Application of absorption spectroscopy for studying behaviour of actinides in molten salts

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Molten salts have a number of potential applications in nuclear technology:

- producing nuclear fuels (metallic, oxide, nitride)
- reprocessing spent nuclear fuels
- acting as a nuclear fuel (molten salt reactor)
- coolant
Introduction

Fuel production
• electrolytic production of uranium (plutonium) metal
• electrolytic production of uranium dioxide, MOX (including granules for “vipac” method)
• precipitation of PuO₂, nitrides

Spent fuel reprocessing
• various molten salts have been tested (chlorides, sulfates, nitrates, molybdates, tungstates…)
MOX → PuO₂

Chlorination 700 °C

First electrolysis 680 °C

PuO₂ crystallization 680 °C

Second electrolysis 700 °C

Melt purification 700 °C

Cl₂ → MOX → PuO₂

Cl₂ + O₂ + Ar

Na₂CO₃, Na₃PO₄

MOX → MOX

Chlorination 650 °C

First electrolysis 630 °C

Main MOX electrolysis 630 °C

Second electrolysis 630 °C

Melt purification 650 °C
## Coolant

- Low melting point (300-500 °C)
- Low vapour pressure (< 1 mm Hg)
- Good thermal physical properties
- Chemical stability
- Acceptable cost

<table>
<thead>
<tr>
<th></th>
<th>Water (PWR)</th>
<th>Na (LMR)</th>
<th>He (HTR)</th>
<th>Salts (MSR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>15.5</td>
<td>0.69</td>
<td>7.07</td>
<td>0.69</td>
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<tr>
<td>Output temperature (°C)</td>
<td>320</td>
<td>540</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Coolant velocity (m/s)</td>
<td>6</td>
<td>6</td>
<td>75</td>
<td>6</td>
</tr>
</tbody>
</table>
Fuel
Acceptable neutron and physical properties
High radiation stability
Good solubility of actinides (U, Pu, Th, MA)
Possibility of reprocessing and recycling
Molten salt reactor

A technology deeply investigated in the 60’s and 70’s

- The successful operation of the MSRE (Molten Salt Reactor Experiment) from 1965 to 1969

  3 fuel types:
  Uranium enriched 30% with $^{235}\text{U}$
  Pure $^{233}\text{U}$
  $^{239}\text{Pu}$

- Fuel salt reprocessing not implemented in MSRE, except the off-gas system

- The detailed design of a 1000 MWe breeder reactor in Th/U cycle, the MSBR (programme stopped in 1976)

  Fuel salt
  71%LiF-16%BeF$_2$-12%ThF$_4$-0.3%UF$_4$
Developing/optimisation of a technological process requires understanding behaviour of fuel components, including actinides.

Spectroscopy offers an attractive tool for studying speciation.

Examples:

• Decomposition of uranyl chloride
• Reaction of uranium dioxide with hydrogen chloride
• Reduction of uranyl chloride by hydrogen
• Reaction of curium(III) with oxide ions
Uranium containing alkali chloride melts can be used
• for producing uranium metal (including powders)
• for producing uranium dioxide (including granules for “vipac” method)
• for reprocessing spent metallic, oxide and nitride fuels
Uranium in chloride melts forms U(III), U(IV), U(V) and U(VI) ions: $\text{UCI}_6^{3-}$, $\text{UCI}_6^{2-}$, $\text{UO}_2\text{Cl}_4^{3-}$ and $\text{UO}_2\text{Cl}_4^{2-}$.

Electronic absorption spectroscopy provides a convenient way of identifying dissolved species.

X-ray absorption spectroscopy allows to probe structure of dissolved species.
For optical spectroscopy and X-ray absorption spectroscopy measurements the melts are held in silica cells.
Experimental set-up for measuring EAS of molten salts

