The synthesis of cementitious compounds in molten salts

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Declaration

“I can confirm the work presented in this thesis is my own. Where information has been derived from other sources, this has been indicated.”

______________________________

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Abstract

This thesis describes an investigation into the synthesis of cementitious compounds in molten salts. These compounds are produced in energy-intensive industries (EIIs), such as the cement process, and are responsible for emitting significant quantities of carbon dioxide (CO\(_2\)) emissions. Molten salt synthesis (MSS) involves dissolving compounds in a molten salt and reacting in solution. If the MSS of cementitious compounds can occur at lower temperatures than EIIs, this could lead to fewer quantities of CO\(_2\) emissions. The cementitious compounds selected for this investigation were dicalcium silicate (\(\beta\)-Ca\(_2\)SiO\(_4\)), tricalcium silicate (Ca\(_3\)SiO\(_5\)), disodium metasilicate (\(\alpha\)-Na\(_2\)SiO\(_3\)), tetrasodium orthosilicate (\(\beta\)-Na\(_4\)SiO\(_4\)) and the salt selected was sodium chloride (NaCl).

Initially, the dissolution behaviour of the reactants; silicon dioxide (SiO\(_2\)), calcium carbonate (CaCO\(_3\)) and sodium carbonate (Na\(_2\)CO\(_3\)) were investigated in NaCl, using calorimetry, potentiometry, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The XRD and SEM data suggested Na\(_2\)CO\(_3\) and CaCO\(_3\) decomposed to CO\(_2\), calcium oxide (CaO) and sodium oxide (Na\(_2\)O), and SiO\(_2\) only dissolved with a limited solubility. The calorimetric data suggested the heat of mixing (\(\Delta H_{\text{mix}}\)) for Na\(_2\)CO\(_3\) in molten NaCl illustrated a maximum positive contribution of \(~2\) kJ mol\(^{-1}\), and its phase diagram illustrated a eutectic point at 638\(^\circ\)C, 47 mol\% Na\(_2\)CO\(_3\). The potentiometric data suggested the solubility products (K\(_{sp}\)) for Na\(_2\)O and CaO in NaCl were -log 1.58 and -log 1.1, demonstrating reasonably high solubilities in comparison to other melts. This information suggests the MSS of cementitious compounds could be possible in industry.

Then, the MSS of cementitious compounds were investigated using SEM and XRD and were depicted on predominance diagrams. The XRD and SEM data suggested \(\beta\)-Ca\(_2\)SiO\(_4\) and \(\alpha\)-Na\(_2\)SiO\(_3\) can be produced, however Ca\(_3\)SiO\(_5\) requires higher temperatures (>1100\(^\circ\)C). This suggests other cementitious compounds can be produced in this manner, thus paving the way for producing complete products, such as cement.
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<td>ARE</td>
<td>Aircraft Reactor Experiment.</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter.</td>
<td>MSRE</td>
<td>Molten Salt Experimental Reactor.</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy of dissociation.</td>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy.</td>
</tr>
<tr>
<td>SEC</td>
<td>Specific energy consumption.</td>
<td>MCFC</td>
<td>Molten carbonate fuel cells.</td>
</tr>
<tr>
<td>EU ETS</td>
<td>EU emission trading scheme.</td>
<td>FFC</td>
<td>Fray, Farthing and Chen.</td>
</tr>
<tr>
<td>SAM</td>
<td>Sequential Addition Method.</td>
<td>ICDD</td>
<td>The International Centre for Diffraction Data database.</td>
</tr>
<tr>
<td>CCGT</td>
<td>Combined Cycle gas Turbine.</td>
<td>IR</td>
<td>Infrared (spectroscopy).</td>
</tr>
<tr>
<td>WHRSG</td>
<td>Waste Heat Recovery Steam Generator.</td>
<td>LSF</td>
<td>Lime saturation factor.</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Wavelength.</td>
<td>TEM</td>
<td>Transmission electron microscopy.</td>
</tr>
<tr>
<td>CCR</td>
<td>Calcium carbide residues.</td>
<td>JI</td>
<td>Joint Implementation Scheme.</td>
</tr>
<tr>
<td>CoP</td>
<td>Conference of Parties.</td>
<td>IGA</td>
<td>Intergranular corrosion.</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>Scattering angle.</td>
<td>YSZ</td>
<td>Yttria stabilized zirconia.</td>
</tr>
<tr>
<td>UKERC</td>
<td>United Kingdom Energy Research Council.</td>
<td>$\mathrm{CO}_2$</td>
<td>Carbon dioxide.</td>
</tr>
<tr>
<td>CDM</td>
<td>Clean Development Mechanism.</td>
<td>$[\mathrm{O}^{2-}]$</td>
<td>Oxide ion activity.</td>
</tr>
<tr>
<td>CRCT</td>
<td>Centre for Research in Computational Thermochemistry.</td>
<td>$\Delta H_{fus}$</td>
<td>Enthalpy of fusion.</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Enthalpy.</td>
<td>AS</td>
<td>Entropy.</td>
</tr>
</tbody>
</table>

*Table N1: Nomenclature.*
<table>
<thead>
<tr>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>g mol(^{-1})</td>
<td>Grammes per mole.</td>
</tr>
<tr>
<td>W</td>
<td>Power.</td>
</tr>
<tr>
<td>kg mol(^{-1})</td>
<td>Kilogrammes per mole.</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percent.</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million.</td>
</tr>
<tr>
<td>Gt</td>
<td>Gigatonnes.</td>
</tr>
<tr>
<td>mol%</td>
<td>Mole percent.</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees centigrade.</td>
</tr>
<tr>
<td>Mt</td>
<td>Metric tonnes.</td>
</tr>
<tr>
<td>kg tonne(^{-1})</td>
<td>Kilogrammes per tonne.</td>
</tr>
<tr>
<td>mm</td>
<td>Millimetre.</td>
</tr>
<tr>
<td>M</td>
<td>Metre.</td>
</tr>
<tr>
<td>V</td>
<td>Voltage.</td>
</tr>
<tr>
<td>°C min(^{-1})</td>
<td>Degrees centigrade per minute.</td>
</tr>
<tr>
<td>kWh tonne(^{-1})</td>
<td>Kilowatt hour per tonne.</td>
</tr>
<tr>
<td>kWh</td>
<td>Kilowatt hour.</td>
</tr>
<tr>
<td>torr</td>
<td>Torr (~133.3 Pa).</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometre (10(^{-6})).</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometre (10(^{-9})).</td>
</tr>
<tr>
<td>Z</td>
<td>Atomic number.</td>
</tr>
<tr>
<td>ρ</td>
<td>Density.</td>
</tr>
<tr>
<td>kV</td>
<td>Kilovolts.</td>
</tr>
<tr>
<td>E(_o)</td>
<td>Incident beam energy.</td>
</tr>
<tr>
<td>A</td>
<td>Atomic weight.</td>
</tr>
<tr>
<td>mW</td>
<td>Megawatts.</td>
</tr>
<tr>
<td>Ω</td>
<td>Resistivity.</td>
</tr>
<tr>
<td>atm</td>
<td>Atmosphere.</td>
</tr>
<tr>
<td>J mol(^{-1}) °C(^{-1})</td>
<td>Joule per mole centigrade.</td>
</tr>
<tr>
<td>cm(^2)</td>
<td>Surface area.</td>
</tr>
<tr>
<td>V s(^{-1})</td>
<td>Volts per second.</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength.</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volts.</td>
</tr>
<tr>
<td>Wh kg(^{-1})</td>
<td>Watts hour per kilogram.</td>
</tr>
<tr>
<td>MJ kg(^{-1})</td>
<td>Mega joules per kilogram.</td>
</tr>
</tbody>
</table>

*Table N2: Units.*
Background & thesis structure

1.1 Global warming and CO\textsubscript{2} emissions

The concept of the molten salt synthesis (MSS) of cementitious compounds initiated in response to the phenomenon of global warming. It is well-known the global average surface temperature of the earth has risen by ~0.8°C during the 20\textsuperscript{th} century (figure 1.1) [1]. This has been attributed to an increase in quantities of greenhouse gases (GHG’s) in the atmosphere, from anthropogenic sources (such as fossil fuels) and changing land use (such as deforestation) [2]. This temperature rise is linked to major catastrophes, such as hurricanes, heat waves, floods, droughts (in localised regions), evaporation of lakes, rising sea levels and the melting of ice glaciers [1-2]. It is also predicted this temperature rise will continue up to ~5.8°C this century, which is greater than the official tipping point of ~2°C, which scientists believe climate change becomes impossible to mitigate [3]. This makes global warming a major environmental problem.

![Figure 1.1: Global earth surface temperature rise (reproduced by author) [4].](image)
There are 24 GHG’s in the atmosphere that contribute towards global warming (figure 1.2) [2]. The main anthropogenic GHG is CO$_2$ and its concentration has increased by ~10 Gt (~1.5 times) between the years 1990-2011, and its concentration in the atmosphere is rising at ~2 ppm per annum [2]. The main anthropogenic sources of CO$_2$ are fossil fuels (~66 wt%) from the manufacturing, power generation and transportation sectors and deforestation (33 wt%), therefore tackling these sectors is likely to reduce CO$_2$ emissions, and therefore global warming [6].
However tackling CO₂ emissions is not an easy task which can vary across the globe. This can be attributed to different population sizes, the effects of regional financial circumstances (such as recessions) and regional strategies used by governments to combat climate change (figure 1.3), for example in 2000, CO₂ emissions from the US increased (up to ~5500 Mt), probably due to an increase in natural gas prices. The gas prices caused an increase in the usage of coal that year instead of natural gas, therefore emitting more CO₂. In 2009, CO₂ emissions from Japan decreased (down to ~1100
Mt) probably due to the effects of a recession which caused its industrial processes to produce significant quantities of materials. CO₂ emissions then rose due to the increased usage of coal energy after the Fukushima incident. In 2002, CO₂ emissions from China increased to ~5300 Mt, probably due to a reduction in electricity prices, which caused customers to use large amounts of electricity. CO₂ emissions from the EU increased to ~4000 Mt in 1996 and 2004, probably due an increase in the usage of fossil fuel. CO₂ emissions from Russia decreased to ~1400 Mt in 2000, after increasing environmental legislation caused an increase in environmental expenditure. CO₂ emissions from India increased to ~1500 Mt probably to an increase in the usage of coal [5-8]. The overall consensus is that although regional differences vary, global CO₂ emissions are still rising and requires addressing.

1.2 Cement process

One of the main sources of CO₂ emissions are energy-intensive industries (EIIs). These emit large quantities of CO₂ directly or indirectly (through electricity usage) [9]. One example of an EII is the cement process, which accounts for 5 wt% of CO₂ emissions [9-11]. In the cement process, ~40 wt% of emissions arise from burning fossil fuels, ~50 wt% from the decomposition of limestone and ~5-10 wt% from electricity usage [11-12]. It has been estimated that the cement process emits between 0.65-0.92 kg tonne⁻¹ of CO₂ annually, and this figure is projected to rise at 4.7% per annum (figure 1.4) [11] [13].
To understand why the cement process is a significant contributor towards CO$_2$ emissions, it is important to understand cement production. Cement contains five phases (including gypsum) which provide different characteristics towards the final product (table 1.1) [14-15]. $\beta$-Ca$_2$SiO$_4$ contributes towards slow hardening and strength, $\beta$-Ca$_3$SiO$_5$ contributes towards rapid hardening and early strength, Ca$_3$Al$_2$O$_6$ contributes towards slow hardening and gives the final product its characteristic grey colour and Ca$_2$(Al, Fe)$_2$O$_5$ contributes towards quick setting and hardening, which is retarded by gypsum. Cement may also contain several minor constituents such as sulphur oxide (SO$_3$), Na$_2$O and potassium oxide (K$_2$O), which appear in small
quantities [14-15]. The final cement product is often described by the quaternary phase system: CaO-SiO$_2$-Al$_2$O$_3$-Fe$_2$O$_3$ [14-15].

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Compound/Solid solution</th>
<th>Name</th>
<th>Compound name</th>
<th>CCN$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45-75</td>
<td>$\beta$-Ca$_3$SiO$_5$</td>
<td>Alite</td>
<td>Tricalcium silicate</td>
<td>C$_3$S</td>
</tr>
<tr>
<td>7-32</td>
<td>$\beta$-Ca$_3$SiO$_4$</td>
<td>Belite</td>
<td>Dicalcium silicate</td>
<td>C$_2$S</td>
</tr>
<tr>
<td>0-13</td>
<td>Ca$_3$Al$_2$O$_8$</td>
<td>Aluminate</td>
<td>Tricalcium aluminate</td>
<td>C$_3$A</td>
</tr>
<tr>
<td>0-18</td>
<td>Ca$_2$(Al, Fe)$_2$O$_5$/Ca$_2$(Al, Fe)$_2$O$_7$</td>
<td>Ferrite</td>
<td>Calcium alumino ferrites</td>
<td>C$_6$A / C$_6$AF</td>
</tr>
<tr>
<td>2-10</td>
<td>CaSO$_4$·2H$_2$O</td>
<td>-</td>
<td>Gypsum</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1.1: Cement composition [14].

Cement production requires excavating limestone and clay from quarries and transporting them to a cement manufacturing site. These are then crushed and grinded in mills to reduce their particle sizes (to ~100 mm in diameter) and blended with additives (such as iron, bauxite, quartzite and/or silica) in silos to produce a “raw meal” [16]. This allows for a specific composition and consistency to be achieved before being sent to the pyroprocessing stage. The pyroprocessing stage contains many different designs according to the type of cement plant which vary according to the characteristics of the raw meal (table 1.2) [14-17].

<table>
<thead>
<tr>
<th>Cement process</th>
<th>Raw meal type</th>
<th>Moisture content (wt%)</th>
<th>Cement kiln type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>Slurry</td>
<td>28-43</td>
<td>Long</td>
</tr>
<tr>
<td>Semi-wet (preheater)</td>
<td>Filter cake</td>
<td>16-21</td>
<td>Long/Leopol</td>
</tr>
<tr>
<td>Semi-dry (preheater)</td>
<td>Pellets</td>
<td>10-12</td>
<td>Long/Leopol</td>
</tr>
<tr>
<td>Dry</td>
<td>Dry powder</td>
<td>0.5-1</td>
<td>Long</td>
</tr>
<tr>
<td>Dry (preheater)</td>
<td>Dry powder</td>
<td>0.5-1</td>
<td>Short</td>
</tr>
<tr>
<td>Dry (precalciners and preheater)</td>
<td>Dry powder</td>
<td>0.5-1</td>
<td>Short</td>
</tr>
<tr>
<td>Shaft</td>
<td>Pellets</td>
<td>-</td>
<td>Shaft</td>
</tr>
</tbody>
</table>

Table 1.2: Pyroprocessing stage designs and raw meal characteristics [14-17].

The wet process involves grinding and mixing the raw meal with water to produce slurry (with a moisture content of ~40 wt%) [14-17]. This allows for the reactants to be easily transported through the kiln, prevents blow back by combustion gases and

$^1$ CCN = Cement Chemist Notation
C = CaO, S = SiO$_2$, A = Al$_2$O$_3$, F = Fe$_2$O$_3$
allows for easier grinding of the reactants. The slurry is then sent to a drier to reduce the moisture content, or to a long cement kiln where the moisture is driven off and cement reactions occur [14-17].

The dry process involves grinding the raw meal to produce a powder (with particle sizes of ~90 µm), which is sent to a precalciner and/or preheater or long cement kiln where cement reactions occur [14-17]. The preheater/precalciners allow ~40% of the raw meal to decompose before the cement kiln [14]. This allows for a reduction in energy consumption and kiln length.

The semi-dry and semi-wet process is a combination of the wet and dry process. The semi-dry process involves mixing and grinding the raw meal to produce pellets (with a moisture content of ~11 wt%) [14-15]. The wet pellets are then sent to a preheater or long cement kiln to drive off the moisture [15]. The semi-wet process involves mixing and grinding the raw meal with water to produce a filter cake (with a moisture content of ~18 wt%) [24]. The wet filter cake is then sent to either a preheater or filter cake drier before the cement kiln [14-17].

The cement kiln is a cylindrical steel tube, inclined between 1-4° to the horizontal (in most cases) [15]. The cement kiln rotates at ~3-5 revolutions per minute upon its axis, causing the reactants to travel from the upper to the lower end [14]. The lower end houses a controlled flame at temperatures exceeding ~1450ºC, which causes the reactants to melt and fuse together to produce cement clinker nodules (table 1.3) [30]. Initially limestone and clay decompose to SiO₂, aluminium(III) oxide (Al₂O₃), calcium oxide (CaO) and iron(III) oxide (Fe₂O₃) (reactions 1-4). Then these compounds react to form the main phases of cement clinker; \( \beta\)-Ca₂SiO₄, Ca₂(Al, Fe)₂O₅, and/or Ca₂(Al, Fe)₂O₁₂, Ca₃Al₂O₆ (reactions 5-8). Then \( \beta\)-Ca₂SiO₄ and CaO react in a secondary reaction to form Ca₃SiO₅ (reactions 9). Ca₆ (Al, Fe)₂ O₁₂, and/or Ca₂(Al, Fe)₂O₅ and \( \alpha\)-Fe₂O₃ form a liquid flux (20-30 wt% of the cement mixture). This liquid flux causes the products to aggregate into cement clinker nodules (with a diameter 1-10 mm) and helps to promote reaction kinetics [14-17].

---

2 A preheater is a series of chambers with moving grates or gas cyclones.
A precalciner is a combustion chamber within a preheater system.
Table 1.3: \( \Delta H_R \) of cement reactions for 1 mol of cement (HSC-Chemistry 6.1) [15] [18-19].

<table>
<thead>
<tr>
<th>Number</th>
<th>Cement reactions</th>
<th>( \Delta H_R ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{CaCO}_3 (s) \rightarrow \text{CaO (s)} + \text{CO}_2 (g) )</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>calcium carbonate ( \rightarrow ) calcium oxide + carbon dioxide</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( \text{Al}_2\text{Si}<em>5\text{O}</em>{11}\text{OH}_2 (s) \rightarrow \alpha\text{-Al}_2\text{O}_3 (s) + 4\text{SiO}_2 (s) + \text{H}_2\text{O} (g) )</td>
<td>82.0</td>
</tr>
<tr>
<td></td>
<td>aluminum silicate di-hydroxide (pyrophyllite) ( \rightarrow ) aluminum(III) oxide + silicon dioxide + water</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \text{Al}_2\text{Si}<em>4\text{O}</em>{10}\text{OH} (s) \rightarrow \alpha\text{-Al}_2\text{O}_3 (s) + 2\text{SiO}_2 (s) + 2\text{H}_2\text{O} (g) )</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>aluminum silicate tetra-hydroxide (kaolinite) ( \rightarrow ) aluminum(III) oxide + silicon dioxide + water</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( 2\text{FeO.OH (s)} \rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O} (g) )</td>
<td>55.2</td>
</tr>
<tr>
<td></td>
<td>iron(III) hydroxide ( \rightarrow ) iron(III) oxide + water</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( 2\text{CaO (s)} + \text{SiO}_2 (s) \rightarrow \beta\text{-Ca}_2\text{SiO}_4 (s) )</td>
<td>-124</td>
</tr>
<tr>
<td></td>
<td>calcium carbonate + silicon dioxide ( \rightarrow ) dicalcium metasilicate (C(_2)S)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( 3\text{CaO (s)} + \alpha\text{-Al}_2\text{O}_3 (s) \rightarrow \text{Ca}_3\text{Al}_2\text{O}_6 (s) )</td>
<td>-16.0</td>
</tr>
<tr>
<td></td>
<td>calcium carbonate + aluminum(III) oxide ( \rightarrow ) tricalcium aluminate (C(_3)A)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( 6\text{CaO (s)} + 2\alpha\text{-Al}_2\text{O}_3 (s) + \alpha\text{-Fe}_2\text{O}_3 (s) \rightarrow \text{Ca}_6(\text{Al, Fe})<em>2\text{O}</em>{12} (s) )</td>
<td>-157</td>
</tr>
<tr>
<td></td>
<td>calcium carbonate + aluminum(III) oxide + iron(III) oxide ( \rightarrow ) hexacalcium aluminoferrite (C(_6)AF)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( 4\text{CaO (s)} + \alpha\text{-Al}_2\text{O}_3 (s) + \alpha\text{-Fe}_2\text{O}_3 (s) \rightarrow \text{Ca}_4(\text{Al, Fe})<em>2\text{O}</em>{12} (s) )</td>
<td>-105</td>
</tr>
<tr>
<td></td>
<td>calcium carbonate + aluminum(III) oxide + iron(III) oxide ( \rightarrow ) tetracalcium aluminoferrite (C(_4)AF)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>( 3\text{CaO (s)} + \text{SiO}_2 (s) \rightarrow \text{Ca}_3\text{SiO}_5 (s) )</td>
<td>-155</td>
</tr>
<tr>
<td></td>
<td>calcium carbonate + silicon dioxide ( \rightarrow ) tricalcium silicate (C(_3)S)</td>
<td></td>
</tr>
</tbody>
</table>

The total residence time in the cement kiln is \( \sim \)3 hours, depending upon the type of process. During this period, pollutants are driven off from the reactants/products in gaseous form or as particulate matter (PM). The main pollutants in cement kilns are nitrogen oxides (NO\(_x\)), sulphur dioxide (SO\(_2\)), cement kiln dust (CKD) and CO\(_2\) [33]. The cement clinker nodules are then cooled (to \( \sim \)170\(^\circ\)C) and solidified in a cooler or cooling zone attached to the cement kiln [14]. The most common coolers are grate coolers, which are horizontal perforated grates with cold air blown from underneath [35]. The clinker nodules are then sent to mills where their particle sizes are reduced (to \( \sim \)5 \( \mu \)m) [14-15]. The most common mills are ball mills which are steel tubes divided into separate chambers, rotating upon a horizontal axis. The final cement product is then mixed with additives, such as gypsum (CaSO\(_4\). 2H\(_2\)O). CaCO\(_3\) or

\(^2\) Data not available in HSC Chemistry 6.1
anhydrite (CaSO$_4$) (up to ~ 2-8 wt%) to achieve the desirable hydraulic properties of cement [15].

