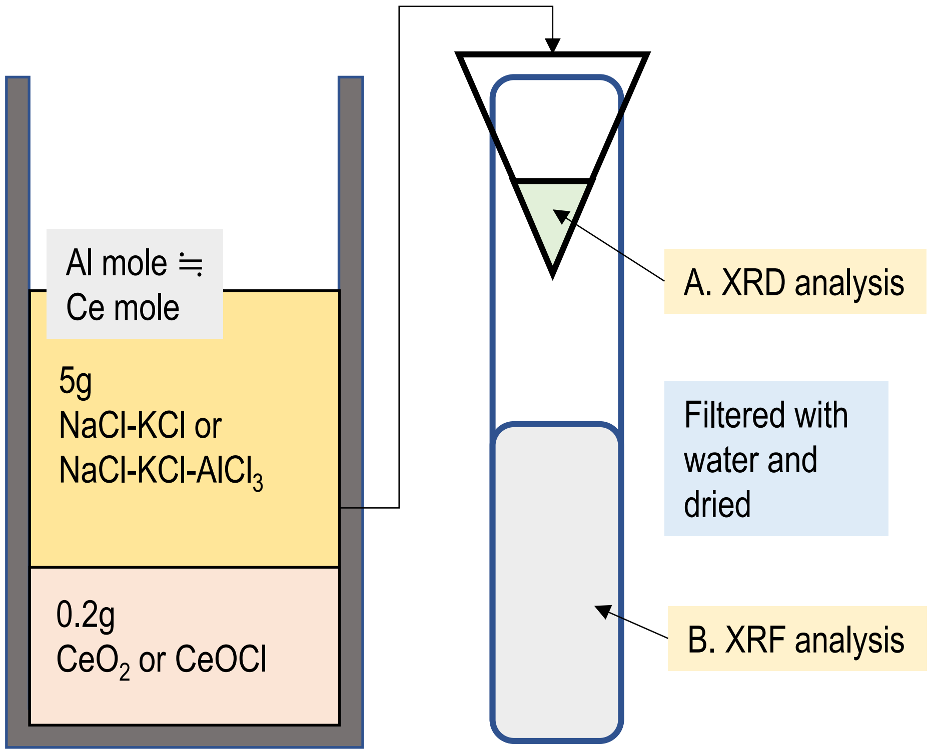
- **Al_2O_3 disperses in molten salt within small particle size at 700 ℃.**
  - In OCP data, discrete peaks were observed in molten salt containing aluminium, suggesting that Al_2O_3 disperses in molten salt.
  - The size of alumina particles seem to be very small. (Al_2O_3 density: 3.8 g/cm^3, NaCl-KCl density at 700 ℃: 1.6 ~ 1.7 g/cm^3).
  - The characteristics of alumina formed in the molten salt environment help alleviate concerns about pipe blockage and local overheating.



Floating alumina particles adhere to and detach from working electrode

Reaction with cerium oxo-species

- **Aluminium chlorides react with cerium oxo-species forming Al_2O_3**
  - Cerium oxide and cerium oxychloride were used as surrogates for uranium oxide and uranium oxychloride.
  - The reacted ratio of $CeOCl/CeO_2$ in the salt containing aluminum chloride (SKA) was higher than that in the salt without aluminum chloride (SKE).
  - The reaction mechanism between aluminium chloride and oxygen is thought to be $2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3$