1, light source; 2 and 6, optical fibre cables; 3 and 5, collimating lenses; 4, furnace; 7, spectrometer; 8, ADC converter; 9, PC
Experimental
Experiments with transuranic elements were performed in a negative pressure box (RIAR)

\[ \text{Cl}_2 \text{ absorption, samples loading} \]
Experimental

Optical furnace attached to a bottom of the box
X-ray absorption spectra of molten and quenched samples (U LIII-edge) were measured at Stations 9.3 (in transmission) and 16.5 (in fluorescence) of the CLRC Daresbury Radiation Source.
Behaviour of U(V) and U(VI)

\[ \text{UO}_2\text{Cl}_4^{2-} + \text{Cl}^- \xrightleftharpoons{} \text{UO}_2\text{Cl}_4^{3-} + \frac{1}{2} \text{Cl}_2 \]

\[ \text{UO}_2\text{Cl}_4^{2-} \xrightleftharpoons{} \text{UO}_2 + \text{Cl}_2 + 2 \text{Cl}^- \]

\[ \text{UO}_2\text{Cl}_4^{3-} \xrightleftharpoons{} \text{UO}_2 + \frac{1}{2} \text{Cl}_2 + 3 \text{Cl}^- \]
Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

At elevated temperatures $\text{UO}_2\text{Cl}_4^{2-}$ decomposes forming $\text{Cl}_2$ and $\text{U}_3\text{O}_8$ [1]
$\text{UO}_2\text{Cl}_4^{3-}$ (below 750 °C) [2]
$\text{UO}_2$ and $\text{UCI}_6^{2-}$ (above 750 °C) [2]
$\text{UO}_2$ and $\text{UO}_2\text{Cl}_4^{3-}$ (by reaction between $\text{UO}_2$ and $\text{UO}_2\text{Cl}_4^{2-}$) [3, 4]
$\text{U}_3\text{O}_8$ and $\text{UCI}_6^{2-}$ [5]

Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

According to the literature the following reactions are possible:

$$\text{UO}_2\text{Cl}_4^{2-} \rightarrow \text{UO}_2 + \text{Cl}_2 + 2 \text{Cl}^-$$

$$\text{UO}_2\text{Cl}_4^{2-} + \text{Cl}^- \rightarrow \text{UO}_2\text{Cl}_4^{3-} + \frac{1}{2} \text{Cl}_2$$

$$4 \text{UO}_2\text{Cl}_4^{2-} \rightarrow \text{U}_3\text{O}_8 + \text{UCl}_6^{2-} + 6 \text{Cl}^- + 2 \text{Cl}_2$$
Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

- NaCl-2CsCl melt, 750°C, 173 min
- NaCl-KCl melt, 750°C, 240 min
- NaCl-2CsCl melt, 850°C, 40 min
- NaCl-KCl melt, 850°C, 206 min
Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

IR spectra of quenched NaCl-KCl based melts containing $\text{UO}_2\text{Cl}_2$ before and after heating under vacuum.
<table>
<thead>
<tr>
<th>Melt</th>
<th>T, °C</th>
<th>Time held under vacuum, min</th>
<th>U conc., wt.%</th>
<th>Final U oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>initial</td>
<td>final</td>
</tr>
<tr>
<td>3LiCl-2KCl</td>
<td>550</td>
<td>340</td>
<td>0.76</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>265</td>
<td>0.90</td>
<td>0.67</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>750</td>
<td>240</td>
<td>0.96</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>206</td>
<td>0.86</td>
<td>0.79</td>
</tr>
<tr>
<td>NaCl-2CsCl</td>
<td>650</td>
<td>92</td>
<td>0.29</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>150</td>
<td>1.15</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>173</td>
<td>1.13</td>
<td>1.59*</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>40</td>
<td>1.18</td>
<td>2.00*</td>
</tr>
</tbody>
</table>

* Volume of the melt was reduced due to solvent-salt sublimation.
Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

**Thermodynamic analysis**

$\text{UO}_2\text{Cl}_4^{3-} = \text{UO}_2 + \frac{1}{2}\text{Cl}_2 + 3 \text{Cl}^-$

$\text{UO}_2\text{Cl}_4^{2-} = \text{UO}_2 + \text{Cl}_2 + 2 \text{Cl}^-$

$\text{UO}_2\text{Cl}_4^{2-} + \text{Cl}^- = \text{UO}_2\text{Cl}_4^{3-} + \frac{1}{2}\text{Cl}_2$

$3\text{LiCl-2KCl based melt, 700 } ^\circ\text{C, total U concentration – 0.005 m.f.}, p_{\text{Cl}_2} = 10^{-7} \text{ atm.}$
Equilibrium partial pressure of Cl₂ above alkali chloride melts containing UO₂Cl₄²⁻, UO₂Cl₄³⁻ and UO₂ is below 10⁻⁵ mm Hg.