The largest energy-intensive step in the cement process is the decomposition of CaCO$_3$ in an endothermic reaction, which is quoted at ~1.76 MJ kg$^{-1}$ at 25°C [39]. The theoretical energy requirement (TER) ranges between 1.57-1.80 MJ kg$^{-1}$ for the wet and dry process respectively [17] [20-22]. The specific energy consumption (SEC) ranges between 3-6 MJ kg$^{-1}$ depending upon the design of the cement process [17]. The average values for the SEC is quoted at ~3.40 GJ tonne$^{-1}$ for the dry process and ~5.29 GJ tonne$^{-1}$ for the wet process [17]. The electrical SEC ranges between ~75-80 kWh tonne$^{-1}$, however values have been reported up to ~110-120 kWh tonne$^{-1}$ in some cases (table 1.4) [20-22].

<table>
<thead>
<tr>
<th>Cement process</th>
<th>SEC</th>
<th>Thermal (MJ kg$^{-1}$)</th>
<th>Electrical (kWh tonne$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td></td>
<td>5-7.5</td>
<td>25</td>
</tr>
<tr>
<td>Semi-wet (with preheater)</td>
<td></td>
<td>3.4-4</td>
<td>30</td>
</tr>
<tr>
<td>Semi-dry (with preheater)</td>
<td></td>
<td>3.2-3.9</td>
<td>30</td>
</tr>
<tr>
<td>Dry</td>
<td></td>
<td>3.6-4.5</td>
<td>25</td>
</tr>
<tr>
<td>Dry (with preheater)</td>
<td></td>
<td>3.1-3.5</td>
<td>22</td>
</tr>
<tr>
<td>Dry (with preheater and precalciner)</td>
<td></td>
<td>3.1-3.2</td>
<td>22</td>
</tr>
<tr>
<td>Shaft</td>
<td></td>
<td>3.7-6.6</td>
<td>30</td>
</tr>
</tbody>
</table>

*Table 1.4: Energy consumption of the cement processes [15] [20-22].*

The energy consumption for the cement process is considered to be a significant source of CO$_2$ emissions. This is mainly attributed to the burning of fossil fuels to heat the kiln, heat losses by conduction, convection and radiation (due to the design of the kiln) and electricity used to grind the final cement product [15]. These areas can be improved which could lead to significant benefits in terms of CO$_2$ emissions.
1.3 Strategies to reduce CO₂ emissions

There have been many strategies to reduce CO₂ emissions, which are divided into adaptation and mitigation. Mitigation strategies are actions to reduce CO₂ emissions or and/or enhance its removal from the atmosphere by switching to low-carbon energy sources (such as wind solar and geothermal) and expanding forests to remove emissions from the atmosphere (carbon sinks). Adaptation strategies are actions to offset the effects of global warming, which involve preparing coasts and river basins for rising sea levels, preparing farms for changing weather conditions and tackling the spread of diseases. The general consensus are that both mitigation and adaptation strategies should be pursued simultaneously as even if CO₂ emissions are stabilized, the effects of global warming will continue for many years [23].

There have been many initiatives to reduce CO₂ emissions. One well-known initiative is the United Nations Framework Convention on Climate Change (UNFCCC) treaty, created by the Intergovernmental Panel on Climate Change (IPCC) [24-26]. This treaty provided a framework for negotiating further international treaties and was further developed during Conference Parties (CoP) meetings [24-26]. However no emission targets or enforcement mechanisms were included thus considered non-legally binding [24-26].

Another initiative was the Kyoto Protocol treaty, which was created in 1997, at the 3rd CoP [27-28]. This treaty represented a shared commitment by 192 countries to reduce their GHG emissions by the implementation of obligatory targets and the mechanisms to tackle climate change, such as Emissions Trading (ET), the Clean Development Mechanism (CDM) and Joint Implementation (JI) scheme [27-28]. Both the CDM and the JI scheme allowed emissions in one country to be reduced by trading emissions reductions in another country. The CDM required the second country to be a developing country and the JI required the second country to be another country that

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The CoP is a committee of signatories to the treaty, formed to assess the goals of the UNFCC and establish measures for the effects of climate change [27-28].

The IPCC is an intergovernmental body containing 196 countries (to date) to stabilize GHG concentrations in the atmosphere to levels which prevent dangerous anthropogenic interferences with the climate system [27-28].
ratified the Kyoto protocol. This treaty set an average CO\textsubscript{2} emissions target from industrialized countries at 5.2% below the 1990 levels by 2012 and between 6-8% for most countries [50]. Unlike the UNFCCC, the US never ratified the Kyoto Protocol which was also the largest GHG emitter [27-28].

Another initiative was the EU emission trading scheme (EU ETS) which was implemented in 2005, as part of the tradable emission allowances scheme of the Kyoto Protocol [29-31]. This was the world’s first international cap and trade system, covering more than 11000 factories, power stations, airlines and other installations in the EU. A limit was set on the total amount of GHG’s emitted which was reduced over time until the total emissions fell. Under the cap, companies received or brought emission allowances and traded with one another as required. This scheme was solely responsible for reducing 45% of EU’s CO\textsubscript{2} emissions and 40% of total GHG emissions by 2012 [29-31].

Another initiative was the Energy and Climate Policy in 2007, (often denoted the 20-20-20 targets) by the EU [30]. This declaration set out goals to reduce GHG emissions by 20% in comparison with the 1990 base-line by 2020 and satisfy 20% of the EU’s energy needs from renewable sources by 2050. The declaration comprised of four pieces of legislation; the reform of the EU ETS, implementation of national targets for emissions not covered by the EU ETS, national targets for renewable energy sources and the introduction of carbon capture and storage (CCS). The reform of the EU ETS included the introduction of a single EU-wide cap on emission allowances to be reduced each year instead of the existing system of national caps [31]. The national targets for emissions not covered by the EU ETS included the housing, agriculture, waste and transport (excluding aviation) sectors and the national targets for renewable energy sources were binding national targets for raising the share of renewable energy by 2020. The introduction of CCS included a legal framework for the environmentally safe use of CCS technologies involves capturing of CO\textsubscript{2} emitted by industrial processes and storing it in underground geological formations. The directive covered all CO\textsubscript{2} storage in geological formations in the EU and laid down requirements over the lifetime of the storage sites [30-31].

Another initiative was the Strategic Energy Technology Plan (SET-Plan) in 2008, by the EU [32]. This set out goals to establish an energy policy for Europe by
accelerating the development and deployment of low-carbon technologies, reducing costs of new technologies by co-ordinating research and helping finance projects and promoting research and innovation efforts across Europe by supporting technologies with the greatest impact on the EU's transformation to a low-carbon energy system [30-32].

Apart from initiatives, many technologies have been developed for EIIIs to reduce CO$_2$ emissions, for example for the cement process ball mills have been replaced with vertical roller mills (VRM), high pressure roller mills (HPGRS) or high roller mills (HRM) [60]. These technologies have higher grinding capacities than conventional ball mills [33-34].

Classifiers and separators are often installed in cement plants to create “grinding circuits” to improve the energy efficiency of the grinding process [33-34]. These circuits can “open” where the feed rate of incoming clinker/raw meal is adjusted to achieve a desired particle size, or “closed” where coarser particles are separated from the finer product and returned for further grinding [33-34].

High activation grinding is a technology at a conceptual level, which is proven to increase the reactivity of blended cements [35]. High activation grinding utilizes vibratory or attrition milling. Current studies suggest activation grinding increases the surface area of the particles and/or mechanically activates compounds within blended cements and hence their reactivity [35].

Wet cement plants are often converted to dry plants in partial or complete conversions. Complete conversions involve converting the cement kiln and initial milling stage to the dry process and partial conversions involve converting solely the cement kiln [35-37]. Preheaters and precalciners are also installed to increase the residence time before the cement kiln to decompose limestone. The most common preheater is the grate preheater which is being succeeded by gas-suspension preheaters.

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5 VMR’s are rollers rotating at different speeds, HPGRS’s are rollers rotating at similar speeds, and a HRM is a roller in a rotating cylinder [33-34].

6 Vibratory mills are grinding chambers attached to vibrating motors. Attrition mills are grinding chambers attached to rotating chambers [33-34].
Cement kilns are also lined with refractory bricks or concrete which insulates the steel shell from the high temperatures inside the cement kiln. This protects the cement kiln from corrosive materials, such as alkali sulphates in cement and reduces heat losses from the cement kiln [35-37].

Thermal energy is often recovered by chains hanging from the cement kiln. These chains are exposed to the high temperature gas stream at the kiln exit, which capture thermal energy and recycle it through a series of heat exchangers [15]. The thermal energy is then redirected to the cement kiln, preheaters and precalciners thus lowering the energy consumption. The thermal energy can also be redirected to waste heat recovery steam generators (WHRSG) to drive an electrical generator. The electricity that is produced offsets a portion of electricity purchased from the national grid which reduces running costs [38].

The reaction temperatures in the cement kiln are often reduced using alternative raw materials that offset a portion of the limestone in the raw meal or alternative fuels. These raw materials include calcareous or decarbonated oil shale, steel or granulated blast furnace slag, fly ash or calcium carbide residues (CCR) [39-42]. Reaction temperatures are also lowered by increasing the limestone content in the raw meal (or lime saturation factor (LSF)) [39-40]. This produces cement with a lower $\text{Ca}_3\text{SiO}_5$ and higher $\beta$-$\text{Ca}_2\text{SiO}_4$, often called Belite cements. This has a lower compressive strength and different hydration characteristics than conventional cement thus lower energy consumption. The final cement product is often blended with additives such as blast furnace slag or fly ash to increase the volume of cement. It is estimated up to 25% of the final product can be diluted without changing the application of cement [39-42].

Carbon capture for cement plants is another technology being investigated at a conceptual level [43-47]. The concentration of $\text{CO}_2$ in flue gases in the cement process are higher (14-33 wt%) than coal power plants (12-14 wt%) or gas power plants (4 wt%) making them ideal for carbon capture [43-46]. The captured $\text{CO}_2$ is then compressed for transportation and taken to reservoirs for underground storage, or used in enhanced oil recovery. The various carbon capture technologies include post-combustion capture, oxy-fuel combustion capture and pre-combustion capture. Post-combustion capture technologies remove $\text{CO}_2$ from flue gases during the combustion
of fuel using CaO (often referred to as a sorbent), which is referred to as carbonate looping technology [43-47]. Other post-combustion capture technologies use an amine solvent or biologically capture CO₂ using algae in water and involve a cleaning process after any cycles [43-47]. Oxy-fuel combustion technologies use O₂ for combustion instead of air. This produces a flue gas containing CO₂ and H₂O and results in a higher flame temperature. The O₂ is often produced by cryogenic air separation [43-47]. Pre-combustion technologies involve burning fuel in insufficient amounts of O₂ or air/steam to produce a ‘synthesis gas” containing carbon monoxide (CO) and water (H₂O) via the water-gas shift reaction [82]. The CO then reacts with steam in a catalytic reactor to produce CO₂ and H₂. The CO₂ is then separated by physical or chemical absorption to produce a fuel that is rich in H₂. The fuel can also be used to generate electricity in a combined-cycle gas turbine (CCGT) [43-48].

1.4 Research objectives and thesis structure

Despite these initiatives, CO₂ emissions are continuing to rise globally and it is important that we continue to investigate new methods of reducing these emissions. One relatively new method of reducing CO₂ emissions is to reduce reaction temperatures in the cement kiln. The cement process requires 1450°C for the cement reactions to occur and melt the phases; Ca₆(Al, Fe)₂O₁₂, and/or Ca₂(Al, Fe)₂O₅ and α-Fe₂O₃. These phases create a liquid flux, allowing sufficient contact between the reactant/product particles for cement reactions to occur [12]. However previous solid-state experiments have suggested only 1250°C is required to obtain Ca₃SiO₅ (the cement phase with the highest temperature requirement) [49]. This suggests if one is able to introduce a liquid phase into the cement kiln at lower reaction temperatures, the energy requirement and CO₂ emissions could be lowered. One method of introducing a liquid phase into the cement kiln is using a molten salt and has led to the synthesis of a variety of compounds (denoted MSS). The concept of MSS is to dissolve the reactants in a molten salt and allow them to react in solution. In this scenario the molten salt behaves as a solvent or as a reactant [50]. Therefore the objective of this thesis is to investigate whether the MSS of cementitious compounds (such as the phases of cement) are possible and whether complete products such as cement can be produced at lower reaction temperatures than industry. The cementitious compounds considered in this thesis will be α-Na₂SiO₃, β-Ca₂SiO₄,
Ca$_3$SiO$_5$ and β-Na$_4$SiO$_4$, which are found in cement and/or share a similar structural chemistry to the phases of cement.  

The structure of this thesis can be described as follows; Chapter 1: Background & thesis structure introduced the effects of global warming, CO$_2$ emissions and strategies to reduce these emissions. It also described the cement process, as an example of an EII that contributes towards CO$_2$ emissions. Chapter 2: Literature review describes molten salts and their applications to readers who are unfamiliar with this topic. It then describes previous investigations into the dissolution of compounds in molten salts (describing investigations into K$_{sp}$, ΔH$_{mix}$ values and phase diagrams). These will help determine whether the MSS of cementitious compounds are possible in industry. This chapter also describes previous investigations into the MSS of compounds, which will determine which compounds/phases can be produced in this manner. Finally it will describe previous investigations into the diagrammatic representation of molten salt reactions (using predominance diagrams), which is a useful topic for describing MSS reactions and the interaction of container materials (crucibles) with the molten salt.

Chapter 3: Characterization, electroanalytical and calorimetric techniques & experimental setup describes the experimental techniques used to investigate the structures and purities of the reactants in the molten salt in the molten salt, behaviour of the molten salt at the reaction conditions, dissolution of the reactants in the molten salt and the MSS of cementitious compounds. These include XRD, SEM, potentiometry, Cyclic Voltammetry (CV), Drop calorimetry and Differential Scanning Calorimetry (DSC). It also provides a description of the setup for each experiment.

Chapter 4: Results & discussion describes the complete investigation into the MSS of cementitious compounds. This initiates with an investigation into the feasibility of the synthesis of cementitious compounds. This will be used to determine the reaction temperatures required to produce cementitious compounds and the selection

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7 “Cementitious compounds” have been selected to replace the phases of cement due to its multi-component nature. The lessons learnt from synthesising cementitious compounds in molten salts will be applied to all the phases of cement.
of a suitable salt for MSS. Then the structures and purities of the reactants in the molten salt will be investigated, which will suggest the purity and phase transitions of the reactants at the reaction conditions. Then, the behaviour of the molten salt at the reaction conditions will be investigated, which will be useful for describing the effects of vapour pressure upon the salt, which can have delirious effects upon the experiments. Then, the dissolution of the reactants in the molten salt will be investigated, which will lead to obtaining $K_{sp}$, $\Delta H_{mix}$ values and phase diagrams. This information will help determine whether the MSS of cementitious compounds are possible in industry. Then the MSS of cementitious compounds will be investigated, and depicted on predominance diagrams. This will help determine which other compounds can be produced in this manner.

Chapter 5: Conclusions & future work describes the conclusions of the thesis and future work for other researchers for the feasibility of the synthesis of cementitious compounds, structures and purities of the reactants in the molten salt, behaviour of the molten salt at the reaction conditions, dissolution of the reactants in the molten salt and MSS of cementitious compounds. The structure of this thesis can also be summarised in a flow diagram (figure 1.5).
Figure 1.5: Decision tree and thesis structure.
Literature review

2.1 Introduction

This chapter provides an understanding of molten salts and their applications to those who are unfamiliar. It then introduces previous investigations describing the dissolution of compounds in molten salts (\(K_{sp}\), \(\Delta H_{mix}\) and phase diagrams), the MSS of compounds and the diagrammatic representation of molten salt reactions.

2.1 Molten salts and their applications

Molten salts (also known as ionized salts) are a class of compounds that are solid at room temperature and pressure, and made liquid by heating [51]. The most common salts that have been used in literature include halides and oxyanionic salts. Halide salts are compounds with a halide ion, i.e. \(F^-\), \(Cl^-\), \(Br^-\) and oxyanionic salts have an \(O^{2-}\) ion, i.e. \(NO_3^-\), \(SO_4^{2-}\), \(OH^-\) complex ions. Complex ions are groups of ions coexisting in localized regions for appreciable periods of time [51-53]. A list of halide and oxyanionic salts can be found in table 2.1.
### Halide salts (with their melting points)

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Chlorides</td>
<td>NaCl (801°C), KCl (770°C), LiCl (605°C)</td>
<td></td>
</tr>
<tr>
<td>Fluorides</td>
<td>NaF (993°C), KF (858°C), LiF (845°C)</td>
<td></td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>NaSCN (287°C), KSCN (173°C), LSCN (unavailable)</td>
<td></td>
</tr>
</tbody>
</table>

### Oxyanionic salts (with their melting points)

<p>| | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Hydroxide</td>
<td>NaOH (318°C), KOH (406°C), LOH (462°C)</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>NaNO₃ (308°C), KNO₃ (334°C), LiNO₃ (255°C)</td>
<td></td>
</tr>
<tr>
<td>Sulphate</td>
<td>Li₂SO₄ (859°C), K₂SO₄ (1069°C), Na₂SO₄ (884°C)</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>Li₂CO₃ (723°C) Na₂CO₃ (851°C) K₂CO₃ (891°C)</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>NaPO₄ (627°C), KPO₄ (450°C), LiPO₄ (unavailable)</td>
<td></td>
</tr>
<tr>
<td>Borates</td>
<td>LiBO₂ (844°C), KBO₂ (947°C), NaBO₂ (967°C)</td>
<td></td>
</tr>
<tr>
<td>Silicates</td>
<td>Na₂SiO₃ (1410°C), K₂SiO₃ (978°C), Li₂SiO₃ (1201°C)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: Halide and oxyanionic salts (with their melting points), 1 atm (produced by author) [18] [51].