Al mole ≒ Ce mole

5g
NaCl-KCl or
NaCl-KCl-$AlCl_3$

0.2g
CeO_2 or CeOCl

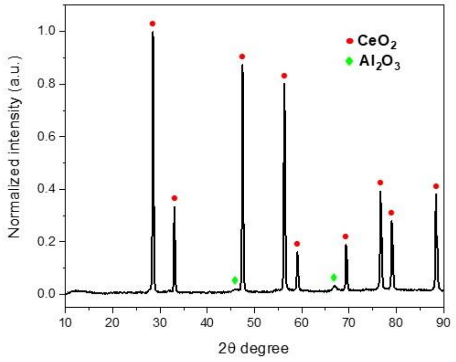
700 ℃, 48 hours

A. XRD analysis

Filtered with water and dried

B. XRF analysis

A. Residual oxides in SKA with CeO_2



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

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

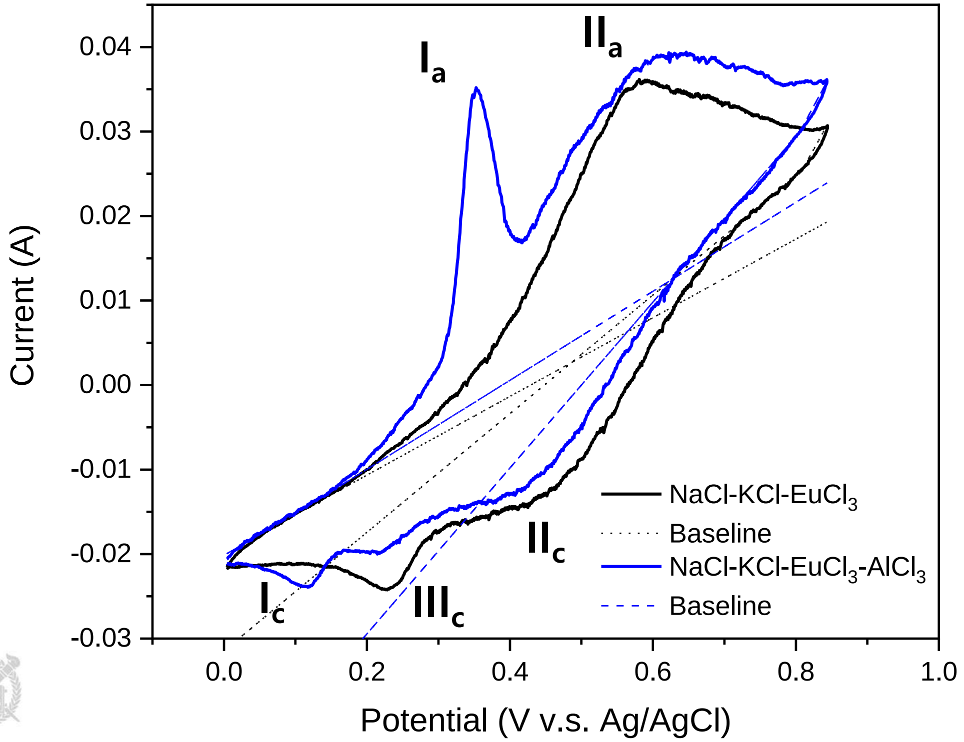
B. Determined quantities of Ce-oxo species reacted

Salt sample	Reacted $CeOCl/CeO_2$ ratio (%)	Reacted Al ratio (%)
SKA with CeOCl	30.7	47.7
SKA with CeO_2	15.3	52.3
SKE with CeOCl	1.3	-
SKE with CeO_2	0.8	-

Inducing oxygen in Eu^{2+}/Eu^{3+} redox system

- **The addition of aluminium chloride doesn't affect main redox couple's redox potential significantly.**
  - 0.0306 g of $AlCl_3$-NaCl-KCl (ASK, 48.2-33.4-18.4 mol%) was added into 10.5 g of NaCl-KCl-$EuCl_3$ (1.29 mol%) at 700 ℃, resulting in a final [Eu]/[Al] molar ratio of 10.
  - The observed peak potential difference (ΔEp) was lower than the predicted value, likely due to a high background current and the presence of impurities.

CV of NaCl-KCl-$EuCl_3$ with/without addition of Na_2O



Redox reactions

Redox peak	Reaction
I_a, I_c	$AlCl_4^-$ associated
II_a, II_c	$Eu^{3+}+e^- \leftrightarrow Eu^{2+}$
III_c	Impurity