To facilitate Cl₂ removal from the atmosphere:

• melt was sparged with argon

• Zr getter was positioned above the melt.

\[
\begin{align*}
\text{Zr + Cl}_2 & \rightarrow \text{ZrCl}_2 \quad (\text{at } 750 \, ^\circ\text{C} \quad K = 3 \cdot 10^{14}) \\
\text{Zr + 2 Cl}_2 & \rightarrow \text{ZrCl}_4 \quad (\text{at } 750 \, ^\circ\text{C} \quad K = 7 \cdot 10^{34})
\end{align*}
\]
Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

Bubbling pure Ar gas through NaCl-2CsCl-UO$_2$Cl$_2$ melt resulted in sweeping forming Cl$_2$ from the atmosphere and assisted conversion of UO$_2$Cl$_4^{2-}$ into UO$_2$Cl$_4^{3-}$.

Presence of O$_2$/air impurities leads to the formation of insoluble alkali metal uranates.
Spectra recorded with Zr turnings positioned in the atmosphere above U(VI) containing melt (NaCl-2CsCl, 650 °C). Concentration of U(V) increased over time (time interval between recording initial and final spectra – 244 min).

Oxidation state of uranium in the final melt – 5.83.

\[ \text{UO}_2\text{Cl}_4^{2-} + \text{Cl}^- \rightarrow \text{UO}_2\text{Cl}_4^{3-} + \frac{1}{2} \text{Cl}_2 \]

Zr reacts with Cl\(_2\) facilitating the decomposition of uranyl(VI) chloride.
Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

Increasing U(V) concentration during reduction of U(VI) using Zr getter

550 °C

3LiCl-2KCl

750 °C

NaCl-KCl

NaCl-2CsCl

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7
absorbance at 780 nm

0 100 200 300 400 500
time / min

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7
absorbance at 780 nm

0 100 200 300 400 500
time / min
Thermal decomposition of $\text{UO}_2\text{Cl}_4^{2-}$

Reduction of $\text{UO}_2\text{Cl}_4^{2-}$ using Zr getter above the melt

<table>
<thead>
<tr>
<th>Melt</th>
<th>$T$, °C</th>
<th>Time, min</th>
<th>U conc., wt.%</th>
<th>Fraction of U remaining in melt, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>initial</td>
<td>final</td>
</tr>
<tr>
<td>$3\text{LiCl-2KCl}$</td>
<td>550</td>
<td>180</td>
<td>0.77</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>380</td>
<td>0.74</td>
<td>0.23</td>
</tr>
<tr>
<td>$\text{NaCl-KCl}$</td>
<td>750</td>
<td>336</td>
<td>0.78</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>410</td>
<td>0.81</td>
<td>0.34</td>
</tr>
<tr>
<td>$\text{NaCl-2CsCl}$</td>
<td>550</td>
<td>123</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>218</td>
<td>0.79</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>235</td>
<td>0.92</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>170</td>
<td>0.65</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Oxidation of uranium dioxide

Reaction of UO₂ with Cl₂ → UO₂Cl₄²⁻:

\[ \text{UO}_2 + \text{Cl}_2 + 2 \text{Cl}^- \rightarrow \text{UO}_2\text{Cl}_4^{2-} \]

Reaction of UO₂ with HCl normally gives UCl₆²⁻:

\[ \text{UO}_2 + 4 \text{HCl} + 2 \text{Cl}^- \rightarrow \text{UCl}_6^{2-} + 2 \text{H}_2\text{O} \]
Reaction of UO$_2$ with HCl

Spectra recorded in the course of reacting UO$_2$ with HCl

- NaCl-KCl melt, 700 °C
- NaCl-2CsCl melt, 600 °C
Reaction of UO$_2$ with HCl

Spectra recorded in the course of reacting UO$_2$ with HCl

LiCl melt, 750 °C
Reaction of UO₂ with HCl

Structural parameters from EXAFS spectra curve fitting of chloride melt samples prepared by reacting UO₂ with HCl