![Figure 2.1: Aqueous and molten NaCl (reproduced by author) [52-53].](image)

Figure 2.1 illustrates a molecule of NaCl in its solid, liquid and aqueous states. When a salt dissolves in an aqueous solution (NaCl in H₂O) polar H₂O molecules are attracted to charged ions (Na⁺, Cl⁻) due to the electric dipole moment of H₂O molecules, thus destroying the lattice arrangement of the solid (often called solvation) [54]. When a salt is heated to its melting temperature (NaCl at 801°C), the cohesive forces and regular arrangement of the lattice is disturbed by thermal energy, causing the charged ions (Na⁺, Cl⁻) to become unbound from the rigid lattice, allowing them to become more ionic in character than conventional liquids. These charged ions interact amongst themselves in a mobile state and even combine to form complex ions. This interaction is often caused by coulomb forces between the particles [55].
Figure 2.2 illustrates the heat capacities ($C_p$) and viscosities of molten salts at 1 atm. It can be seen that molten salts have similar $C_p$ values to aqueous media which allows them to store or transfer large quantities of thermal energy. Molten salts also have viscosities similar to aqueous media which allows them to be transported at low pressures [53]. This can be useful for chemical processes as it removes the need for auxiliary equipment (such as pumps).
Figure 2.3: Stability ranges (top) and vapour pressures (bottom) of common salts (with Na\(^+\) ion), 1 atm (produced by author) [56].

Figure 2.3 shows the stability ranges and vapour pressures of common salts. Molten salts can have large stability ranges (801-1413°C for NaCl), higher than aqueous media, which is useful for high temperature processes. Molten salts also have similar vapour pressures to aqueous media (0.302 mmHg °C\(^{-1}\) for NaCl at 801°C, 26.5 mmHg °C\(^{-1}\) for H\(_2\)O at 25°C) beyond their melting temperatures [18]. This can be useful for chemical processes as it avoids the loss of reactants.

The properties of molten salts are useful for many commercial and conceptual technologies, for example molten beryllium and lithium fluorides are used as primary fuel/coolants in molten salt nuclear reactors [57-64]. These salts dissolve fissile and
fertile elements, such as uranium, plutonium and thorium [57-64]. The molten salts become critical in the reactor core, generating thermal energy which is then transferred to an external heat exchanger. The thermal energy is then transferred to a secondary molten salt which is pumped to a CCGT to generate electricity [98]. Molten salt nuclear reactors are generally safer than conventional nuclear reactors as in the event of power failures, the salt is drained immediately to a cooled storage facility to terminate the nuclear reaction. The start-up costs are also lower as molten salts have generally low viscosities, thus reducing the cost of auxiliary equipment (such as pumps) [57-64]. Also it has been estimated the thermal to electrical efficiency of molten salt nuclear reactors are ~45%, which is 40% higher than conventional nuclear reactors with similar fuel consumptions [57-64].

Molten salt nuclear reactors were developed in 1954, as part of the U.S. Aircraft Nuclear Propulsion (ANP) program at the Oak Ridge National Laboratory (ORL) in Texas [59-61]. The objective was to create a nuclear propulsion engine for aircraft, to increase their flight range. The project resulted in a 2.5 MWt molten salt nuclear reactor called the Aircraft Reactor Experiment (ARE), containing a molten fluoride mixture as a primary and secondary coolant in conjunction with a solid ceramic fuel [59-61]. Another example was the Molten Salt Experimental Reactor (MSRE), developed in the 1960’s, by the United States Atomic Energy Commission (AEC). The project resulted in a 7.4 MWt molten salt nuclear reactor containing a graphite reactor core and tested with uranium dissolved in a molten fluoride mixture [59-61]. Recently there has been a growing interest in advancing the development of molten salt nuclear reactors and in 2011, they were identified by the Generation IV International Forum as one of six possible nuclear reactors candidates to be commercialised by 2030 [64].

Molten salts such as molten bromides, chlorides and fluorides are used as electrolytes in thermal and high temperature rechargeable batteries. Thermal batteries contain solid non-conductive salts at room temperature, which are mobilized by a pyrotechnic heat source. When heated the salt becomes a liquid to provide short bursts of power until the salt is no longer molten [65-72]. High temperature rechargeable batteries contain a conductive molten electrolyte which is powered externally through the mains [65-72]. The “Durathon” battery is an example of a high temperature
rechargeable battery, developed by GE Energy Storage [70-72]. The battery contains a molten chloride electrolyte, with a sodium anode and nickel chloride (NiCl$_2$) cathode. The anode and cathode are connected to a β-Al$_2$O$_3$ solid electrolyte that is conductive to Na$^+$ ions. The battery operates between 270-350ºC with an energy density of 115 Wh kg$^{-1}$ [70-72].

Molten salts such as molten lithium and potassium carbonates are used as electrolytes in molten carbonate fuel cells (MCFCs) [73-78]. These operate at higher temperatures (~650ºC) than fuel cells (~90ºC), resulting in improved reaction kinetics and greater electrical efficiencies (~50%) [73-78]. A typical molten carbonate fuel cell contains a nickel anode and nickel oxide (NiO) cathode catalyst, coupled with a molten carbonate electrolyte suspended in a porous ceramic membrane. The nickel anode splits H$_2$ to H$^+$ ions to release an electron, which travels through an external circuit to generate electricity, and the H$^+$ ion reacts with CO$_3^{2-}$ ions to form H$_2$O and CO$_2$ and an electron. The electron then travels to the cell cathode to complete the reaction and the H$_2$O and CO$_2$ is expelled from the system [73-78]. “DFC 300A combined heat and power system”, and “HotModule unit”, are examples of molten carbonate fuel cells developed by FuelCell Energy and MTU Friedrichshafen respectively. These are used as decentralized energy units and provide ~250 kW of power [73-78].

Molten salts such as chlorides are used as reactants and electrolytes in the electrolytic extraction of sodium and lithium. Sodium is produced by placing NaCl in a Downs cell and heating above its melting point [79-81]. A typical Downs cell contains 3 chambers, 4 carbon anodes, surrounded by steel cathodes to split molten NaCl into Cl$_2$ and sodium. These operate at 590ºC at 7 V, higher than the decomposition potential of NaCl (3.21V), caused by high anodic and cathodic overpotentials [79-81]. Companies such as DuPont are known to produce sodium in a Downs cell [81].

Molten salts such as cryolite (Na$_3$AlF$_6$) are used as solvents and electrolytes in the electrolytic extraction of aluminium (Hall-Héroult process) [82-85]. The process involves dissolving Al$_2$O$_3$ (~6 wt%) in molten cryolite (Na$_3$AlF$_6$) and other additives such as aluminium fluoride (AlF$_3$), calcium fluoride (CaF$_2$), magnesium fluoride (MgF$_2$), lithium fluoride (LiF) and NaCl (~12 wt%), which increases the melt’s electrical conductivity and lowers the reaction temperature in comparison with pure
Na$_3$AlF$_6$ [82-85]. In the process, the reactants are placed in a carbon-lined cell and carbon anodes inserted into the molten salt. Then an electrical current is passed through the cell (at ~960ºC) which causes aluminium to deposit, as a liquid, at the bottom of the cell (due to its higher density then Na$_3$AlF$_6$). O$_2$ is also released from Al$_2$O$_3$ which combines with the carbon anodes to produce CO$_2$ and CO, causing them to be consumed [82-85]. A typical Hall-Héroult cell requires 4.5 V of which 2.8 V is taken up by ohmic losses making the process ~40% efficient. A typical aluminium smelter produces 200,000 tonnes of aluminium per annum, and requires between ~100-200 Hall-Héroult cells connected electrically in series. Rio Tinto Alcan is a well-known producer of aluminium via electrolytic extraction.

Molten salts such as chlorides are used as electrolytes in titanium extraction (FFC Cambridge process) [86-90]. Traditionally, titanium is produced in the Kroll process, by reacting impure TiO$_2$ (Rutile) with coke (at ~1000ºC) and Cl$_2$ to produce titanium tetrachloride (TiCl$_4$). Then the TiCl$_4$ is reduced by molten magnesium (at ~800ºC), producing titanium and magnesium chloride (MgCl$_2$) which is separated by vacuum distillation [86-90]. In the FFC Cambridge process, a graphite anode and TiO$_2$ cathode is immersed in a molten chloride (at ~900ºC). Then an electrical current is passed through the molten salt causing TiO$_2$ to reduce to titanium and O$_2$. The O$_2$ reacts with the graphite anode to produce either CO$_2$ or CO, causing them to be consumed in the process [86-90]. The FFC Cambridge process can produce ~10 tonnes of titanium over several days using 160 kg of TiO$_2$ to produce 100 kg of titanium. This is an improvement from the Kroll process, which uses 380 kg of TiCl$_4$ and ~100 kg of magnesium to produce 100 kg of titanium and 380 kg of MgCl$_2$ [83-87]. The process doesn’t involve hazardous materials such as Cl$_2$, TiCl$_4$ and MgCl$_2$, which is more environmentally friendly [86-90].

Molten salts such as sodium and potassium nitrates are used as thermal energy storage mediums in solar power plants [91-94]. A typical molten salt solar plant contains a central tower receiver, a heliostat and molten salt storage system. The heliostat contains a parabolic mirror which concentrates thermal radiation from the sun (factor of ~80) onto a focal point which is then transferred to a molten salt. The molten salt is then pumped to a power CCGT to generate electricity [91-94]. Often a thermal energy storage system is integrated into the plant which allows it to work on overcast days.
and at night “Archimede” is a molten salt solar plant in Sicily, by ENEL and Archimede Solar Energy, which generates 5 MW of electrical power (at 550°C) [91-94].

Molten salts such as nitrates, nitrite, chlorides and cyanides, are used in the heat treatments of metals, to enhance mechanical toughness and surface hardness [95-97]. Molten salts offer more controllable heat transfer rates than heat treatments in air due to a uniform temperature distribution across the alloy [95-97]. A typical heat treatment involves heating iron in steel beyond its phase transformation temperature, to transform the ferrite phase to austenite, followed by quenching to form martensite [95-97].

2.2 Dissolution of compounds in molten salts

Dissolution of compounds in molten salts has been investigated through phase diagrams, $\Delta H_{\text{mix}}$ and $K_{sp}$ values. These have been useful for many conceptual and commercial applications of molten salts, which can no doubt affect the quality of the final product and/or process.

2.2.1 Heats of mixing of compounds in molten salts

Dissolution of compounds in molten salts has been investigated through $\Delta H_{\text{mix}}$ values. $\Delta H_{\text{mix}}$ or “excess enthalpy” is the enthalpy change associated with the dissolution of a compound in a liquid at constant pressure and temperature [98-99].
Figure 2.4 illustrates the $\Delta H_{\text{mix}}$ of a binary system for components A and B, where $H_A$ and $H_B$ are the enthalpies of the pure substances (available in thermodynamic tables) and $\Delta H_{\text{mix}}$ is the heat of mixing (an integral quantity) at mole fraction $X_1$, obtainable directly from calorimetric measurements [98-99]. Symmetrical representations of the heats of mixing (denoted ideal mixing behaviour) between two components are represented by a regular solution model [98-99].

$$\Delta H_{\text{mix}} = x_A(1 - X_A) A$$

Equation 2.1

Equation 2.1 describes the regular solution model, where $X_A$ is the composition of component A, $\Delta H_{\text{mix}}$ is the heat of mixing and A is a constant. Most experimental data do not conform to symmetrical representations (denoted non-ideal mixing behaviour), thus a sub-regular solution model is often used [98-99].

$$\Delta H_{\text{mix}} = x_A(1 - X_A) (A + Bx_A + C x_A(1 - X_A))$$

Equation 2.2

Equation 2.2 describes the sub-regular solution model, where $X_A$ is the composition of component A, $\Delta H_{\text{mix}}$ is the heat of mixing, and A, B and C are sub-regular solution coefficients (when B and C approach zero, the regular solution model is obtainable).
There has been considerable interest in the $\Delta H_{\text{mix}}$ values of various molten salt binary systems, such as molten chlorides, iodides, nitrates and fluorides (including their ternary mixtures) [100-105]. For example, in 1965, Hersh and Kleppa investigated the $\Delta H_{\text{mix}}$ in molten LiCl-NaCl, LiCl-KCl, LiCl-RbCl, LiCl-CsCl, NaCl-KCl, NaCl-RbCl, NaCl-CsCl, KCl-RbCl, KCl-CsCl, and RbCl-CsCl, between 810-670ºC, using drop calorimetry, under argon. The melts were either used as received or vacuum dried, melted and filtered through quartz wool, before being placed in fused silica (SiO$_2$) crucibles. It was shown the $\Delta H_{\text{mix}}$ data for most systems (with the exception of the last three) displayed negative contributions, which increased the larger the size differences between the two cations i.e. the sub-regular solution coefficient; A is -1120 for the LiCl-NaCl binary system and -490 for molten NaCl-KCl [102].

In 1976, Anderson and Kleppa investigated the $\Delta H_{\text{mix}}$ values of molten Li$_2$CO$_3$-Na$_2$CO$_3$, Li$_2$CO$_3$-K$_2$CO$_3$, Li$_2$CO$_3$-Rb$_2$CO$_3$, Li$_2$CO$_3$-Cs$_2$CO$_3$, Na$_2$CO$_3$-Rb$_2$CO$_3$, Na$_2$CO$_3$-Cs$_2$CO$_3$, K$_2$CO$_3$-Rb$_2$CO$_3$, K$_2$CO$_3$-Cs$_2$CO$_3$ and Rb$_2$CO$_3$-Cs$_2$CO$_3$, between 857-907°C, using drop calorimetry, under CO$_2$. The purpose of CO$_2$ was to inhibit the decomposition of the carbonates at the reaction temperatures. The reactants were previously dried under vacuum to remove any residual moisture and placed in a palladium-gold (Pd-Au) alloy crucible. The $\Delta H_{\text{mix}}$ data showed most systems had negative $\Delta H_{\text{mix}}$ values, with the minimum value at $\sim$-2.864, $\sim$-8.229, $\sim$-8.326, $\sim$-9.966, $\sim$1.347, $\sim$2.141 and $\sim$2.124 kJ mol$^{-1}$ respectively. For molten K$_2$CO$_3$-Rb$_2$CO$_3$, K$_2$CO$_3$-Cs$_2$CO$_3$ and Rb$_2$CO$_3$-Cs$_2$CO$_3$, the heat effects demonstrated small positive contributions at 0.0002 kJ mol$^{-1}$, 0.0567 kJ mol$^{-1}$ and 0.0473 kJ mol$^{-1}$ respectively. This was largely attributed to the association reaction between CO$_2$ and O$_2$ to the CO$_3^{2-}$ complex ion [103].

In 1990, Dessurealt et al compiled a list of $\Delta H_{\text{mix}}$ (and phase diagrams) for 24 binary systems (A$_2$CO$_3$-AX, A$_2$SO$_4$-AX (where A = Li, Na, K and X = F, Cl, OH, NO$_3$) to create a set of optimized thermodynamic functions. In four of the 24 systems the $\Delta H_{\text{mix}}$ values in the liquid phase were measured using a drop calorimeter and fitted to an appropriate model. The Gibbs free energies of mixing ($\Delta G_{\text{mix}}$) were evaluated, and combined with the calorimetric data to obtain excess liquid entropies. When calorimetric data was not available, the entropy was set to zero and the $\Delta G_{\text{mix}}$ and $\Delta H_{\text{mix}}$ values were obtained from phase diagrams [106].
In 1994, Gaune-Escard et al investigated the $\Delta H_{\text{mix}}$ values in molten NaCl-NdCl$_3$, KCl-NdCl$_3$, RbCl-NdCl$_3$, CsCl-NdCl$_3$, between 792-576ºC, using a drop calorimeter, under argon. The reactants were melted under hydrochloric (HCl) and argon by progressive heating, in an alumina crucible, inside a quartz tube. To remove trace impurities, the authors performed distillation under a reduced pressure. The $\Delta H_{\text{mix}}$ data displayed negative contributions with minimum values at -5.7, -16.6, -20.2 and -23.4 kJ mol$^{-1}$ respectively. These minimum values were shifted towards the chloride rich compositions, suggesting the existence of Cl$_6^{3-}$ complex ions [107].

In 2005, Rycerz et al investigated the $\Delta H_{\text{mix}}$ values in molten PrCl$_3$-CaCl$_2$ and NdCl$_3$-CaCl$_2$, at 800ºC, using drop calorimetry, under argon. The reactants were melted under HCl and argon by progressive heating in an alumina crucible, inside a quartz tube. To remove trace impurities, distillation was performed under reduced pressure. The $\Delta H_{\text{mix}}$ data demonstrated “S” shaped functions (positive for PrCl$_3$ and NdCl$_3$ rich compositions). This behaviour was attributed to the existence of complex ions, possibly Pr$_2$Cl$_{11}^{5-}$ and Nd$_2$Cl$_{11}^{5-}$ which may have existed in the liquid. These $\Delta H_{\text{mix}}$ values were considered low (between -200-180 J mol$^{-1}$) thus the systems were assumed to be ideal [108].

<table>
<thead>
<tr>
<th>Binary system</th>
<th>Temperature (°C)</th>
<th>Sub-regular solution coefficients ($\Delta H_{\text{mix}}$ in kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>810</td>
<td>-2.05</td>
</tr>
<tr>
<td>NaCl-LiCl</td>
<td>740</td>
<td>-4.69</td>
</tr>
<tr>
<td>NaCl-RbCl</td>
<td>810</td>
<td>-3.22</td>
</tr>
<tr>
<td>NaCl-CsCl</td>
<td>810</td>
<td>-4.31</td>
</tr>
<tr>
<td>NaCl-Na$_2$CO$_3$</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>Na$_2$CO$_3$-K$_2$CO$_3$</td>
<td>857</td>
<td>-5.03</td>
</tr>
<tr>
<td>Na$_2$CO$_3$-Li$_2$CO$_3$</td>
<td>905</td>
<td>-9.90</td>
</tr>
<tr>
<td>Na$_2$CO$_3$-Rb$_2$CO$_3$</td>
<td>905</td>
<td>-8.26</td>
</tr>
<tr>
<td>Na$_2$CO$_3$-Cs$_2$CO$_3$</td>
<td>862</td>
<td>-8.89</td>
</tr>
</tbody>
</table>

Table 2.2: $\Delta H_{\text{mix}}$ in chloride-carbonate, chloride and carbonate binary systems (with a Na$^+$ ion) (produced by author) [102-106].

8 Calculated from the phase diagram of the Na$_2$CO$_3$-NaCl binary system.
Table 2.2 summaries the sub-regular solution coefficients for chloride, carbonate and chloride-carbonate binary systems, sharing a common Na\(^+\) ion. The effect of temperature upon $\Delta H_{\text{mix}}$ are assumed to be negligible, therefore these coefficients can be used to calculate the liquidus and solidus points for phase diagrams at any temperature [109].

2.2.2 Phase diagrams of compounds in molten salts

Dissolution of compounds in molten salts has been investigated through phase diagrams [119-128]. Phase diagrams represent thermodynamically stable regions of systems at specific temperatures, pressures and compositions [110-115]. These regions are separated by phase boundaries, marking conditions where multiple phases coexist at equilibrium conditions. They are classified by the different phase behaviours encountered, governed by the number of species in the system, including one component (unary), two component (binary) systems and three component (ternary) systems [110-115]. A one component (unary) system can exist in three different phases (solid, liquid or gas), as a function of pressure and temperature at fixed composition [110-115].

![Figure 2.5: One component system; SiO\(_2\) (reproduced by author) [112]](image-url)
Figure 2.5 illustrates the many crystalline forms of SiO$_2$, at different temperatures and pressures. The most common form is α-quartz which undergoes a non-reversible phase transition (at 570ºC) to β-quartz [112]. Metastable (non-equilibrium) phases of SiO$_2$ also occur, at these temperatures but not represented on phase diagrams [116]. A eutectic system represents two solid solutions with miscibility (in some proportion). If comparable differences in atomic radii and crystal structure between the components are present (larger than isomorphous systems), a miscible region arises, extending to the liquid phase [110-115].