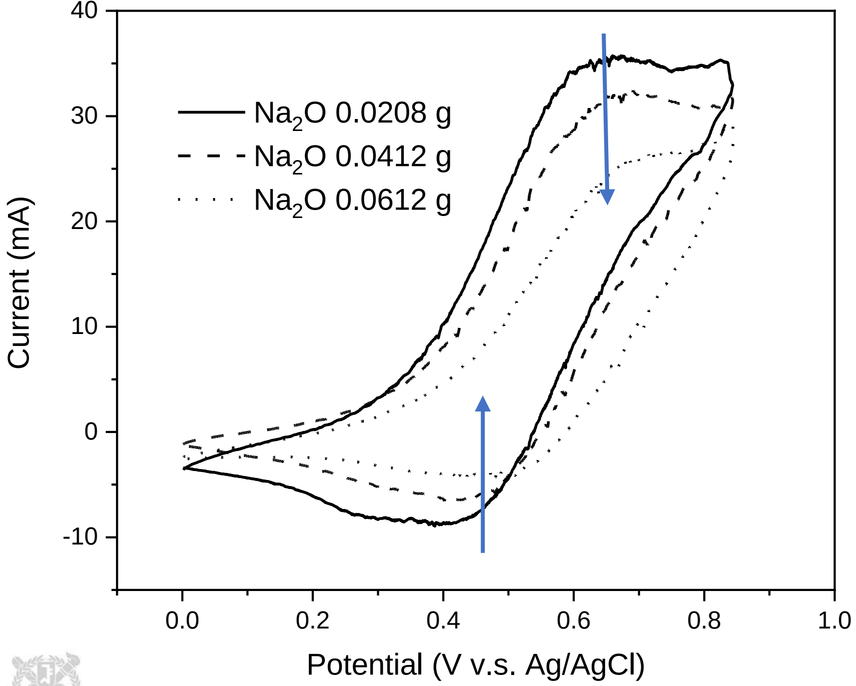
Peak potential difference

Salt system	ΔE_p (V)
NaCl-KCl-$EuCl_3$ (theoretical)	>0.19
NaCl-KCl-$EuCl_3$	0.12
NaCl-KCl-$EuCl_3$-$AlCl_3$	0.13

Inducing oxygen in Eu^{2+}/Eu^{3+} redox system

- **Intruded oxides significantly affect redox potential of main redox species.**
  - Intruded oxides react with Eu to form Eu_2O_3, reducing the concentration of soluble Eu in molten salt.
  - The ratio of Eu^{3+}/Eu^{2+} can be calculated from peak potential difference.
  - Intruded O^{2-} evokes highly reducing environment, opposed to O_2, resulting in increasing Eu^{2+} ratio.

CV of NaCl-KCl-$EuCl_3$ with addition of Na_2O



Calculated concentration ratio of Eu^{3+} to Eu^{2+} via peak potential difference [15]

Na_2O input (g)	ΔE_p (V)	$\frac{RT}{nF}\Delta E_p$	$\frac{C_{Eu}^{3+}}{C_{Eu}^{2+}}\sqrt{\frac{D_{Eu}^{3+}}{D_{Eu}^{2+}}}$	$\frac{C_{Eu}^{3+}}{C_{Eu}^{2+}}$
0.0208	0.272969	3.26	0.306	2.39
0.0412	0.264381	3.15	2.63	2.07
0.0612	0.198132	2.36	2.28	0.278

[15] Guo, Shaoqiang, et al. "Measurement of europium (III)/europium (II) couple in fluoride molten salt for redox control in a molten salt reactor concept." Journal of Nuclear Materials 496 (2017): 197-206

Summary and future work

- **Aluminium chloride is highly effective removing oxygen intruded (O_2^-) or contacting (O_2) with molten salt.**
- **In molten salt reactors, oxygen scavenger should compete with UO_2.**
  - Oxychlorides seem to be not stable at high temtperature (~700 ℃), which converts to oxide rapidly.
- **Aluminium chloride has potential that can convert uranium oxides to chlorides.**
  - Effectively reacted with cerium oxide forming aluminium oxide with a small particle size.
  - $3UO_2 + 4AlCl_3 \rightarrow 3UCl_4 + 2Al_2O_3$ (ΔG^0_{973K} = -185 kJ/mol.)
  - The efficiency of aluminum chloride in converting uranium oxides (UO_2, U_3O_8, UO_3) to uranium chlorides will be assessed.
- **Intruded oxygen can not only reduce the concentration of uranium, but also change its redox potential (U^{3+}/U^{4+}).**
  - The effect of aluminum chloride on maintaining the redox potential will be evaluated.
- **From a corrosion perspective, introducing a small amount of bubbling $AlCl_3$ in molten salt reactors may help mitigate oxygen-induced corrosion.**

THANK YOU