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell</th>
<th>CN</th>
<th>Distance, Å</th>
<th>Debye-Waller factor, 2σ², Å²</th>
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</thead>
<tbody>
<tr>
<td>UO₂+HCl in LiCl, 750 °C (4.88 wt.% U)</td>
<td>U-O</td>
<td>2</td>
<td>1.80</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>U-Cl</td>
<td>4</td>
<td>2.71</td>
<td>0.046</td>
</tr>
<tr>
<td>As above, quenched melt</td>
<td>U-O</td>
<td>2</td>
<td>1.76</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>U-Cl</td>
<td>4</td>
<td>2.76</td>
<td>0.024</td>
</tr>
<tr>
<td>UO₂+HCl in 3LiCl-2KCl, 450 °C (0.72 wt.% U)</td>
<td>U-Cl</td>
<td>6</td>
<td>2.44</td>
<td>0.028</td>
</tr>
<tr>
<td>As above, quenched melt</td>
<td>U-Cl</td>
<td>6</td>
<td>2.61</td>
<td>0.013</td>
</tr>
</tbody>
</table>
Reaction of UO$_2$ with HCl

EAS recorded upon reacting UO$_2$ with HCl in 3LiCl-2KCl melt at 450 °C (bottom) and 600 °C (top)
EAS recorded during reaction of $\text{UO}_2$ with HCl in 3LiCl-2KCl melt at 750 °C. Total time of HCl bubbling 160 min.
Possible reactions

\[ \text{UO}_2 + 4 \text{ HCl} \rightarrow \text{UCl}_4 + 2 \text{ H}_2\text{O} \]
\[ 2 \text{ UO}_2 + 2 \text{ HCl} \rightarrow 2 \text{ UO}_2\text{Cl} + \text{H}_2 \]

In a chloride melt the reaction products dissolve forming \( \text{UCl}_6^{2-} \) and \( \text{UO}_2\text{Cl}_4^{3-} \), respectively:

\[ \text{UO}_2 + 4 \text{ HCl} + 2 \text{ Cl}^- \rightarrow \text{UCl}_6^{2-} + 2 \text{ H}_2\text{O} \]
\[ 2 \text{ UO}_2 + 2 \text{ HCl} + 6 \text{ Cl}^- \rightarrow 2 \text{ UO}_2\text{Cl}_4^{3-} + \text{H}_2 \]
Thermodynamic analysis

For gaseous species

$$\Delta G_{(\text{gas})} = \Delta G^0_{(\text{gas})} + R \cdot T \cdot \ln(p),$$

and

$$\Delta G_{(\text{melt})} = \Delta G^0_{(l)} + R \cdot T \cdot \ln(N) + \Delta G_{(\text{mix})},$$

$p$ is the partial pressure of the gaseous species in the atmosphere above the melt and $N$ is that gaseous species molar fraction in the melt.

$p(HCl) \sim 1 \text{ atm.}$, if the system is close to equilibrium then $\Delta G_{(\text{melt})} \approx \Delta G_{(\text{gas})}$

For uranium chlorides

$$\Delta G_{(\text{melt})} = \Delta G^0_{(l)} + R \cdot T \cdot \ln(N) + \Delta G_{(\text{mix})},$$

$$\Delta G_{(\text{mix})} = \Delta G^* - \Delta G^0_{(l)},$$

(Gibbs free energy of the formation of a uranium chloride in the melt - standard Gibbs free energy of the formation of pure liquid uranium chloride)

$$\Delta G_{(\text{melt})} = \Delta G^* + R \cdot T \cdot \ln(N)$$

$\Delta G^*$ of $\text{UCl}_6^{2-}$ and $\text{UO}_2\text{Cl}_4^{3-}$ can be calculated from known values of the electrode potentials for $\text{U}^{\text{III}}/\text{U}^{0}$, $\text{U}^{\text{IV}}/\text{U}^{\text{III}}$ and $\text{UO}_2^{V}/\text{UO}_2$ red-ox couples measured versus $\text{Cl}_2/\text{Cl}^-$ reference electrode.

The order of $p(\text{H}_2\text{O})$ and $p(\text{H}_2)$ was estimated from known volumes of the experimental cells, rate of HCl flow through the system and amounts of $\text{H}_2\text{O}$ and $\text{H}_2$ formed.
Reaction of UO$_2$ with HCl

Calculated values of change of Gibbs free energy $\Delta G$ of reactions of UO$_2$ with HCl leading to the formation of UO$_2$Cl$_4$$^{3-}$ (1) and UCl$_6$$^{2-}$ (2) in:

A, melts of various cationic compositions at 750 °C, r(M$^+$) is average radius of alkali cation in the melt;

B, 3LiCl-2KCl melt at various temperatures.

\[ p(\text{H}_2\text{O}) = p(\text{H}_2) = 2 \times 10^{-4} \text{ atm}, \ [\text{U}] = 1 \text{ mol.\%}. \]
### Reaction of UO$_2$ with HCl