A two component (binary) system exists in three different phases (solid, liquid or gas), as a function of pressure, temperature and composition [110-115]. There are four types of binary systems; isomorphous, eutectic, peritectic and monotectic, each resulting in different representations [110-115]. An isomorphous system is the simplest type of binary system, representing two components dissolving into each other in all (or some proportion). This dissolution behaviour arises from both components having similar crystal structures and atomic radii [110-115].
Figure 2.6: Two component isomorphous systems; Cu-Ni (middle), NaCl-KCl (bottom) and eutectic system; Au-Si (top) (reproduced by author) [113] [117-119].
Figure 2.6 illustrates the isomorphous systems for copper-nickel (Cu-Ni), NaCl-KCl binary system and the eutectic system for gold-silicon (Au-Si) [117-119]. The boundary lines between the liquid mixture region and liquid + solid or solid solution regions is denoted the liquidus and between the liquid + solid and solid (or solid solution region) is denoted the solidus. The liquidus and solidus lines meet at the fusion temperatures for copper (at 1085°C), nickel (at 1085°C), NaCl (at 801°C) and KCl (at 770°C). If comparable differences in atomic radii and crystal structure between the components are present, a miscible region arises (denoted a miscibility gap). Peritectic and monotectic systems consider additional reactions to a phase diagram. During a peritectic reaction, a liquid phase and solid phase react together to form a new solid phase and during a monotectic reaction, a liquid phase cools to form a new liquid phase and solid mixture [113]. Often phase diagrams can involve three (or multiple) components which represent solid, liquid or gas phases as a function of pressure, temperature and composition of multiple components.

Figure 2.7 illustrates a space model for a ternary eutectic system for components A, B and C, being combinations of binary systems; A and B, B and C and C and A. Space models serve limited practical purpose, thus often represented in two dimensions, as liquidus/solidus or composition triangles (a horizontal section of a space model).
There has been considerable interest in the phase diagrams of various binary systems, such as molten chlorides and carbonates [120-128]. For example, in 1990, Dessureault et al compiled a list of phase diagrams (and $\Delta H_{\text{mix}}$) for 24 binary systems (A$_2$CO$_3$-AX, A$_2$SO$_4$-AX) where A = Li, Na, K and X = F, Cl, OH, NO$_3$, to create a set of optimized thermodynamic functions to calculate phase diagrams and $\Delta H_{\text{mix}}$ using the CALPHAD method (CALculation of PHAse Diagrams). All carbonate-chloride mixtures represented a eutectic system, with no solid solubility (assumed to be 0 in most cases). More specifically, the transition temperatures for Na$_2$CO$_3$ were 359ºC and 485ºC, and fusion temperature was 858ºC and the phase diagram for molten NaCl-Na$_2$CO$_3$ demonstrated a eutectic point at 643ºC at 43 mol% Na$_2$CO$_3$ [106].

In 2000, Iwasawa and Maeda investigated the phase diagram for molten NaCl-Na$_2$CO$_3$, NaCl-Na$_2$SiO$_3$, and LiCl-Li$_2$SiO$_3$, using a novel hot filament technique, to allow solid, liquid-solid and liquid phases to be visually observed. These mixtures were slowly heated in a hot filament cell, purged with argon to eliminate H$_2$O. This allowed the fusion temperature of NaCl, Na$_2$CO$_3$ and the eutectic point for molten NaCl-Na$_2$CO$_3$, to be determined at 801ºC, at 851ºC, and at 643ºC at 43 mol% Na$_2$CO$_3$ [124].

In 2007, Yaokawa et al investigated the phase diagram for molten NaCl-Na$_2$CO$_3$, NaCl-Na$_2$SO$_4$, KCl-K$_2$SO$_4$, KCl-K$_2$CO$_3$, NaCl-KCl, Na$_2$SO$_4$-K$_2$SO$_4$, Na$_2$CO$_3$-K$_2$CO$_3$, Na$_2$SO$_4$-Na$_2$CO$_3$, K$_2$SO$_4$-K$_2$CO$_3$, NaCl-Na$_2$SO$_4$-Na$_2$CO$_3$, KCl-K$_2$SO$_4$-K$_2$CO$_3$, NaCl-Na$_2$SO$_4$-KCl-K$_2$SO$_4$, NaCl-Na$_2$CO$_3$-KCl-K$_2$CO$_3$, and Na$_2$SO$_4$-Na$_2$CO$_3$-K$_2$CO$_3$-K$_2$SO$_4$. These were used to calculate the phase diagram for the molten NaCl-Na$_2$SO$_4$-KCl-K$_2$SO$_4$-K$_2$CO$_3$, using a Modified Quasichemical solution model. The phase diagram exhibited no solid solution or intermediate phases and the eutectic point was found (at 631ºC, 45 mol% Na$_2$CO$_3$) [125].

Also in 2007, Lindberg et al investigated phase diagrams and thermodynamic functions for molten NaCl-Na$_2$CO$_3$, KCl-K$_2$CO$_3$, Na$_2$CO$_3$-K$_2$CO$_3$ and NaCl-KCl to calculate the phase diagram for molten KCl-K$_2$CO$_3$-NaCl-Na$_2$CO$_3$. Initially the phase diagram for molten NaCl-Na$_2$CO$_3$ was calculated and compared with previous measured liquidus and solidus points. The melting point of Na$_2$CO$_3$ (at 851ºC) was
found to be lower than the extrapolated value of the calculated liquidus line (at 858ºC) and the eutectic point was found to be 632ºC, 45 mol% Na$_2$CO$_3$ [126].

In 2011, Kochkarov et al investigated the phase diagram for molten NaCl-Na$_2$CO$_3$, including the fusion temperatures for NaCl and Na$_2$CO$_3$ using DTA. The NaCl and Na$_2$CO$_3$ were initially fused and placed inside a platinum crucible. The fusion temperatures were found to be 801ºC and 851ºC respectively, which were used in combination with the phase diagram for molten NaBO$_2$-Na$_2$CO$_3$ and NaCl-NaBO$_2$ to calculate the phase diagram for molten NaBO$_2$-NaCl-Na$_2$CO$_3$, with a eutectic point, at 612ºC, 16 mol% NaBO$_2$, 42 mol% NaCl and 42 mol% Na$_2$CO$_3$. A similar approach was used to calculate the phase diagram for molten NaBO$_2$-Na$_2$CO$_3$-Na$_2$WO$_4$, and NaBO$_2$-NaCl-Na$_2$WO$_4$ and the eutectic point were found to be at 568ºC, 12 mol%, NaBO$_2$, 28 mol% NaBO$_2$, 60 mol% Na$_2$MoO$_4$ and 655ºC, 9 mol% NaBO$_2$, 53 mol% NaCl, 38 mol% Na$_2$WO$_4$ [127].

In 2014, Longgang et al investigated the density, viscosity, volatilization, decomposition, melting point, eutectic composition and enthalpy of fusion for molten NaCl-Na$_2$CO$_3$, using a DTA, rotating-cylinder, horizontal-hammer method, transpiration method, XRD, SEM, and EDS, under argon. The Na$_2$CO$_3$ and NaCl were placed in a corundum (Al$_2$O$_3$) crucible and heated to melt completely, to remove residual moisture, and then ground in a ball mill. They found the melting point of the mixture was 636ºC, the enthalpy of fusion was 101.12 J g$^{-1}$ and the density was 1.83 g cm$^{-3}$ at 700ºC, and 1.67 g cm$^{-3}$ at 1000ºC, showing that the density decreased linearly with temperature. The viscosity was 17.02 cp at 700ºC and 1.21 cp at 1000ºC, showing that the viscosity had an exponential dependence upon temperature in its liquid state. The vapour pressure was 13.34 Pa at 700ºC and 151.06 Pa at 900ºC, showing that the vapour pressure increased with temperature. The evaporation of NaCl became evident after 804ºC and ~90 wt% was lost at 1000ºC. The weight loss of Na$_2$CO$_3$ was slow indicating its decomposition to Na$_2$O and CO$_2$. The XRD showed the composition and phase of the mixture remained unchanged after high-temperature treatment. The SEM and EDS showed particles of Na$_2$CO$_3$ and NaCl in the mixture were randomly distributed with no uniform phase [128].
2.2.3 Solubility products of compounds in molten salts

Dissolution of compounds in molten salts has been investigated by obtaining $K_{sp}$ values. $K_{sp}$ values describe the activity of “free ions” in a saturated solution, and are often accompanied by dissociation constants ($K_d$), describing the extent of dissociation of the compound in an unsaturated solution, and formation constants ($K_f$), describing the formation of a complex ion in solution [129-130]. These terms can be used to describe a compound at equilibrium with its ions/complex ions, at a specific temperature and pressure, and are independent of the initial and final concentration of the reactants and products.

$$K_{sp} = [\text{Me}^{2+}][\text{O}^{2-}]$$  \hspace{1cm} \text{Equation 2.3}

$$K_d = \frac{[\text{Me}^{2+}][\text{O}^{2-}]}{[\text{MeO}]} = \frac{K_{sp}}{[\text{MeO}]}$$  \hspace{1cm} \text{Equation 2.4}

$$K_f = \frac{[\text{MeO}]}{[\text{Me}^{2+}][\text{O}^{2-}]} = \frac{[\text{MeO}]}{[K_{sp}]}$$  \hspace{1cm} \text{Equation 2.5}^9

Equations 2.3-2.5 describe the $K_{sp}$, $K_d$ and $K_f$ values for a two-charged metal cation oxide, where $[\text{Me}^{2+}]$ is the activity of the metal cation, $[\text{O}^{2-}]$ is the activity of the O$^{2-}$ ion and $[\text{MeO}]$ is the activity of the dissolved non-dissociated oxide. $K_{sp}$, $K_{sp}$, and $K_f$ values in molten salts can be found using techniques such as isothermal saturation, potentiometric titration or the sequential addition method (SAM) [129-131].

---

*Only for the case of a two-charged metal cation oxide.*

*Equilibrium thermodynamic constants units are dimensionless.*
• **Isothermal saturation method**
  This method has been employed for studying oxide solubilities over a limited concentration range. The procedure involves the addition of oxides to a molten salt and removing samples at regular intervals to analyse the $\text{Me}^{2+}$ or $\text{O}^{2-}$ ion activity (using techniques such as radiochemical or complexometric analysis). This is often accompanied by a potentiometry to detect the activity of $\text{Me}^{2+}$ or $\text{O}^{2-}$ ions in the molten salt (to detect the saturation limit). Upon knowledge of the $\text{Me}^{2+}$ or $\text{O}^{2-}$ ion activity, $K_{sp}$, $K_d$ and $K_f$ values of compounds and complexes can be determined [130].

• **Potentiometric titration method**
  This method is employed for studying oxide solubilities over a wide concentration range. The procedure involves the addition of a compound (such as an oxide) to a molten salt (often saturated with a metal chloride (or vice versa)). This is accompanied by a potentiometry to detect the activity of $\text{Me}^{2+}$ or $\text{O}^{2-}$ ions in the molten salt (to detect the formation of a complex or insoluble compound). The addition of the oxide causes complexes and/or insoluble compounds to form in a “titration reaction”, which can be followed by potentiometry. Upon knowledge of the $\text{Me}^{2+}$ or $\text{O}^{2-}$ ion activity, $K_{sp}$, $K_d$ and $K_f$ values of compounds and complexes can be determined [130].

• **Sequential addition method**
  This method is employed for studying oxide solubilities over a wide concentration range. The procedure involves the addition of a compound (such as an oxide) to a molten salt (often saturated with a metal chloride (or vice versa)). This is accompanied by potentiometry to detect the activity of $\text{Me}^{2+}$ or $\text{O}^{2-}$ ions in the molten salt (to detect the saturation limit). The addition of the compound causes a “dissolution reaction” up to the saturation limit of the molten salt, which can be followed by potentiometry. Upon knowledge of the $\text{Me}^{2+}$ or $\text{O}^{2-}$ ion activity, $K_{sp}$ values of compounds can be determined [130].
There has been considerable interest in obtaining $K_{sp}$ values in various melts, such as molten chlorides, nitrates and fluorides (and their binary and ternary mixtures) [132-160]. The scale of literature is extensive therefore we will focus upon $K_{sp}$ values in molten NaCl, KCl, LiCl-KCl, NaCl-KCl and CaCl$_2$-NaCl.

### 2.3.1.1 Solubility products of compounds in molten LiCl-KCl

Molten LiCl-KCl is used as electrolytes in molten salt batteries, molten carbonate fuel cells and as solvents for the pyrochemical reprocessing of nuclear fuel, due to its low melting temperature (at 348°C) and high proliferation resistance over aqueous solvents [57-58]. These applications are highly dependent upon the $O^{2-}$ ion activity in the molten salt therefore $K_{sp}$ values of oxides in this molten salt are frequently investigated.

One of the first authors to measure $K_{sp}$ values in molten LiCl-KCl was Delarue in 1959, where he qualitatively investigated the solubility of cadmium oxide (CdO), lead oxide (PbO), barium oxide (BaO), CaO, silver oxide (Ag$_2$O), cobalt oxide (CoO), NiO, zinc oxide (ZnO), magnesium oxide (MgO), beryllium oxide (BeO) and Al$_2$O$_3$ in molten LiCl-KCl, at 500°C, by visual inspection. The molten salt was contained in a Pyrex tube, which was heated to the experimental temperature, followed by the addition of oxide pellets. When no deposit of oxide appeared in the molten salt, they considered it to be soluble, and when a deposit formed, the oxide was considered slightly soluble or insoluble. He found that CdO, PbO, BaO, CaO and Ag$_2$O were soluble in the molten salt, CoO, NiO, ZnO were slightly soluble and MgO, BeO and Al$_2$O$_3$ were insoluble. He also found the solubility of oxides, added as pellets were greater than powders, which can be attributed to its larger surface area [132].

In 1960, Laitinen and Bhatia investigated the $K_{sp}$ values of NiO, palladium oxide (PdO), PtO$_2$ and copper oxide (Cu$_2$O) in molten LiCl-KCl, by potentiometry, at 450°C, under nitrogen (N$_2$). The technique involved an ISE and reference electrode immersed in the molten salt at the experimental temperature. The ISE was constructed from graphite with a platinum wire in the centre, and the reference electrode was a platinum wire, immersed in molten platinum chloride (PtCl$_2$). They found the behaviour of the reference electrode wasn’t reversible which was attributed to the
reaction of platinum with molten LiCl-KCl at highly acidic conditions. Therefore the Cl\(^-\) ions in the electrode were analysed after each experiment, to determine the amount of PtCl\(^2-\) present. The reference electrode potential was then corrected for a PtCl\(^2-\) activity of 1. They found the K\(_{sp}\) values for NiO, PdO, PtO\(_2\) and Cu\(_2\)O to be -log 1.46, -log 1.95, -log 1.49, -log 1.56 respectively. They also found heavier metal oxides were more soluble than lighter ones in these melts [133].

In 1979, Picard et al investigated the K\(_{sp}\) values for Al\(_2\)O\(_3\) in molten LiCl-KCl, at 470\(^\circ\)C, by potentiometry, under CO\(_2\). The technique involved a reference electrode and an ISE immersed in the molten salt. The ISE was constructed from Y\(_2\)O\(_3\)-ZrO\(_2\) (YSZ) and contained a silver wire, immersed in molten LiCl-KCl and Ag\(_2\)O, and the reference electrode contained a silver wire immersed in molten LiCl-KCl and Ag\(_2\)O. The experimental procedure involved the addition of Na\(_2\)CO\(_3\) to the molten salt, containing metal ions. They found a titration curve displaying two equivalence points at 1 and 1.5, which was attributed to the formation of AlOCl\(^2-\) and AlCl\(^4-\) complex ions. The K\(_{sp}\) values of Al\(_2\)O\(_3\) were reported to be -log 27.4 and K\(_f\) values for the AlO\(^+\) complex ion at -log 10.7, and -log 6 respectively [134].

In 1986, Martinot and Fuger investigated the K\(_{sp}\) values for thorium oxide (ThO\(_2\)), protactinium dioxide (PaO\(_2\)), uranium dioxide (UO\(_2\)), neptunium dioxide (NpO\(_2\)), uranium(IV) oxide (UO\(_3\)) and plutonium(III) oxide (PuO\(_2\)) in molten LiCl-KCl, at 500\(^\circ\)C, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from calcia-stabilized zirconia (CaO-ZrO\(_2\)), which contained a silver wire immersed in molten AgCl, Li\(_2\)O and molten LiCl-KCl and the reference electrode contained a silver wire immersed in molten AgCl and molten LiCl-KCl. The experimental procedure involved the addition of Na\(_2\)CO\(_3\) to the molten salt, containing thorium chloride (ThCl\(_2\)), protactinium chloride (PaCl\(_2\)), uranium chloride (UCl\(_2\)), neptunium chloride (NpCl\(_2\)) and plutonium chloride (PuCl\(_2\)). They found a titration curve displaying one equivalence point, attributed to the formation of ThO\(_2\), PaO\(_2\), UO\(_2\), NpO\(_2\), UO\(_3\) and PuO\(_2\). The K\(_{sp}\) values for ThO\(_2\), PaO\(_2\), UO\(_2\), NpO\(_2\), UO\(_3\) and PuO\(_2\) were reported to be -log 13.3, -log 15.2, -log 14.0, log 5.1, -log 7.12 and -log 25.7 respectively [135].
In 1994, Rouault-Rogeze et al investigated the $K_{sp}$ values of ZnO in molten LiCl-KCl, at 450°C, by potentiometry and electrolysis, under $N_2$. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, and contained a silver wire, immersed in molten AgCl, Ag$_2$O and molten LiCl-KCl, and the reference electrode contained a silver wire immersed in molten AgCl and molten LiCl-KCl. The electrolysis arrangement involved a tungsten wire immersed in the molten salt, serving as an anode, and a tungsten wire in a Pyrex tube, containing molten zinc, Na$_2$CO$_3$ and molten LiCl-KCl, serving as a cathode. The experimental procedure involved the addition of Na$_2$CO$_3$ to the molten salt; however this was disturbed by the slow reaction kinetics of carbonate decomposition, therefore they precipitated ZnO by the anodic oxidation of zinc chloride (ZnCl$_2$), using electrolysis, under CO$_2$. The $K_{sp}$ values for ZnO were reported to be -log 5.6 [136].

In 1999, Cherginets investigated the $K_{sp}$ values of CoO, MgO and NiO in molten LiCl-KCl, at 700°C using potentiometry, under $N_2$. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, and contained a platinum wire immersed in molten Ag$_2$O and molten LiCl-KCl, under O$_2$, and the reference electrode contained a platinum wire, immersed in molten AgCl, and molten LiCl-KCl. The molten salt was initially melted under $N_2$ saturated with CCl$_4$ which was followed by the addition of argon and ammonium chloride (NH$_4$Cl) to remove any residual $O^{2-}$ impurities. A calibration curve was then realized by additions of Na$_2$CO$_3$ to the molten salt, which displayed an inflection point at -log 2.3, attributed to the formation of $O^{2-}$ ions on the platinum wire surface (in the ISE). This was followed by the addition of Na$_2$CO$_3$ to the molten salt containing MgCl$_2$, NiCl$_2$ or CoCl$_2$. They found a titration curve displaying one equivalence point attributed to the formation of CoO, MgO and NiO. The titration curve for CoO displayed an appreciable non-saturated solution region, suggesting that CoO was soluble. The titration curve for MgO and NiO didn’t include a non-saturated solution region, suggesting these were insoluble in the molten salt. The $K_{sp}$ values for MgO, CoO and NiO were reported to be -log 4.43, -log 5.34, and -log 5.87 respectively and the $K_d$ value for CoO at -log 1.18 [137].