<table>
<thead>
<tr>
<th>Melt</th>
<th>$m$(UO$_2$)/$m$(salt)</th>
<th>$T$, °C</th>
<th>Time, min</th>
<th>Final U conc., wt.%</th>
<th>$n_U^{ox}$ in the final melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>0.17</td>
<td>750</td>
<td>261</td>
<td>4.88</td>
<td>5.27</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>750</td>
<td>180</td>
<td>0.65</td>
<td>5.09</td>
</tr>
<tr>
<td>3LiCl-2KCl</td>
<td>0.01</td>
<td>450</td>
<td>90</td>
<td>0.38</td>
<td>3.91</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>600</td>
<td>60</td>
<td>1.84</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>750</td>
<td>160</td>
<td>1.06</td>
<td>4.75</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>0.08</td>
<td>700</td>
<td>259</td>
<td>2.50</td>
<td>4.02</td>
</tr>
<tr>
<td>NaCl-2CsCl</td>
<td>0.07</td>
<td>600</td>
<td>162</td>
<td>0.90</td>
<td>3.98</td>
</tr>
</tbody>
</table>
Chemical reduction of $\text{UO}_2\text{Cl}_4^{2-}$

Reaction of $\text{UO}_2\text{Cl}_2$ with hydrogen

Reprocessing oxide nuclear fuels using alkali chloride melts and hydrogen

$$\text{UO}_2 + \text{Cl}_2 + 2 \text{Cl}^- \rightarrow \text{UO}_2\text{Cl}_4^{2-}$$

$$\text{UO}_2\text{Cl}_4^{2-} + \text{H}_2 \rightarrow \text{UO}_2 + 2 \text{HCl} + 2 \text{Cl}^-$$

Chemical reduction of $\text{UO}_2\text{Cl}_4^{2-}$

Reaction of $\text{UO}_2\text{Cl}_4^{2-}$ with $\text{H}_2$ in NaCl-2CsCl at 750 °C

![Absorbance spectra](image)
Chemical reduction of $\text{UO}_2\text{Cl}_4^{2-}$

Variation of U(V) concentration during reduction of $\text{UO}_2\text{Cl}_4^{2-}$ by $\text{H}_2$
Chemical reduction of $\text{UO}_2\text{Cl}_4^{2-}$

**Reaction of $\text{UO}_2\text{Cl}_4^{2-}$ containing melts with hydrogen**

<table>
<thead>
<tr>
<th>Melt</th>
<th>T, °C</th>
<th>U(VI) initial conc., wt.%</th>
<th>Time, min</th>
<th>U final conc., wt.%</th>
<th>Fraction of U remaining in the melt, %</th>
<th>U oxidation state</th>
<th>Time of reaching max. U(V) conc., min</th>
</tr>
</thead>
<tbody>
<tr>
<td>3LiCl-2KCl</td>
<td>550</td>
<td>0.71</td>
<td>44</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.42</td>
<td>56</td>
<td>0.014</td>
<td>3</td>
<td>5.62</td>
<td>7</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>550</td>
<td>0.76</td>
<td>23</td>
<td>0.62</td>
<td>82</td>
<td>5.41</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>0.83</td>
<td>45</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.74</td>
<td>48</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.71</td>
<td>86</td>
<td>0</td>
<td>0</td>
<td>--</td>
<td>5</td>
</tr>
</tbody>
</table>

$\text{UO}_2\text{Cl}_4^{2-} + \frac{1}{2} \text{H}_2 + \text{Cl}^- \rightarrow \text{UO}_2\text{Cl}_4^{3-} + \text{HCl}$ \hspace{1cm} (1)

$\text{UO}_2\text{Cl}_4^{3-} + \frac{1}{2} \text{H}_2 \rightarrow \text{UO}_2 + \text{HCl} + 3 \text{Cl}^-$ \hspace{1cm} (2)

in NaCl-2CsCl at total [U]~0.7 wt.% $\Delta G_{(1)} = \Delta G_{(2)}$ at n$_U$~5.67 (550 °C) or n$_u$~5.45 (750 °C) – around half of U(VI) can be reduced to U(V).
Chemical reduction of $\text{UO}_2\text{Cl}_4^{2-}$

Reaction of $\text{UO}_2\text{Cl}_4^{2-}$ with $\text{H}_2$ in NaCl-2CsCl at 750 °C