In 2001, Caravaca et al investigated the $K_{sp}$ values of cerium oxychloride (CeOCl), lanthanum oxychloride (LaOCl), praseodymium oxychloride (PrOCl) and yttrium(III)
oxide (Y$_2$O$_3$) in molten LiCl-KCl, at 450ºC, by potentiometry, under argon. The technique involved an ISE and a reference electrode immersed in the molten salt. The ISE was constructed from YSZ, and contained a silver wire, Ag$_2$O and AgCl with molten CaCl$_2$-NaCl or molten LiCl-KCl, and the reference electrode contained molten AgCl with molten LiCl-KCl. Initially the salt was prepared under vacuum, to remove residual O$^{2-}$ ion impurities. Then a calibration curve was realized by additions of Na$_2$CO$_3$ and BaO, which demonstrated good Nernstian behaviour. The experimental procedure involved the addition of Na$_2$CO$_3$ or BaO to the molten salt containing CeCl$_3$, LaCl$_3$, praseodymium(III) chloride (PrCl$_3$), yttrium(III) chloride (YCl$_3$). They found the titration curves displayed one equivalence point at -log 1 and -log 1.5 corresponding to the formation of oxychloride compounds and Y$_2$O$_3$ respectively. The K$_{sp}$ values for CeOCl, LaOCl, PrOCl and Y$_2$O$_3$ were reported to be -log 7.45, -log 7, -log 7.45 and -log 19.9 respectively [138].

In 2003, Casterillego et al investigated the K$_{sp}$ values of LaOCl, CeOCl, neodymium oxychloride (NdOCl) and PrOCl in molten LiCl-KCl, at 450ºC, by potentiometry, under argon. The technique involved an ISE and a reference electrode immersed in the molten salt. The ISE was constructed from YSZ containing a silver wire immersed in molten AgCl, Na$_2$CO$_3$ and molten LiCl-KCl, and the reference electrode contained a silver wire, immersed in molten AgCl and molten LiCl-KCl. Initially the molten salt was calibrated by additions of Na$_2$CO$_3$ or BaO, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of Na$_2$CO$_3$ or BaO to the molten salt. They found titration curves which demonstrated an equivalence point at -log 1, corresponding to the formation of oxychloride species. The K$_{sp}$ values for CeOCl, LaOCl, NdOCl and PrOCl were reported to be -log 7.45, -log 7, -log 7.45 and -log 7.67 respectively [139].

In 2004, Cherginet al investigated the K$_{sp}$ values of MgO in molten LiCl-KCl, between 600-800ºC, under argon and CO$_2$, at 0.1 MPa. The technique involved an ISE and a reference electrode immersed in the molten salt. The ISE was constructed from YSZ, containing a platinum wire under O$_2$, and the reference electrode, contained a silver wire, immersed in molten AgCl in molten LiCl-KCl. Initially the molten salt was treated with CCl$_4$ and argon, followed by NH$_4$Cl to remove residual O$^{2-}$ ion impurities. Then a calibration curve was realized by additions of potassium hydroxide
(KOH), which displayed an inflection point at -log 2, corresponding to the formation of O$_2^{2-}$ ions in the ISE. The experimental procedure involved the addition of MgO to the molten salt up to the saturation limit. The K$_{sp}$ values for MgO were reported to be -log 6.99 at 600ºC, -log 5.87 at 700ºC and -log 5.41 at 800ºC [140].

In 2007, Cordoba and Caravaca investigated the K$_{sp}$ values for SmOCl in molten LiCl-KCl, at 450ºC, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, containing a silver wire, molten AgCl, BaO, Li$_2$CO$_3$ or Na$_2$CO$_3$, and molten LiCl-KCl and the reference electrode contained a silver wire immersed in molten AgCl and molten LiCl-KCl. The salt was prepared by bubbling HCl and argon, to remove residual O$_2^{-}$ ion impurities. Initially the molten salt was calibrated by additions of Na$_2$CO$_3$, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of Li$_2$CO$_3$, Na$_2$CO$_3$ and BaO to the molten salt containing samarium(III) chloride (SmCl$_3$). The titration curve displayed one equivalence point at -log 1, corresponding to the formation SmOCl. The K$_{sp}$ values for SmOCl were reported to be ~-log 7.54. In addition, the K$_{sp}$ values for SmOCl and Sm$_2$O$_3$ were calculated from thermodynamic data, at -log 7.76 and -15.93 respectively, at the same experimental temperature [141].

In the same year, Kado et al investigated the solubility of Li$_2$O in molten LiCl-KCl, between 400-650ºC, by CV. The technique involved a three electrode arrangement; an anode, a cathode and a reference electrode immersed in the molten salt. The anode and cathode electrodes were constructed from glassy carbon and the reference electrode contained a silver wire immersed in molten AgCl and molten LiCl-KCl. The experimental procedure involved the addition of Li$_2$O to the molten salt at 58.5, 75, 90 and 100 mol% LiCl. They found the current of the electrochemical cell increased linearly as the amount of Li$_2$O increased, up to the saturation limit. The CV curves demonstrated the solubility of Li$_2$O at 1.12 mol%, 0.708 mol%, 1.14 mol% and 1.32 mol% at 400ºC, 450ºC, 500ºC and 550ºC respectively and the highest solubility of Li$_2$O was reported to be 12.0 mol% at 650ºC [142].

In 2012, Osipenko et al investigated the K$_{sp}$ values of CmOCl and curium(III) oxide (Cm$_2$O$_3$) in molten LiCl-KCl, at 450ºC, by potentiometry, under argon. The ISE
electrode was constructed from YSZ, containing a platinum wire under O₂ and the reference electrode, containing a silver wire immersed in molten AgCl and molten LiCl-KCl. Initially the salt was prepared under vacuum, and melted under argon to remove residual O²⁻ ion impurities. The experimental procedure involved the addition of Na₂CO₃ to the molten salt containing curium chloride (CuCl₃). The titration curve displayed three equivalence points corresponding to the formation of CmOCl, CmO⁺ and Cm₂O₃. The Kₘₚ and Kₙ values for CmOCl, the CmO⁺ complex ion and Cm₂O₃ were reported to be -log 2.5, -log 7.5 and -log 15.5 at 450°C, -log 2.4, -log 5.7 and -log 12.7 at 550°C and -log 0.8, -log 5.2 and -log 12.5 at 650°C respectively [143]. A complete list of Kₘₚ values for various oxides in molten LiCl-KCl are reported in table 2.3.
<table>
<thead>
<tr>
<th>Name</th>
<th>Compound</th>
<th>-(\log K_{sp})</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel oxide</td>
<td>NiO</td>
<td>1.46</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.87</td>
<td>700</td>
</tr>
<tr>
<td>Palladium oxide</td>
<td>PdO</td>
<td>1.95</td>
<td>450</td>
</tr>
<tr>
<td>Platinum oxide</td>
<td>PtO₂</td>
<td>1.49</td>
<td>450</td>
</tr>
<tr>
<td>Copper(II) oxide</td>
<td>Cu₂O</td>
<td>1.56</td>
<td>400</td>
</tr>
<tr>
<td>Aluminium(III) oxide</td>
<td>Al₂O₃</td>
<td>27.4</td>
<td>470</td>
</tr>
<tr>
<td>Thorium(IV) oxide</td>
<td>ThO₂</td>
<td>13.3</td>
<td>500</td>
</tr>
<tr>
<td>Protactinium diox</td>
<td>PaO₂</td>
<td>15.2</td>
<td>500</td>
</tr>
<tr>
<td>Uranium dioxide</td>
<td>UO₂</td>
<td>14.0</td>
<td>500</td>
</tr>
<tr>
<td>Neptunium dioxide</td>
<td>NpO₂</td>
<td>5.1</td>
<td>500</td>
</tr>
<tr>
<td>Uranium(IV) oxide</td>
<td>UO₃</td>
<td>7.12</td>
<td>500</td>
</tr>
<tr>
<td>Plutonium(IV) oxide</td>
<td>Pu₃O₅</td>
<td>25.7</td>
<td>500</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>ZnO</td>
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<td>450</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>MgO</td>
<td>4.43</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.99</td>
<td>600</td>
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<td></td>
<td></td>
<td>5.41</td>
<td>800</td>
</tr>
<tr>
<td>Cobalt oxide</td>
<td>CoO</td>
<td>5.34</td>
<td>700</td>
</tr>
<tr>
<td>Cerium oxychloride</td>
<td>CeOCl</td>
<td>7.45</td>
<td>450</td>
</tr>
<tr>
<td>Lanthanum oxychloride</td>
<td>LaOCl</td>
<td>7.00</td>
<td>450</td>
</tr>
<tr>
<td>Protactinium oxychloride</td>
<td>PrOCl</td>
<td>7.45</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.67</td>
<td>450</td>
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<tr>
<td>Yttrium(III) oxide</td>
<td>Y₂O₃</td>
<td>19.9</td>
<td>19.9</td>
</tr>
<tr>
<td>Lithium oxide</td>
<td>Li₂O</td>
<td><strong>1.12 (wt%)</strong></td>
<td>400</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>0.108 (wt%)</strong></td>
<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>1.14 (wt%)</strong></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>1.32 (wt%)</strong></td>
<td>550</td>
</tr>
<tr>
<td>Samarium oxychloride</td>
<td>SmOCl</td>
<td>7.54</td>
<td>450</td>
</tr>
<tr>
<td>Curium oxychloride</td>
<td>CmOCl</td>
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<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.4</td>
<td>550</td>
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<td></td>
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<td>650</td>
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<td>Cm₂O₃</td>
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<tr>
<td></td>
<td></td>
<td>12.7</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.5</td>
<td>650</td>
</tr>
<tr>
<td>Indium oxychloride</td>
<td>NdOCl</td>
<td>7.45</td>
<td>450</td>
</tr>
</tbody>
</table>

*Table 2.3: \(K_{sp}\) values of compounds in molten LiCl-KCl (produced by author) [132-143].*
2.3.3.2 Solubility products of compounds in molten NaCl, KCl and NaCl-KCl

Molten NaCl, KCl and NaCl-KCl are used as solvents for the growth of crystals, as electrolytes for molten carbonate fuel cells, and as solvents for the pyrochemical reprocessing of nuclear fuel, due to its low melting temperature (at 727°C), high electrical conductivity and high proliferation resistance over aqueous solvents [57]. These applications are dependent upon the O\(^2-\) ion activity in the molten salt therefore \(K_{sp}\) values of oxides in these melts are frequently investigated.

In 1966, Neumann and Reinhard investigated the \(K_{sp}\) values of CaO, strontium oxide (SrO) and BaO in molten NaCl-KCl, molten NaCl and molten KCl, between 727-900°C, by isothermal saturation, under argon. Initially the molten salt was dried between 160-200°C for 24 hours, to remove residual O\(^2-\) ion impurities. The experimental procedure involved the addition of CaO, SrO and BaO to the molten salt, until the saturation limit. The molten salt was then filtered using a nickel frit and analysed by complexometric titration. The \(K_{sp}\) values for CaO, SrO and BaO were reported to be -log 1.60, -log 1.77, -log 1.36 in molten NaCl, -1.77, -1.77, -log 1.75 in molten KCl and -log 1.11, -log 0.93, -log 1.08 in molten NaCl-KCl, at 900°C respectively. They also found the \(K_{sp}\) values increased in the sequence CaO > SrO > BaO, with the \(K_{sp}\) values for molten KCl-NaCl and molten KCl being similar and those for molten NaCl being higher [144].

In 1975, Combes et al investigated the \(K_{sp}\) values for CaO and NiO in molten NaCl-KCl, between 706-800°C, by potentiometry, under argon. The technique involved an ISE and a reference electrode immersed in the molten salt. The ISE was constructed from CaO-ZrO\(_2\), containing a silver wire, immersed in molten NaCl-KCl and Ag\(_2\)O, and the reference electrode, contained a nickel wire immersed in molten NaCl-KCl, and NiO. Initially, the molten salt was dehydrated at 10\(^{-2}\) Torr, between 200-500°C, to remove residual O\(^2-\) ion impurities. Then the molten salt was calibrated by additions of CaO and the potentiometric plots displayed good Nernstian behaviour. The experimental procedure then involved the addition CaO or Na\(_2\)CO\(_3\) to the molten salt, containing NiCl\(_2\) and copper chloride (CuCl\(_2\)) and the \(K_{sp}\) values for CaO and NiO were reported to be -log 14.6 at 706°C and -log 12.4 at 800°C respectively. The values
were also calculated from thermodynamic data and experimental activity coefficients from Me$^{2+}$ ions; Ag$_2$O, Cu$_2$O, ZnO, CoO, PdO, FeO, SnO, CuO, NiO, FeO, CrO and ZrO$_2$ at -log 0.8, -log 5.4, -log 8.3, -log 9.3, -log 9.6, -log 9.8, -log 10, -log 10.1, -log 11.2, -log 21.1, -log 23.1, -log 33.6 respectively [145].

In the same year, Combes et al investigated the $K_{sp}$ values of CaO in molten NaCl-KCl, between 710-820ºC, by potentiometry, under argon. The technique involved an ISE and reference electrode, immersed in the molten salt. The ISE were constructed from CaO-ZrO$_2$, containing a silver wire, with molten NaCl-KCl and Ag$_2$O and the reference electrode contained a nickel wire immersed in molten NaCl-KCl and NiO. The experimental procedure involved the addition of CaO to the molten salt, and the partial pressure of H$_2$O over the molten salt was modified to allow specific Ca$^{2+}$ ion activities to be achieved. The $K_{sp}$ values for CaO in the molten salt were reported at -log 5.4 at 710ºC, -log 5.0 at 727ºC and -4.3 at 820ºC. Then WO$_3$ was added to the molten salt after an O$^{2-}$ ion activity was imposed and a titration curve was obtained with two equivalence points at -log 0.5 and -log 0.6. This corresponded to the formation of WO$_4^{2-}$ and W$_3$O$_{10}^{2-}$ complex ions and $K_d$ values for WO$_4^{2-}$ and W$_3$O$_{10}^{2-}$ complex ions were found to be -log 10 and -log 12.7 respectively. The $K_{sp}$ values for CaO and CaWO$_4$ were also calculated from thermodynamic data at -log 7.6 and -log 3.5 respectively [146].

In 1978, Combes et al investigated the $K_{sp}$ values of cerium(III) oxide (Ce$_2$O$_3$) in molten NaCl-KCl, at 727ºC, by potentiometry, under CO$_2$ at 10$^{-2}$ atm. The technique involved a reference electrode and ISE immersed in the molten salt. The reference electrode contained a silver wire, immersed in molten NaCl-KCl and Ag$_2$O, and the ISE was constructed from CaO-ZrO$_2$, containing a nickel wire immersed in molten NaCl-KCl and NiO. Initially, the molten salt was heated to 400ºC, under vacuum and melted under HCl, CO$_2$ and argon to remove residual O$^{2-}$ ion impurities. The molten salt was then calibrated by adding Na$_2$CO$_3$ and the potentiometric curve demonstrated good Nernstian behaviour. Then the experimental procedure involved the addition of Na$_2$CO$_3$ to the molten salt, containing cerium(III) chloride (CeCl$_3$). The titration curve demonstrated two equivalence points, corresponding to the formation of Ce$_2$O$_3$ and CeO$^+$ complex ions. The $K_d$ values for CeO$^+$ complex ions and Ce$_2$O$_3$ were found to be -log 11 and -log 7.9 respectively, and the $K_{sp}$ values for Ce$_2$O$_3$ at -log 30 [147].
In 1979, Combes et al investigated the $K_{sp}$ values of MgO, CaO and BaO in molten NaCl-KCl at 727ºC, by potentiometry, under argon. The technique involved a reference electrode and ISE immersed in the molten salt. The reference electrode contained a silver wire immersed in molten NaCl-KCl and Ag$_2$O, and the ISE was constructed from CaO-ZrO$_2$, containing a nickel wire immersed in molten NaCl-KCl and NiO. The first experimental procedure involved the addition of BaO, CaO or MgO to the molten salt, and then measuring the activity of Ba$^{2+}$, Ca$^{2+}$ or Mg$^{2+}$ ions at the saturation limit. The second experimental procedure involved the addition of BaO to the molten salt, after calibration, containing MgCl$_2$. The titration curve displayed two equivalence points at -log 0.5 and -log 1, corresponding to the formation of Mg$_2$O$^{2+}$ complex ions and MgO. They also found the $K_d$ for Mg$_2$O$^{2+}$ complex ions and MgO at -log 9.35, -log 8.5 respectively and $K_{sp}$ values for BaO, CaO and MgO at -log 2.31, -log 9 and -log 5 respectively [148].

In 1981, Stern and Deanhard investigated the $K_{sp}$ values for NiO and CoO in molten NaCl, at 827ºC, by potentiometry, under O$_2$ at 0.2 atm. The technique involved a reference electrode and ISE immersed in the molten salt. The reference electrode a silver wire immersed in molten NaCl and AgCl, and the ISE, was constructed from YSZ, containing a silver wire immersed in molten NaCl, AgCl and Na$_2$O. Initially, the salt was dried at 500ºC under vacuum to remove residual O$^{2-}$ ion impurities. Then the molten salt was calibrated by additions of Na$_2$O, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of Na$_2$O to the molten salt containing NiCl$_2$ and cobalt chloride (CoCl$_2$). The titration curve demonstrated 2 equivalence points, corresponding to the formation of NiO and nickel(III) sodium oxide (NaNiO$_2$). The titration curve demonstrated 3 equivalence points, corresponding to the formation of cobalt (II, III) oxide (CO$_3$O$_4$), CoO and cobalt(III) sodium dioxide (NaCoO$_2$), showing competing equilibrium within the system. The $K_{sp}$ values for NiO and CO$_3$O$_4$ were reported to be $2.18 \times 10^{-12}$ and $9.0 \times 10^{-12}$ respectively (in mole fraction scale) [149].

In 1986, Martinot and Fuger investigated the $K_{sp}$ values of ThO$_2$ and UO$_2$ in molten NaCl-KCl, at 700ºC, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from CaO-ZrO$_2$ containing a silver wire, immersed in molten AgCl, Na$_2$CO$_3$ and molten NaCl-KCl.
and the reference electrode contained a silver wire immersed in molten NaCl-KCl and AgCl. The molten salt was calibrated by additions of Na₂CO₃, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of Na₂CO₃ to the molten salt, containing ThCl₂ and UCl₂. The titration curve showed one equivalence point, corresponding to the formation of ThO₂ and UO₂ respectively. The K<sub>sp</sub> values for ThO₂ and UO₂ were reported to be -log 15.5 and -log 18.0 respectively [134].

In 1991, Volovich investigated the K<sub>sp</sub> values of CaO, Li₂O and BaO in molten NaCl-KCl, between 700-800°C, by isothermal saturation, under argon. Initially the NaCl was dried between 160-200°C to remove residual O²⁻ ion impurities. The experimental procedure involved the addition of CaO to the molten salt up to the saturation limit. Then samples of the salt were analysed by complexometric titration. The K<sub>sp</sub> values for CaO, Li₂O and BaO were reported to be -log 1.84, -log 1.37, -log 0.96 respectively [150].

In the same year, Volovich investigated the K<sub>sp</sub> values of PbO in molten NaCl-KCl, at 700°C, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, with a platinum wire immersed in molten NaCl-KCl and Ag₂O, and the reference electrode contained a silver wire immersed in molten NaCl-KCl and AgCl. Initially the salt was dried, between 160-200°C to remove residual O²⁻ ion impurities. The molten salt was calibrated by additions of Na₂CO₃, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of Na₂CO₃ to the molten salt containing PbCl₂. The titration curve exhibited one equivalence point at 1, corresponding to the formation of PbO. The K<sub>sp</sub> value for PbO was reported to be -log 4.72 [129].