3 $\text{UO}_2\text{Cl}_4^{3-} + \text{H}_2 \rightarrow \text{UOCl}_5^{2-} + 2 \text{UO}_2 + \text{H}_2\text{O} + 7 \text{Cl}^-$
2 $\text{UO}_2\text{Cl}_4^{2-} + \text{H}_2 + \text{Cl}^- \rightarrow \text{UOCl}_5^{2-} + \text{UO}_2\text{Cl}_4^{3-} + \text{H}_2\text{O}$

In chloride melts Cm is present in the form of Cm(III) ions.

$$3\text{LiCl}-2\text{KCl}, \ 550 \degree\text{C}$$

0.0177 mol/kg Cm

$$\text{Cm(III)} + 3\bar{e} \leftrightarrow \text{Cm(0)}$$

WE – W

$$\nu = 0.5 \text{ V/s}$$

RE – Ag\(^+\)/Ag

$$n = 3$$
Behaviour of curium in chloride melts

Cm\(^{3+}\) (similar to lanthanides) reacts with oxide ions to form oxychloride (soluble ?) and oxide:

\[
\begin{align*}
\text{Cm}^{3+} + \text{O}^{2-} + \text{Cl}^- & \rightarrow \text{CmOCl} \\
2 \text{Cm}^{3+} + 3 \text{O}^{2-} & \rightarrow \text{Cm}_2\text{O}_3
\end{align*}
\]
Behaviour of curium in chloride melts

Electronic absorption spectra of Cm(III)

NaCl-2CsCl
(550, 650, 750 °C)
Behaviour of curium in chloride melts

Addition of $O^{2-}$ ions into chloride melts

**Dissolution of oxides – Na$_2$O, BaO**

**Bubbling Cl$_2$-O$_2$ mixtures**

$$\frac{1}{2}O_2^{(g)} + 2Cl^- \leftrightarrow O^{2-} + Cl_2^{(g)}$$

**Bubbling HCl-H$_2$O mixtures**

$$2H_2O + 4Cl^- \leftrightarrow O^{2-} + 4HCl^{(g)}$$
Behaviour of curium in chloride melts

Reaction of Cm(III) with H₂O

NaCl-2CsCl, 550 °C

\[ \log\left(\frac{p_{2\text{HCl}}}{p_{\text{H}_2\text{O}}}\right) \]

-1.4
-2.1
-2.9
-3.6
-4.3
-5.0
-5.7
Behaviour of curium in chloride melts

Electronic absorption spectra of Cm species

NaCl-2CsCl, 550 °C

$\log(p^2_{HCl}/p_{H_2O}) = -10$

$\log(p^2_{HCl}/p_{H_2O}) = -1.4$

$\text{CmO}^+$ ?
The peak around 358 nm appears:
- after bubbling HCl-H₂O mixtures with high p(H₂O)
- after bubbling Cl₂-O₂ mixtures with high p(O₂)
- after dissolving BaO

The peak remains after bubbling Cl₂ through the melt:
\[ \text{CmO}^+ + \text{Cl}_2 \rightarrow X \]

The peak disappears after bubbling Cl₂ through the melt in the presence of C (graphite):
\[ 2 \text{CmO}^+ + 2 \text{Cl}_2 + \text{C} \rightarrow 2 \text{Cm}^{3+} + \text{CO}_2 + 4 \text{Cl}^- \]
Behaviour of curium in chloride melts

Cm in NaCl-2CsCl melt, 550 °C

![Graph showing the behavior of curium in NaCl-2CsCl melt at 550 °C. The graph plots the Cm fraction against the logarithm of the ratio of p_{HCl}/p_{H_2O}. Two curves are shown: one for Cm^{3+} and another for CmO^{+}. The Cm fraction decreases as the logarithm of the ratio increases.]
Behaviour of curium in chloride melts

Cm in 3LiCl-2KCl melt, 450 °C

- Cm\(^{3+}\)
- CmO\(^{+}\)
- Cm\(_2\)O\(_3\)

Cm fraction vs. \(\log(p_{\text{HCl}}^2/p_{\text{H}_2\text{O}})\)
Conclusion

• Absorption spectroscopy techniques (i.e., electronic and X-ray) offer a convenient tool for \textit{in situ} studying behaviour of actinides in high temperature melts and can answer many questions some of which otherwise would never have been asked…
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