In the same year, Watson and Perry investigated the K<sub>sp</sub> values of ZnO in molten KCl, at 800°C, by potentiometry, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, containing and a platinum wire immersed in molten KCl and NiO and the reference electrode contained a silver wire immersed in molten AgCl and KCl. Initially the salt was prepared by bubbling through HCl to remove residual O²⁻ ion impurities. The molten salt was calibrated by additions of Na₂O, demonstrating good Nernstian behaviour.
The first experimental procedure involved additions of Na$_2$O to the molten salt containing ZnCl$_2$. The titration curve demonstrated an equivalence point at 1, corresponding to the formation of ZnO. The second experimental procedure involved the addition of ZnCl$_2$ to the molten salt, containing ZnO. The titration curve demonstrated an equivalence point at 0.5, corresponding to the formation of ZnO$_2^{2-}$ complex ions. The $K_{sp}$ values of ZnO was reported to be $2.3 \times 10^{-8}$ mol kg$^{-1}$ (-log 1.18) and the $K_f$ values for the ZnO$_2^{2-}$ complex ion was reported to be $3 \times 10^{-12}$ mol$^3$ kg$^{-3}$ [151].

In 1999, Koeller and Combes investigated the $K_{sp}$ values of SrO in molten NaCl-KCl, at 727°C, by potentiometry, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from ZrO$_2$-ZrO$_2$ containing a nickel wire, NiO and molten NaCl-KCl, and the reference electrode contained a silver wire, AgCl and molten NaCl-KCl. Initially the salt was dried under vacuum to remove residual O$^{2-}$ ion impurities. Then the molten salt was calibrated by additions of BaO, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of BaO to the molten salt containing strontium chloride (SrCl$_2$). The titration curve demonstrated an equivalence point at 1, corresponding to the formation of SrO. The $K_{sp}$ value for SrO was reported to be -log 4.2 [152].

In the same year, Barbin et al investigated the solubility of Li$_2$O in molten KCl-NaCl, between 700-800°C, by isothermal saturation, under argon. Initially the salt was dehydrated under vacuum, and treated with HCl, Cl$_2$ and helium (to remove residual O$^{2-}$ ion impurities. The experimental procedure involved the addition of a sintered Li$_2$O pellet to the molten salt. Samples of the salt was analysed at regular intervals, and the solubility of Li$_2$O determined using an alkalinity test. The solubility of Li$_2$O was reported to be -log 0.107 (in mole fraction) [153].

In 2002, Koeller and Combes investigated the $K_{sp}$ values of CaO in molten NaCl, between 827-927°C, using potentiometry, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from CaO-ZrO$_2$, containing a nickel wire, Na$_2$CO$_3$ and molten NaCl, and the reference electrode contained a nickel wire immersed in molten NaCl. Then the molten salt was
calibrated by additions of Na$_2$CO$_3$, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of CaO to the molten salt up to the saturation limit. The $K_{sp}$ values for CaO are reported to be -log 4.3 at 827°C, -log 4.1 at 877°C and -log 3.9 at 927°C [154].

In the same year, Cherginet investigated the $K_{sp}$ values of CaO in molten NaCl-KCl at 830°C, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, containing a platinum wire under O$_2$, and the reference electrode contained a platinum wire immersed in molten NaCl-KCl and AgCl. Then the molten salt was calibrated by additions of NaOH, demonstrating two linear sections with an inflection point at -log 2 corresponding to the formation of O$_{2^{2-}}$ ions. The experimental procedure involved adding CaO to the molten salt up to the saturation limit. The $K_{sp}$ values of CaO was reported to be -log 3.77, $K_d$ value at -log 2.59, amount of non-dissociated oxide at 0.066 mol kg$^{-1}$ and Ca$^{2+}$ ion activity at 0.013 mol kg$^{-1}$ [156]. A complete list of $K_{sp}$ values for various oxides in molten NaCl, KCl and NaCl-KCl are reported in table 2.4.
<table>
<thead>
<tr>
<th>Name</th>
<th>Compound</th>
<th>-log $K_{sp}$</th>
<th>Temperature (°C)</th>
<th>Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium oxide</td>
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<td>NaCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.11</td>
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<td>NaCl-KCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.77</td>
<td>900</td>
<td>KCl</td>
</tr>
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<td></td>
<td>14.6</td>
<td>706</td>
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</tr>
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<td>9</td>
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</tr>
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<td></td>
<td>$9.0 \times 10^{-12}$ (mole fraction)</td>
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<td></td>
<td>1.75</td>
<td>900</td>
<td>KCl</td>
</tr>
<tr>
<td>Cerium(III) oxide</td>
<td>Ce$_2$O$_3$</td>
<td>30</td>
<td>727</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>MgO</td>
<td>2.31</td>
<td>727</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Nickel oxide</td>
<td>NiO</td>
<td>12.4</td>
<td>827</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Thorium oxide</td>
<td>ThO$_2$</td>
<td>15.5</td>
<td>727</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Uranium oxide</td>
<td>UO$_2$</td>
<td>18</td>
<td>727</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Lithium oxide</td>
<td>Li$_2$O</td>
<td>0.107</td>
<td>727</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Lead oxide</td>
<td>PbO</td>
<td>4.72</td>
<td>700</td>
<td>NaCl-KCl</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>ZnO</td>
<td>$2.3 \times 10^8$ (mole fraction)</td>
<td>800</td>
<td>NaCl-KCl</td>
</tr>
</tbody>
</table>

Table 2.4: $K_{sp}$ values of compounds in molten NaCl-KCl, NaCl and KCl (produced by author) [144-155].
2.3.3.3 Solubility products of compounds in molten CaCl$_2$-NaCl

Molten CaCl$_2$-NaCl is used as a solvent for the pyrochemical reprocessing of nuclear fuel, due to its low eutectic point (at 504°C) [156]. This application is dependent upon the O$^{2-}$ ion activity in the molten salt, which can have a detrimental influence upon the preferred reactions therefore $K_{sp}$ values in this molten salt are frequently investigated.

In 1997, Castrillego et al investigated the $K_{sp}$ values of MgO in molten CaCl$_2$-NaCl, at 575°C, using potentiometry, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, containing a silver wire immersed in molten CaCl$_2$-NaCl and Ag$_2$O and the reference electrode contained a silver wire immersed in molten CaCl$_2$-NaCl and AgCl. Initially, the molten salt was treated under vacuum and HCl and argon to remove residual O$^{2-}$ impurities. The experimental procedure then involved the addition of Na$_2$CO$_3$ to the molten salt containing MgCl$_2$. The molten salt was calibrated with additions of Na$_2$CO$_3$, demonstrating a Nernstian response. The titration curve displayed one equivalence point corresponding to the formation of MgO. The $K_{sp}$ value for MgO was reported to be -log 5.3 [157].

In 1998, Martinez et al investigated the $K_{sp}$ values for titanium oxide (TiO) and titanium(III) oxide (Ti$_2$O$_3$) in molten CaCl$_2$-NaCl, at 550°C, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, containing a silver wire immersed in molten CaCl$_2$-NaCl, AgCl and Ag$_2$O, and the reference electrode contained a silver wire immersed in molten CaCl$_2$-NaCl and AgCl. The experimental procedure involved the addition of Na$_2$CO$_3$ to the molten salt, containing titanium tetrachloride (TiCl$_3$) or titanium dichloride (TiCl$_2$) solution. The titration curve demonstrated one equivalence point at 1 and 1.5 corresponding to the formation of TiO and Ti$_2$O$_3$. The $K_{sp}$ values for TiO and Ti$_2$O$_3$ were reported to be -log 9.01 and -log 25.7 respectively [158].

In 2002, Lambertin et al investigated the $K_{sp}$ values of Pu$_2$O$_3$ in molten CaCl$_2$-NaCl, at 550°C, by potentiometry, under argon. The technique involved an ISE and reference electrode immersed in the molten salt. The ISE was constructed from YSZ, containing a silver wire immersed in molten NaCl-CaCl$_2$, AgCl and Na$_2$CO$_3$, and the reference electrode contained a silver wire immersed in molten NaCl-CaCl$_2$ and AgCl. Initially,
the salt was fused under argon, followed by the addition of graphite powder and bubbling Cl\textsubscript{2} to remove residual O\textsuperscript{2-} ion impurities. The molten salt was then calibrated by additions of Na\textsubscript{2}CO\textsubscript{3}, demonstrating good Nernstian behaviour. The experimental procedure involved the addition of Na\textsubscript{2}CO\textsubscript{3} to the molten salt containing PuCl\textsubscript{3}. The titration curve displayed one equivalence point at 1, corresponding to the formation of Pu\textsubscript{2}O\textsubscript{3}. The K\textsubscript{sp} value for Pu\textsubscript{2}O\textsubscript{3} was reported to be -log 17.5 [159].

In 2008, Wang et al investigated the solubility of CaO in molten CaCl\textsubscript{2}-NaCl, CaCl\textsubscript{2}-KCl, CaCl\textsubscript{2}-SrCl\textsubscript{2}, CaCl\textsubscript{2}-BaCl\textsubscript{2}, CaCl\textsubscript{2}-LiCl, between 600-950ºC, by isothermal saturation. The salts were dried at between 100-200ºC to remove residual O\textsuperscript{2-} ion impurities. The experimental procedure involved the addition of CaO to the molten salt and then removing samples at regular intervals. These samples were analysed by NaOH solution and then titrated with dibutyl orthophthalate, NaOH, and HCl solution. They found the K\textsubscript{sp} values for CaO to be at 15 wt% (CaCl\textsubscript{2} at 877ºC), 5 wt% (CaCl\textsubscript{2}-NaCl at 727ºC), 4 wt% (CaCl\textsubscript{2}-KCl at 877ºC), 6 wt% at (CaCl\textsubscript{2}-SrCl\textsubscript{2} at 877ºC), 6 wt% (CaCl\textsubscript{2}-BaCl\textsubscript{2} at 877ºC) and 7 wt% (CaCl\textsubscript{2}-LiCl at 627ºC) [160]. A complete list of K\textsubscript{sp} values for various oxides in molten CaCl\textsubscript{2}-NaCl are reported in table 2.5.

<table>
<thead>
<tr>
<th>Name</th>
<th>Compound</th>
<th>-log K\textsubscript{sp}</th>
<th>Temperature (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium oxide</td>
<td>MgO</td>
<td>5.3</td>
<td>575</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>CaO</td>
<td>5 (wt%)</td>
<td>600-950</td>
</tr>
<tr>
<td>Titanium oxide</td>
<td>TiO</td>
<td>9.01</td>
<td>550</td>
</tr>
<tr>
<td>Titanium(III) oxide</td>
<td>Ti\textsubscript{2}O\textsubscript{3}</td>
<td>25.7</td>
<td>550</td>
</tr>
<tr>
<td>Plutonium(III) oxide</td>
<td>Pu\textsubscript{2}O\textsubscript{3}</td>
<td>17.5</td>
<td>550</td>
</tr>
</tbody>
</table>

*Table 2.5: K\textsubscript{sp} values of compounds in molten CaCl\textsubscript{2}-NaCl (produced by author) [157-160].*
2.3 Molten salt synthesis of compounds

MSS of compounds involve mixing reactant(s) with an excess of salt, in a crucible, under a modified atmosphere or under air. The crucibles are made from either alumina ($\text{Al}_2\text{O}_3$), zirconia ($\text{ZrO}_2$) or $\text{SiO}_2$, depending upon the selection of the molten salt, to avoid any interaction with the container materials [50] [161]. The crucible is then heated in a furnace above the melting point of the salt, where the reactants dissolve and react with in solution. During this process, the salt behaves as a solvent and/or as a reactant and upon completion, the molten salt is cooled and washed with $\text{H}_2\text{O}$, alcohol, or mechanically separated to obtain the final product [50]. When using hydroscopic salts (such as nitrates), the salt is pre-treated (such as drying under vacuum) to eliminate any $\text{H}_2\text{O}$ attached to the salt [215]. The product is then analysed using thermo gravimetric analysis (TGA), XRD, infrared (IR) spectroscopy, gas chromatography (GC), or transmission electron microscopy (TEM) [161-188].

There have been many investigations into the MSS of compounds in molten chlorides, nitrates and fluorides [161-188]. The scale of materials synthesised are extensive therefore the author has selected the compounds; $\text{ZrO}_2$, $\text{Al}_2\text{O}_3$, and titanium dioxide ($\text{TiO}_2$) and previous studies for the MSS of cement compounds. These are examples of oxides and silicates due to the assimilation of the $\text{O}^{2-}$ and $\text{Si}^{4+}$ ions into the crystal structure, similar to the cementitious compounds being synthesised.

2.3.1 Molten salt synthesis of $\text{ZrO}_2$

$\text{ZrO}_2$ is used in gas sensors, fuel cells, coatings and catalytic agents, advanced metal oxide semiconductors (MOS) and dynamic random-access memory (DRAM) devices due to its wide band gap and high dielectric constant ($\varepsilon \sim 25$) [161]. It also exhibits several polymorphic transitions including a monoclinic polymorph (m-$\text{ZrO}_2$), below 1170°C, a tetragonal polymorph (t-$\text{ZrO}_2$), between 1170-2370°C, and a cubic polymorph (c-$\text{ZrO}_2$) between 2370-2706°C [162]. This makes the synthesis of $\text{ZrO}_2$ complicated and doping with additives is required to stabilize the phases, making the MSS of $\text{ZrO}_2$ attractive to many scientists/technologists.
The first authors to produce crystals of ZrO$_2$ in molten salts were Kerridge and Rey, in 1975, using thermo gravimetric analysis (TGA), XRD, infrared spectroscopy (IR) and gas chromatography (GC). They produced crystals of m-ZrO$_2$ by reacting zirconium(IV) sulphate (Zr(SO$_4$)$_2$) in molten LiNO$_3$-KNO$_3$ at ~200ºC. They also increased the basicity of the molten salt, by adding sodium peroxide (Na$_2$O$_2$), sodium oxide (Na$_2$O) or sodium hydroxide (NaOH), which was found to reduce reaction temperatures, to 150ºC. In all cases, they found a soluble intermediate forming, before the formation of m-ZrO$_2$, deduced to be zirconium nitrate (Zr(NO$_3$)$_4$). They also found m-ZrO$_2$ depleted slowly after being formed, probably due to the formation of a zirconate, which was stronger as the basicity of the molten salt increased [163].

In 1994, Raihani et al investigated the MSS of ZrO$_2$ using TGA, XRD and transmission electron microscopy (TEM), by reacting Zr(SO$_4$)$_2$ in molten sodium nitrate (NaNO$_3$), LiNO$_3$-KNO$_3$, NaNO$_3$-KNO$_3$, NaNO$_2$-KNO$_2$, between 300-500ºC. They found that multi-stage reactions occurred in molten NaNO$_3$ at 500ºC, which didn’t go to completion. They also increased the molten salt basicity, by adding NaCl and Na$_2$CO$_3$. In both cases, the reactions went to completion but for different reasons. In molten NaCl-NaNO$_3$, this was probably due to the complexing effect of Cl$^-$ ions. In molten Na$_2$CO$_3$-NaNO$_3$, this was probably due to the formation of sodium zirconate (Na$_2$ZrO$_3$), forming at a lower reaction temperature (at ~440ºC). Upon adding KNO$_2$ to molten LiNO$_3$-KNO$_3$, both m-ZrO$_2$ and t-ZrO$_2$ crystals were formed by multi-stage reactions. When using molten NaNO$_2$-KNO$_2$, only t-ZrO$_2$ crystals were formed a single reaction occurred (below 200ºC). The t-ZrO$_2$ crystals obtained at 450ºC in molten NaNO$_2$-KNO$_2$ were agglomerates; with spherical grains ~6 nm in diameter and a specific surface area greater than 150 m$^2$ g. The t-ZrO$_2$ crystals obtained at 300ºC in molten NaNO$_2$-KNO$_2$ were agglomerates with smaller grains ~3 nm in diameter and a specific surface area of ~250 m$^2$ g [164].

In 1995, Afanasiev and Geantet investigated the MSS of ZrO$_2$ using XRD and TEM, by reacting zirconyl(IV) chloride, octahydrate (ZrOCl$_2$.8H$_2$O) or zirconyl nitrate dihydrate (ZrO(NO$_3$)$_2$.2H$_2$O) in molten NaNO$_3$-KNO$_3$, LiNO$_3$, NaNO$_3$ or molten potassium nitrate (KNO$_3$), between 300-500ºC. They found poor or amorphous crystalline phases were produced (at ~370ºC) and, crystalline phases of m-ZrO$_2$ and t-ZrO$_2$ were produced (between 400-500ºC). They also found the surface area of the
crystals varied according to the reaction temperatures and molten salt, which ranged between 50-220m² g⁻¹. The crystallite sizes of the final products also ranged for the different salts and temperatures; between 300-370°C, (from highest to lowest) was LiNO₃ > NaNO₃ > KNO₃, between 400-430°C, was NaNO₃ > LiNO₃ > KNO₃, and between 430-500°C, was LiNO₃ > NaNO₃ > KNO₃. Above 430°C, the crystallite sizes were small in all melts, probably due to the increasing growth of nuclei and division of crystals. In all cases, the product purities were high as the residual element activity was low, at ~0.2 wt% [165].

In the same year, Du and Inman investigated the MSS of ZrO₂, using XRD, TG, DTG and DTA, by reacting Zr(SO₄)₂ in molten NaNO₃, LiNO₃-KNO₃, NaNO₃-KNO₃ and NaNO₂-KNO₂, between 170-460°C. They found a single reaction occurred in molten NaNO₂-KNO₂, between 170-250°C, and multiple reactions occurred in molten NaNO₃-KNO₃, LiNO₃-KNO₃ and molten NaNO₃, between 200-460°C. In general, m-ZrO₂ and t-ZrO₂ crystals were produced in the nitrate melts, and only t-ZrO₂ crystals in the nitrite melt. Also in the nitrate melts, the crystallite sizes were between 1-20 nm and lower than 10 nm in the nitrite melts, probably due to the increase of reactivity of the melt. They also found the reaction in the nitrite melt to be second order with activation energy of ~183 kJ mol⁻¹ [166].

In 1996, Du and Inman investigated the MSS of ZrO₂, using TGA and XRD, by reacting α-Zr(SO₄)₂ or β-Zr(SO₄)₂ in molten NaNO₂-KNO₂, LiNO₃-KNO₃ and NaNO₃-KNO₃, between 300-450°C. They found t-ZrO₂ crystals were produced in molten NaNO₂-KNO₂ below 270°C, producing crystallite sizes of ~3.8 nm. Upon increasing the temperature to 450°C, the crystallite sizes became smaller (at ~3.5 nm) and reducing the temperature to 320°C, caused the crystallite sizes to become larger (at ~4.6 nm), probably due to faster reaction times. In the LiNO₃-KNO₃ binary system and molten NaNO₃-KNO₃, both t-ZrO₂ and m-ZrO₂ crystals were produced with crystallite sizes between 10-20 nm, probably due to multiple or side reactions. In all cases, an increase in temperature (higher than 400°C) favoured the formation of crystalline phases, and reducing the temperature (to ~350°C) favoured non-crystalline or amorphous phases. This was probably caused by a slow reaction rate, leading to fewer nuclei, but larger crystal sizes. In all cases, the product purities were high as the residual element activity was low, at ~1.5 wt% [167].
In the same year, Du et al investigated the MSS of ZrO$_2$, using XRD and TEM, by reacting Zr(SO$_4$)$_2$ in molten NaNO$_3$-KNO$_3$, between 200-450°C. They found that m-ZrO$_2$ and t-ZrO$_2$ crystals were produced via two reactions in molten NaNO$_3$-KNO$_3$, at ~200°C. Also by increasing the melt basicity, through the addition of Na$_2$O$_2$ and Na$_2$CO$_3$ and using molten NaNO$_2$-KNO$_2$, the reaction temperature was lowered to ~130°C. This was probably caused by the increase of O$^{2-}$ ions in the molten salt, causing multiple or side reactions to take place. A direct relationship was found between the proportion of the t-ZrO$_2$ phase in the final product, and basicity of the molten salt (reaching 100% at 20 mol% of Na$_2$O$_2$, 20 mol% of Na$_2$CO$_3$, and 40% mol of NaNO$_2$-KNO$_2$). The crystallite sizes were also found to decrease according to the same relationship [168].

In 1997, Afanasiev investigated the MSS of ZrO$_2$, using XRD, atomic emission spectroscopy (AES) and N$_2$ gas adsorption, by reacting ZrOCl$_2$.8H$_2$O in molten NaNO$_3$-KNO$_3$, at 500°C. They also investigated the effect of adding fluoride ions to the molten salt, by adding ammonium hydrogen fluoride (NH$_4$HF$_2$). They found that NH$_4$HF$_2$ promoted the formation of m-ZrO$_2$ crystals, with mean radiuses, surface areas and pore volumes increasing up to 0.05 wt% NH$_4$HF$_2$ and decreasing up to 1 wt% NH$_4$HF$_2$. The amount of residual Na$^+$ and F$^-$ ions in the final product were also low and irregular, between 0.1-0.2 wt%. This was probably caused by F$^-$ ions becoming partially bound to the final precipitate [169].

In 2002, Maroto et al investigated the MSS of ZrO$_2$, using XRD DTA, TGA and SEM, by reacting ZrOCl$_2$.8H$_2$O or zirconium dichloride (ZrCl$_2$) in molten lithium nitrate (LiNO$_3$) or NaNO$_3$, at 450°C. They found that in molten LiNO$_3$ and NaNO$_3$, ZrOCl$_2$.8H$_2$O promoted the formation of the m-ZrO$_2$ crystals with t-ZrO$_2$ only present lower than 10 wt%. In molten LiNO$_3$ and NaNO$_3$, ZrOCl$_2$.8H$_2$O promoted the formation of the t-ZrO$_2$ crystals, with only the t-ZrO$_2$ crystals present lower than 70 wt%. Also, in molten LiNO$_3$ and NaNO$_3$, ZrOCl$_2$.8H$_2$O promoted larger crystallite sizes of m-ZrO$_2$, of ~10 nm and ~8 nm respectively, and t-ZrO$_2$, of ~13 nm and ~8 nm respectively. When using ZrCl$_2$ in the same melts, crystallite sizes of t-ZrO$_2$ and m-ZrO$_2$ were much larger and more dispersed, between 12-20 nm and 8-16 nm respectively. The crystal surface areas were also larger when using ZrOCl$_2$.8H$_2$O, between 104-204 m$^2$.g$^{-1}$ than using ZrCl$_2$, between 63-91 m$^2$.g$^{-1}$. In all cases, the
product purities were high as the residual element activity was low, between 0.3-3.4 wt% [170].

The MSS of ZrO₂ are not limited to nitrate and nitrite melts. In 1982, Finch and Belcher investigated the MSS of m-ZrO₂ using atomic emission spectroscopy (AES), by passing H₂O through molten LiF-NaF, between 650-800°C and adding zirconium fluoride (ZrF₄). The final product formed crystallite sizes up to ~3 mm, with an etched appearance, probably caused by the low solubility of ZrO₂ in the molten salt. The impurity levels of the residual elements were also low, with the highest element detected being nickel (at 0.5 wt%) [171].

2.3.2 Molten salt synthesis of Al₂O₃

Al₂O₃ has been used as a catalyst, catalyst carrier and adsorbent, due to its high catalytic activity and high surface area [50]. In addition, its main mineral form, bauxite, is used as a reactant in aluminium smelting [57]. However the synthesis of Al₂O₃ is complicated, due to its many metastable polymorphs (γ, η, κ, θ, α, τ, δ, ε, χ), besides its main stable alpha-alumina (α-Al₂O₃) form. These polymorphs are dependent upon the choice of starting materials and conditions. The most common method of producing Al₂O₃ is by precipitation or sol-gel methods, however more recently, MSS has proven to be successful route [172-178].

The first MSS study of Al₂O₃ was by Kerridge and Shakir in 1990, where they investigated the MSS of Al₂O₃ by reacting aluminium(III) chloride (AlCl₃) or aluminium sulphate (Al₂(SO₄)₃) in molten LiNO₃-KNO₃, between 140-450°C. When using AlCl₃, a yellow suspension initially formed, at 200°C, which led to the formation of α-Al₂O₃, and evolution of NO₂ and O₂. When using Al₂(SO₄)₃ at 320°C, the reactants were incompletely soluble, with evidence of a yellow-white suspension, forming γ-Al₂O₃ along with the evolution of NO₂ and O₂ [172].

In 1996, Du and Inman investigated the MSS of Al₂O₃, using XRD, atomic adsorption spectroscopy (AAS) and TEM, by reacting Al₂(SO₄)₃ or AlCl₃ in molten NaNO₃ the NaN₃-KNO₃ binary system, molten LiNO₃-KNO₃, and the NaN₂O₂-KNO₂ binary system at ~400°C. They also investigated the effects of increasing the basicity of the molten salt, by adding Na₂O₂ and Na₂CO₃. They found that in molten NaNO₂-KNO₂,
reaction temperatures were lower than molten nitrates. Also when using AlCl$_3$ in molten NaNO$_2$-KNO$_2$, reaction temperatures were lower at $\sim$160$^\circ$C, than using Al$_2$(SO$_4$)$_3$, at $\sim$210$^\circ$C. This probably occurred due to the rise of O$^{2-}$ ions in the salt, accelerating the reaction between Al$^{3+}$ and O$^{2-}$ ions to form Al$_2$O$_3$. In all cases, fine or poorly crystallite powders of $\alpha$-Al$_2$O$_3$ were produced. Also, when using AlCl$_3$ in molten NaNO$_2$-KNO$_2$, the crystallite sizes were below 10 nm, in comparison to when using Al$_2$(SO$_4$)$_3$, causing crystallite between 1-2 nm. The total impurity levels of the elements; sodium and potassium were also low (at $\sim$0.5 wt%) indicating a high product purity [173].

In 1998, Hashimoto and Yamaguchi investigated the MSS of Al$_2$O$_3$, using SEM, XRD, DTA and TG, by reacting Al$_2$(SO$_4$)$_3$ in molten potassium sulphate (K$_2$SO$_4$), between 1000-1300$^\circ$C. The final product was washed with hydrochloric acid (HCl), between 70-80$^\circ$C, to produce porous aggregations of $\alpha$-Al$_2$O$_3$ platelets, with crystallite sizes of $\sim$10 µm. They found the surface area of the crystals reached a maximum of 5.2 m$^2$ g$^{-1}$ at 1000$^\circ$C, and minimum of 0.7 m$^2$ g$^{-1}$ at 1100$^\circ$C. They also found increasing the amount of K$_2$SO$_4$, increased the Al$_2$O$_3$ crystallite sizes [174].

In 1999, Hashimoto and Yamaguchi investigated the MSS of Al$_2$O$_3$, using SEM, XRD, DTA and TG, by reacting Al$_2$(SO$_4$)$_3$ or $\gamma$-Al$_2$O$_3$ in molten sodium sulphate (Na$_2$SO$_4$) at 1100$^\circ$C. The final product was then washed with HCl, between 70-80$^\circ$C, to produce porous aggregations of $\alpha$-Al$_2$O$_3$ platelets, with crystallite sizes of $\sim$5 µm. They found that increasing the amount of Na$_2$SO$_4$, caused hexagonal $\alpha$-Al$_2$O$_3$ platelets to form, which increased in size up to 120 µm. They also found when using $\gamma$-Al$_2$O$_3$, platelets of $\alpha$-Al$_2$O$_3$ were produced with average diameters of 3.7 µm and thickness of 0.3 µm. Upon increasing the amount of Na$_2$SO$_4$, hexagonal $\alpha$-Al$_2$O$_3$ platelets with crystallite sizes of 5 µm were produced [175].

In 2008, Li-Hui et al investigated the MSS of Al$_2$O$_3$, using SEM and XRD, by reacting aluminium hydroxide (Al(OH)$_3$), amorphous Al$_2$O$_3$ or $\alpha$-Al$_2$O$_3$ in the NaCl-KCl binary system, between 900-1000$^\circ$C. They found when using Al(OH)$_3$, both $\gamma$-Al$_2$O$_3$ and $\kappa$-Al$_2$O$_3$ platelets were produced, at 900$^\circ$C and only $\alpha$-Al$_2$O$_3$, at 1100$^\circ$C. The surface area of the platelets decreased at higher temperatures, from 62 m$^2$ g$^{-1}$ at 900$^\circ$C, to 16 m$^2$ g$^{-1}$ at 1100$^\circ$C. When amorphous $\alpha$-Al$_2$O$_3$ was used, only $\alpha$-Al$_2$O$_3$
platelets were produced, between 900-1100°C. There was no significant difference, between increasing temperature and the surface area of the platelets, shown by sizes of 1.7 m² g⁻¹ at 900°C, and 1.6 m² g⁻¹ at 1100°C. When using molten NaCl-KCl and amorphous Al₂O₃ crystals as reactants, the formation of α-Al₂O₃ crystals was favoured, probably because the salt would remain inside the crystal, increasing the interfacial area [176].

In 2011, Li-Hui and Huang investigated the MSS of Al₂O₃, using SEM and XRD, by reacting aluminium sulphate octadecahydrate ((Al₂(SO₄)₃.18H₂O)) in molten Na₂SO₄-K₂SO₄ or NaCl-KCl, between 1100-1300°C. They also investigated the effect of using Na₂CO₃, trisodium phosphate dodecahydrate (Na₃PO₄.12H₂O), titanium(IV) oxysulfate (TiOSO₄) and α-Al₂O₃ as additives. They found most α-Al₂O₃ platelets were hexagonal, with some overlapping and upon increasing the amount of salt, caused their diameters and number of crystals to increase. This was probably because more space was available inside the molten salt, allowing a higher diffusivity of the reactants. Upon the addition of Na₃PO₄.12H₂O, α-Al₂O₃ platelets of irregular shapes were obtained whilst the addition of TiOSO₄ allowed thick α-Al₂O₃ particles of hexagonal shapes to be produced. When both Na₃PO₄.12H₂O and titanium(IV) oxysulfate (TiOSO₄) were used, thin α-Al₂O₃ platelets of discal shapes would form. The addition of α-Al₂O₃ increased the size of α-Al₂O₃ platelets, but caused overlapping and abnormal crystal growth [177].

In 2011, Li-Hui et al investigated the MSS of Al₂O₃, using SEM and XRD, by reacting NaAlO₂ in molten Na₂SO₄-K₂SO₄ and molten NaCl-KCl, between 900-1400°C. They also investigated the effect of using TiOSO₄, Na₃PO₄.12H₂O and α-Al₂O₃ as additives. They found as the temperature increased (up to 1200°C), and amount of salt increased, the size distribution of α-Al₂O₃ platelets also increased, with minimal overlapping. They also found in molten Na₂SO₄-K₂SO₄ at 1200°C, platelets with diameters of 7.5 µm were produced and platelets with diameters of 5.8 µm in molten NaCl-KCl. Upon the addition of α-Al₂O₃, the diameter of platelets decreased in both molten Na₂SO₄-K₂SO₄ and molten NaCl-KCl, to 5.8 µm and 1.5 µm respectively. When both Na₃PO₄.12H₂O and TiOSO₄ were added, thinner platelets of discal shapes were obtained [178].
2.3.3 Molten salt synthesis of TiO$_2$

TiO$_2$ has been used in environmental remediation, solar cells, lithium ion batteries, gas sensors, photonic crystals and self cleaning coatings, due to its chemical stability, environmental friendliness and low cost [50]. The production of TiO$_2$ is complicated due to its several polymorphs; including rutile, antase (which is metastable) and brookite phases. In addition, up to five polymorphs also exist at high pressures [50]. TiO$_2$ is currently produced by flame aerosol synthesis, hydrothermal synthesis, sol-gel synthesis, and more recently, MSS has proven to be successful route [179-184].

One of the first MSS studies of TiO$_2$ was by Kerridge and Rey, in 1977 using TGA, where they produced antase crystals of TiO$_2$ and other titanates by reacting potassium(IV) hexafluorotitanate ($K_2TiF_6$) in molten LiNO$_3$-KNO$_3$, between 130-320ºC. They also investigated the effects of increasing the basicity of the salt, by adding Na$_2$O$_2$, Na$_2$O or NaOH. They found reactions in molten LiNO$_3$-KNO$_3$ were rapid, at 320ºC, producing TiO$_2$ along with NO$_2$ and O$_2$ and slower at lower temperatures. Upon increasing the melt basicity, different reactions were observed, for example, upon the addition of Na$_2$O$_2$, antase TiO$_2$ was produced, with only the evolution of O$_2$, at lower temperatures. When using excess quantities of Na$_2$O$_2$, at 230ºC, Na$_2$O$_2$ decomposed to Na$_2$O to produce a titanate, instead of TiO$_2$. Upon the addition of Na$_2$O and excess quantities of $K_2TiF_6$, antase TiO$_2$ was produced, at 200ºC, without the evolution of a gas. When Na$_2$O was used in excess, various titanates were produced instead of TiO$_2$. Upon the addition of NaOH, antase TiO$_2$ was produced, at 180ºC, with the evolution of H$_2$. When using excess quantities of NaOH, titanates were produced instead of TiO$_2$ and finally when using excess quantities of $K_2TiF_6$, with Na$_2$O, a mixture of antase TiO$_2$ and titanates were produced [179].

In 2006, Afanasiev investigated the MSS of TiO$_2$ using mass spectroscopy (MS) and SEM, by reacting titanium oxysulfate (TiOSO$_4$) or TiO$_2$ in molten lithium nitrate (LiNO$_3$), molten KNO$_3$ or molten NaNO$_3$, between 400-550ºC. They also investigated the effect of increasing the basicity of the melt by adding potassium hydroxide (KOH), NaOH, Na$_2$CO$_3$, and potassium carbonate ($K_2CO_3$). They found shorter reaction times at temperatures below 500ºC were insufficient to produce pure titanates, leading to mixtures of TiO$_2$ and titanates to be produced. As the temperature or basicity of the salt decreased, the sequence of compounds obtained were; TiOSO$_4$, 

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TiO$_2$, Alk$_2$Ti$_6$O$_{13}$, Alk$_2$Ti$_4$O$_9$, Alk$_2$Ti$_2$O$_5$ and Alk$_2$TiO$_3$. When salts were used in excess quantities, a single phase TiO$_2$ was produced over a wide temperature range. They also found the morphology and composition varied as a function of the reaction conditions, for example when potassium based preparations were used, particles formed rods, whiskers, lamellae and when using sodium based preparations, fine dispersions were used. This was probably because the rod-like particles were intermediate phases, due to reactants not being fully dissolved in the salt, which underwent pseudomorphic transformations or the ionic salt promoted the selective growth of specific crystallographic planes. The final products produced were rod-like dispersions of TiO$_2$ and other titanates, with crystallite sizes, between 1-10 µm [180].

In 2011, Kozakova et al investigated the MSS of TiO$_2$ nanorods, using XRD and SEM, by reacting TiO$_2$ in molten NaCl-Na$_2$HPO$_4$.12H$_2$O, above 735ºC, after exposure to 750W microwaves. They found that samples prepared by dry homogenization produced pure rutile TiO$_2$ whilst wet homogenisation resulted in mixture of antase and rutile TiO$_2$ or the formation of elongated particles. This was probably due to the encompassment of TiO$_2$ particles, forming of diffusion barrier, causing the reactants to coalesce into complex structures. The final products produced were nanorods of antase TiO$_2$ with crystallite sizes between 2-10 µm [181].

In 2012, Han et al investigated the MSS of rutile TiO$_2$, using XRD and SEM, by reacting TiO$_2$ slag in molten NaOH, at 500ºC. The final product was washed and treated with H$_2$SO$_4$ (at 50ºC) and hydrolyzed to sodium metatitanate (Na$_2$TiO$_3$), which was then calcined, at 940ºC, and doped to produce dispersed rutile TiO$_2$. They found impurities in the initial slag, such as chromium, aluminium, manganese and silicon could be separated during the washing process, and impurities such as iron, calcium and magnesium could be separated in the acid dissolution process. They also found at lower temperatures (at ~350ºC), the crystallinity of the final product was low, with a titanium conversion rate of 67.6%. As the temperature increased, to 500ºC, the crystallinity improved with a titanium conversion rate of 92.3%. After treating with Na$_2$TiO$_3$, coating and crushing, the TiO$_2$ content in the final product was 98.6 wt%. The final product had crystallite sizes between 0.1-0.4 µm [182].
Also in 2012, Wu et al investigated the MSS of rutile TiO$_2$ microrods, using XRD, SEM, photoluminescence (PL) and UV-visible spectroscopy (UV-vis), by reacting TiOSO$_4$.H$_2$SO$_4$ in molten hydrogen fluoride (HF), hydrogen peroxide (H$_2$O$_2$) and NaCl, at 810ºC. They found the transformation process of TiO$_2$ microrods was rapid, achieving a length of 100 µm and diameters between 1-5 µm. After 4 hours, the quantity of microrods increased and micro-particles decreased, and after 8 hours, ultra-long microrods were produced of lengths, between 200-500 µm and ~2 µm in diameter [183].

Also in 2012, Peining et al investigated the MSS of antase TiO$_2$ nanorods, using SEM and XRD, by reacting TiOSO$_4$.H$_2$SO$_4$ in molten LiNO$_3$ and molten LiCl at 280ºC. They found agglomerated nanostructures of diameters between 100-300 nm were produced, with aggregate sizes between 40-60 nm in diameter. These were each composed of smaller particles with an average diameter of ~5 nm with a surface area of ~200 m$^2$ g$^{-1}$ [184].

### 2.3.4 Molten salt synthesis of cement compounds

The effects of global warming and the rise of CO$_2$ emissions from the cement process led to the EPSRC funded project ULECES: Ultra low energy cement synthesis: A radical process change to achieve green and sustainable technologies project grant (EP/FO144499/1) in 2008 [185]. The objective of the project was to reduce reaction temperatures, energy consumption and hence CO$_2$ emissions by synthesising individual phases of cement in molten salts. The results of the project were reported in the following publications [185-188].

In 2011, Photiadis et al investigated the MSS of the cement compounds; β-Ca$_2$SiO$_4$ and Ca$_3$SiO$_5$, using SEM, XRD and Raman scattering, by reacting CaCO$_3$ and SiO$_2$ in molten NaCl, at 908ºC. They found that β-Ca$_2$SiO$_4$ was successfully synthesised, however the synthesis of Ca$_3$SiO$_5$ led to the formation of β-Ca$_2$SiO$_4$ and CaO, suggesting higher reaction temperatures were required. These observations also suggested that β-Ca$_2$SiO$_4$ was an intermediate compound during the formation of Ca$_3$SiO$_5$ [185].
In 2012, Maries et al investigated the resource efficiency (energy consumption and waste output), supply chain influences and management of a molten salt cement production process in comparison with the cement process, using a risk-based model. It was suggested a molten salt cement process would have lower reaction temperatures, lower fossil fuel consumption and lower CO$_2$ emissions than the conventional process. Also the possibility of using renewable sources of electricity to power the process and sequestering CO$_2$ into the molten salt were highlighted [186].

In 2014, Photiadis et al investigated the MSS of the cement compound; β-Ca$_2$SiO$_4$, by reacting CaCO$_3$ with SiO$_2$ in molten NaCl-CaCl$_2$ and CaCl$_2$, using Raman scattering and XRD at 900°C. However it was found the reaction in molten CaCl$_2$ produced calcium chlorosilicate (Ca$_2$SiO$_4$·CaCl$_2$) and the reaction in molten CaCl$_2$-NaCl produced mixtures of β-Ca$_2$SiO$_4$ and Ca$_2$SiO$_4$·CaCl$_2$ [187].

In 2015, Photiadis et al investigated the MSS of the cement compound; Ca$_3$Al$_2$O$_4$ by reacting CaCO$_3$ with Al$_2$O$_3$ in molten NaCl and CaCl$_2$ between 900-1100°C. However it was found the reaction in molten NaCl produced dodecacalcium heptaaluminate (Ca$_{12}$Al$_{14}$O$_{33}$) and the reaction in molten CaCl$_2$ produced 11CaO.7Al$_2$O$_3$.CaCl$_2$ [188].

2.4 Diagrammatic representation of molten salt reactions

Molten salt reactions (including K$_{sp}$ and K$_f$ values) have been depicted on predominance diagrams [189-191]. These diagrams show the stability areas of dissolved or precipitated compounds at a specific molten salt activity and temperature [189-191]. These are analogous to Pourbaix diagrams (potential-pH diagrams), used to represent stability areas of species in aqueous solutions, where the specific ion activity is the H$^+$ ion [192]. The construction of predominance diagrams requires plotting the equilibrium potential (or redox potentials) of electrochemical reactions against the negative logarithm of a specific ion activity, often selected to be the O$^{2-}$ ion for molten salts.

\[ pO^{2-} = -\log [O^{2-}] \]  
\[ \text{Equation 2.5} \]

Equation 2.5 describes the definition for O$^{2-}$ ion activity in molten salts, where [O$^{2-}$] is the O$^{2-}$ ion activity in the electrolyte and $pO^{2-}$ is its negative logarithm and it is for this
reason that predominance diagrams are often denoted potential-pO$_2$- diagrams. The equilibrium potentials are often equated to the standard redox potentials of electrochemical reactions, by neglecting the activity coefficient of the species in the electrolyte. The equilibrium (or standard redox potentials) and O$_2^-$ ion activity can be calculated using decomposition potentials of electrolytes, equilibrium potentials (by voltammetry), $K_{sp}$ values (by potentiometry) and thermodynamic data [189-191]. Predominance diagrams can be used to describe the following processes.

- **Corrosion reactions of metals in molten salts;**
  These diagrams show stability domains of chemical species, where metals are immune to corrosion, where metals corrode, and where passivity of metals occur, at a specific temperature, pressure, O$_2^-$ ion and Me$_{2+}$ ion activity.

- **Electrowinning of metals from molten salts;**
  The diagrams show the electrowinning pathways of metals and alloys from their ores (metal oxides) in molten salts. This can be obtained by following the equilibrium potential at a specific temperature, pressure, O$_2^-$ ion and Me$_{2+}$ ion activity.

- **Precipitation of oxides from molten salts;**
  The diagrams show the $K_{sp}$ and $K_f$ values of oxides in molten salts (on the x-axis) which can be used to precipitate or dissolve compounds such as metal oxides, by knowledge of temperature, pressure, O$_2^-$ ion and Me$_{2+}$ ion activity.

The construction of predominance diagrams is based upon representing chemical and electrochemical equilibria in molten salts in three combinations (according to Trémillon and Littlewood) [189-191].

- Chemical reactions (involving no electron transfer) are represented as vertical lines (on the x-axis) on predominance diagrams and independent of equilibrium potential (on the y-axis).

$\Delta G^\circ = -RT\ln K$ \hspace{1cm} \textbf{Equation 2.6}
Equation 2.6 describe the equilibria of a chemical reaction where $\Delta G^\circ$ is the Gibbs free energy of the chemical reaction and $K$ is the equilibrium constant of the chemical reaction. These can be substituted into each other to provide the following relationship.

$$\Delta G^\circ = -RTpO^{2-}$$ \hspace{1cm} \text{Equation 2.7}$$

Equation 2.7 describes the equilibria of a chemical reaction involving $O^{2-}$ ions, where $\Delta G^\circ$ is the Gibbs free energy of the chemical reaction, $pO^{2-}$ is the negative logarithm of the oxide ion activity, $R$ is the universal gas constant and $T$ is the temperature of the chemical reaction.

- Electrochemical reactions (involving electron transfer) are represented as horizontal lines (on the x-axis) on predominance diagrams and are independent of $pO^{2-}$ (on the x-axis).

$$\Delta G^\circ = -nF E^\circ$$ \hspace{1cm} \text{Equation 2.8}$$

Equation 2.8 describes the equilibria of an electrochemical reaction, where $E_\circ$ is the equilibrium potential of the electrochemical reaction, $n$ is the number of electrons, $\Delta Go$ is the Gibbs free energy of the electrochemical reaction and $F$ is the Faradays constant.

- Electrochemical and chemical equilibria (with electron transfer) are represented by straight lines on predominance diagrams and are dependent upon equilibrium potential (on the y-axis) and $pO^{2-}$ (on the x-axis).

$$E = E_\circ + \frac{RT}{nF} K$$ \hspace{1cm} \text{Equation 2.9}$$

$$E = E_\circ + \frac{RT}{n_F}pO^{2-}$$ \hspace{1cm} \text{Equation 2.10}$$

Equation 2.9-10 describes the equilibria for chemical and electrochemical reactions in molten salts, where $E_\circ$ is the equilibrium potential of the electrochemical reaction, $n$ is the number of electrons, $R$ is the universal gas constant and $K$ is the equilibrium constant of the electrochemical/chemical reaction.
Figure 2.8: Predominance diagram for a metal in a molten chloride (produced by author) and plutonium in molten NaCl-KCl at 800°C, metal ion activity = 0.01 (in mole fraction) [189-191] [196].

Figure 2.8 shows a fundamental predominance diagram for a metal in a molten chloride, at a specific temperature and pressure, relative to a metal/metal chloride reduction potential and a preominance diagram for plutonium compounds in molten NaCl-KCl. The O\(^{2-}\) ion activity in a molten salt can be obtained by knowledge of the equilibrium potential (on the vertical axis), pressure (the dotted lines), Me\(^{2+}\) ion activity (on the horizontal [Me\(^{2+}\)] axis) and temperature, therefore Pu\(_2\)O\(_3\) dissociates in molten NaCl-KCl at -log 10.2. Alternatively, the activity of a metal ion (on the vertical log [Me] axis) can be determined by knowledge of the O\(^{2-}\) ion activity.

Predominance diagrams have been constructed for molten chlorides, sulphates, carbonates and hydroxides (including their binary mixtures) [189-208]. The literature is extensive, thus predominance diagrams for metals in molten CaCl\(_2\)-NaCl, NaCl-KCl, KCl, NaCl and CaCl\(_2\) will be investigated.
2.4.1 Diagrammatic representation of reactions in molten NaCl, KCl and NaCl-KCl

As described earlier, molten NaCl, KCl and NaCl-KCl have been used as electrolytes in molten carbonate fuel cells, and as solvents for the pyrochemical reprocessing of nuclear fuel, due to their low melting temperatures (at 801ºC and 770ºC and 727ºC), high electrical conductivity and high proliferation resistance over aqueous solvents [57]. These applications are dependent upon the \(\text{O}^{2-}\) ion activity in the molten salt; therefore predominance diagrams in these molten salts are frequently constructed.

The construction of predominance diagrams in molten salts initiated in 1962 when Littlewood, constructed the diagrams for magnesium, zirconium, nickel and titanium in molten MgCl\(_2\), LiCl, potassium chloride (KCl) and NaCl, at 800ºC, relative to the Cl\(^-\)/Cl\(_2\) reduction potential, at metal ion activities of 1, \(10^{-2}\), \(10^{-4}\) and \(10^{-6}\). These diagrams showed the stability domains for Li\(_2\)O, potassium oxide (K\(_2\)O), Na\(_2\)O, NiO, MgO, ZrO\(_2\), TiO, TiO\(_2\), titanium(III) carbonate (Ti\(_2\)CO\(_3\)) and Mg\(^{2+}\), Ni\(^{2+}\), Zr\(^{2+}\), Zr\(^{3+}\), Zr\(^{4+}\), Ti\(^{2+}\), Ti\(^{3+}\), Ti\(^{4+}\) ions in the molten salt. These were used to describe \(\text{O}^{2-}\) ion and metal ion activity in molten salts and applied to corrosion processes of metals in molten salts, electrowinning processes of metals from molten salts and reduction processes of molten salt by reactive metals. The diagrams also depicted the K\(_{sp}\) values for MgO in molten KCl, NiO in molten KCl, NiO in molten LiCl, ZrO\(_2\) in molten KCl and titanium in molten MgCl\(_2\), NaCl and KCl at -log 23, -log 19, -log 8, -log 19, and \(\sim\)log 22 respectively [189].

In 1974, Trémillon constructed predominance diagrams for nickel in molten NaCl and zirconium in molten KCl, at 800ºC, relative to the Na\(^+\)/Na reduction potential at metal ion activities of \(10^{-2}\), \(10^{-4}\) and \(10^{-6}\). These diagrams were used to show the stability domains for NiO, ZrO\(_2\), K\(_2\)O and Ni\(^{2+}\), Zr\(^{3+}\), Zr\(^{2+}\), Zr\(^{4+}\) ions in the molten salt. The diagrams also showed the K\(_{sp}\) values for NiO and ZrO\(_2\) in molten NaCl at -log 17 and -log 20 respectively [190].

In 1991, Nishikata et al constructed the predominance diagrams for nickel, magnesium zirconium and titanium in molten KCl, at 800ºC, relative to the Cl\(^-\)/Cl\(_2\) reduction potential, at metal ion activities of \(10^{-2}\) and \(10^{-6}\). These diagrams showed the
stability domains for NiO, MgO, ZrO$_2$, TiO$_2$, TiO, titanium(V) oxide (Ti$_3$O$_4$),
titanium(III) oxide (Ti$_2$O$_3$) and Ni$^{2+}$, Zr$^{2+}$, Ti$^{4+}$ ions in the molten salt and were used to
describe the corrosion of metals in the molten salt. They suggested that although the
diagrams illustrated the existence of oxide layers at high O$^{2-}$ ion activities, these were
most likely broken down by reactions with Cl$^-$ ions in the molten salt. Also the K$_{sp}$
values for NiO, MgO, ZrO$_2$ and TiO$_2$ in molten KCl were shown at -log19, -log 21, -
log 20 and -log 25 respectively [194].

In 2000, Ishitsuka and Nose constructed the predominance diagram for chromium in
molten NaCl-KCl. These were plotted at 727ºC, relative to the Cl$^-$/Cl$_2$ reduction
potential, at metal ion activities of 10$^{-2}$, 10$^{-4}$ and 10$^{-6}$. These diagrams showed the
stability domains for the chromium(II) oxide (Cr$_2$O$_3$), Cr$^{2+}$, Cr$^{3+}$, Cr$^{6+}$ ions and Cr$_2$O$_7^{2-}$
, CrO$_4^{2-}$ complex ions in the molten salt. These were used to describe the behaviour of
Cr$_2$O$_3$ film in the molten salt, suggesting that these dissolve at high O$^{2-}$ ion activities,
forming CrO$_4^{2-}$ complex ions. Also the K$_{sp}$ values for Cr$_2$O$_3$ in molten NaCl-KCl were
shown at -log 12 [195].

In 2005, Lambertin et al constructed the predominance diagrams for plutonium in
molten NaCl-KCl and CaCl$_2$. These were plotted at 900ºC, relative to the Cl$^-$/Cl$_2$
reduction potential at metal ion activities of 10$^{-2}$. These diagrams showed the stability
domains for Pu$_2$O$_3$, plutonium(IV) oxide (PuO$_2$) and the Pu$^{2+}$ ion in the molten salt. It
was shown that the stability domain for the Pu$^{2+}$ ion was higher in molten CaCl$_2$ than
NaCl-KCl. Also the K$_{sp}$ values for Pu$_2$O$_3$ in molten NaCl-KCl and CaCl$_2$ were shown
to be -log 10 and -log 6 respectively [196].

### 2.4.2 Diagrammatic representation of reactions in molten LiCl-KCl

As described earlier, molten LiCl-KCl is used as electrolytes in molten salt batteries,
molten carbonate fuel cells and solvents for the pyrochemical reprocessing of nuclear
fuel, due to its low melting temperature (at 348ºC) and high proliferation resistance
over aqueous solvents [57-58]. These applications are dependent upon the O$^{2-}$ ion
activity in the molten salt; therefore predominance diagrams in this molten salt are
frequently constructed.
In 1975, Takahashi et al constructed the predominance diagram for platinum in molten LiCl-KCl, at 450°C, relative to the Ag⁺/Ag and Cl⁻/Cl₂ reduction potential, at metal ion activities of 10⁻², 10⁻⁴, 10⁻⁶ and 10⁻⁸. This diagram showed the stability domains for platinum oxide (PtO₂) and Pt²⁺ ion in the molten salt. It was shown how platinum was probably passivated by a PtO₂ film at high O²⁻ ion activities and a PtCl₂, lithium tetrachloroplatinate (LiPtCl₄) or potassium tetrachloroplatinate (K₂PtCl₄) film at low O²⁻ ion activities. The passivation characteristics of platinum were shown to be independent of temperature within the range of 400-450°C [197].

In the same year, Uchida et al constructed the predominance diagram for uranium in molten LiCl-KCl, at 450°C, relative to the Pt²⁺/Pt reduction potential at a metal ion activity of 10⁻². These diagrams showed the stability domains for UO₃, UO₂ compounds, U⁴⁺, U³⁺ ions and UO₂²⁺ complex ions in the molten salt. Also the stability constants for UO₂²⁺ complex ions and the U⁴⁺ ion in molten LiCl-KCl was shown to be -log 4.6 and -log 9 respectively [198].

In 1973, Landresse constructed the predominance diagram for uranium in molten LiCl-KCl, at 450°C, relative to the Cl⁻/Cl₂ reduction potential at a metal ion activity of 10⁻². These showed the stability domains for UO₃, UO₂, UO²⁺, UO₂²⁺ complex ions and U⁴⁺, U³⁺ ions in the molten salt. Also the K_sp values for UO₂ and UO₃ in molten LiCl-KCl was shown to be -log 3.5 and -log 2.6 respectively [199].

In 1982, Seon et al constructed the predominance diagram for iron in molten LiCl-KCl at 470°C, relative to the Cl⁻/Cl₂ reduction potential at metal ion activities of 1, 6.18 x 10⁻², 1.68 x 10⁻² and 0.108. This showed the stability domains for iron oxide (FeO), iron (II, III) oxide (Fe₃O₄), iron(III) oxide (Fe₂O₃), Fe-Li₂O compounds, FeO²⁻ complex ions and Fe²⁺ ions in the molten salt. Also the stability constants for the FeO²⁻ ion in molten LiCl-KCl was shown to be -log 1.7 [200].

In 2004, Rouquette-Sanches and Picard constructed the predominance diagrams for selenium in molten LiCl-KCl at 450°C, 500°C, 550°C and 600°C, relative to the Cl⁻/Cl₂ reduction potential at a metal ion activity of 1. These showed the stability domains for lithium(II) sulphide (Li₂S₃), selenium chloride (SeCl₂) and SeO₂ compounds, and Se₂O₇⁻⁶, SeO₃²⁻ complex ions in the molten salt. Also the K_sp values
for Se$_2$O$_7^{6-}$ complex ions at 450°C, 500°C and 600°C were shown to be -log 6, -log 4 and -log 3 respectively [201].

In 2005, Hayashi and Minato constructed the predominance diagrams for lanthanide, gadolinium and neodymium in molten LiCl-KCl, at 450°C, relative to the Cl$^-$/Cl$_2$ reduction potential at metal ion activities of $10^{-2}$, $5 \times 10^{-3}$ and $10^{-3}$. These showed the stability domains for LaOCl, lanthanum chloride (LaCl$_3$), neodymium(III) oxide (Nd$_2$O$_3$), neodymium oxychloride (NdOCl), NdCl$_3$, gadolinium(III) oxide (Gd$_2$O$_3$), gadolinium oxychloride (GdOCl) and gadolinium chloride (GdCl$_3$) compounds in the molten salt. Also $K_{sp}$ values for neodymium oxychloride (LaOCl), neodymium(III) oxide (Nd$_2$O$_3$) and gadolinium oxychloride (GdCOCl) in molten LiCl-KCl were shown to be -log 6, -log 4 and -log 9.37 respectively [202].

In 2007, Cordoba and Caravaca constructed the predominance diagram for samarium in molten LiCl-KCl, at 450°C, relative to the Cl$^-$/Cl$_2$ reduction potential, at a metal ion activity of 0.1. This showed the stability domains for samarium oxide (Sm$_2$O$_3$), samarium oxychloride (SmOCl) and Sm$^{3+}$, Sm$^{2+}$ ions in the molten salt. It was stated how Sm$^{3+}$ ions could not removed due to their equilibrium potential being more electronegative than the molten salt. Also the $K_{sp}$ values for SmOCl in molten LiCl-KCl was shown to be -log 7.54 [203].

In 2008, Caravaca et al constructed the predominance diagram for plutonium in molten LiCl-KCl, at 550°C, relative to the Cl$^-$/Cl$_2$ reduction potential at a metal ion activity of $10^{-2}$. This showed the stability domains for Pu$_2$O$_3$, plutonium chloride (PuCl$_3$), plutonium(IV) oxide (PuO$_2$) in the molten salt. It was suggested the diagram could be used to predict the precipitation of PuOCl from the molten salt, although this wasn’t observed during the experiment. This could have been due to Pu$^{3+}$ ions becoming stabilized by complexation which could shift its stability domain to higher O$_2^-$ ion activities. Also the $K_{sp}$ values for Pu$_2$O$_3$ in molten LiCl-KCl were shown to be -log 22.1 [137].

In 2013, Brown et al constructed the predominance diagram for uranium in molten LiCl-KCl, at 500°C, relative to the Cl$^-$/Cl$_2$ reduction potential at a metal ion activity of 1. This showed the stability domains for lithium uranium oxide (Li$_2$UO$_3$), UO$_2$,
uranium (IV, V) oxide ($U_4O_9$), uranium (V, VI) oxide ($U_3O_8$), uranium (VI) oxide), uranium oxydichloride ($UCl_2O$), uranium pentaoxychloride ($U_2Cl_5O_2$), uranium (III) chloride ($UCl_3$), uranium tetrachloride ($UCl_4$) compounds in the molten salt. They suggested the reduction of $UO_2$ to uranium was easier at higher temperatures, as it required less control over the $O^{2-}$ ion activity. Also the $K_{sp}$ values for $Pu_2O_3$ in molten LiCl-KCl was shown to be -log 16 [204].

2.4.3 Diagrammatic representation of reactions in molten CaCl$_2$-NaCl

As described earlier, molten CaCl$_2$-NaCl is used as a solvent for the pyrochemical reprocessing of nuclear fuel, due to its low eutectic point (at 504ºC) [156]. This application is dependent upon the $O^{2-}$ ion activity in the molten salt, which can have a detrimental influence upon the preferred reactions; therefore predominance diagrams in this molten salt are frequently constructed.

In 2000, Martinez et al constructed the predominance diagram for chromium in molten CaCl$_2$-NaCl, at 550ºC, relative to the Cl$^-$/Cl$_2$ reduction potential, at metal ion activities of 1 and $10^{-1}$. The diagram showed the stability areas for $Cr_2O_3$ and $Cr_2O^{2+}$, $Cr^{2+}$, $Cr^{3+}$ complex ions in the molten salt. They suggested how these diagrams could be used in conjunction with a predominance diagram of chlorinating gaseous mixtures to predict the operating conditions for chlorinating chromium oxides. These operating conditions include the chlorination of the sample and electrowinning to obtain the final metal. Also the stability constants for the $Cr_2O^{2+}$ complex ion, and $K_{sp}$ values for CrO and $Cr_2O_3$ in molten CaCl$_2$-NaCl was shown to be -log 1.23, -log 7.75 and -log 26.5 respectively [158].

2.4.4 Diagrammatic representation of reactions in molten CaCl$_2$

Molten CaCl$_2$ has been used as a solvent for the extraction of metals, such as titanium [87]. This application is dependent upon the $O^{2-}$ ion activity in the molten salt, which can have a detrimental influence upon the preferred reactions; therefore predominance diagrams in this molten salt are frequently constructed.
In 2005, Dring et al constructed the predominance diagram for titanium in molten \( \text{CaCl}_2 \) at 800ºC, 900ºC and 1100ºC, relative to the \( \text{Cl}^-/\text{Cl}_2 \) reduction potential, at a metal ion activity of 1. This showed the stability domains for calcium titanate (\( \text{CaTiO}_2 \)), \( \text{Ti}_3\text{O}_5 \), trititanium dioxide (\( \text{Ti}_3\text{O}_2 \)), titanium oxide (\( \text{TiO} \)), titanium(III) oxide (\( \text{Ti}_2\text{O}_3 \)), \( \text{TiO}_2 \), titanium(III) oxychloride (\( \text{TiClO} \)) compounds and \( \text{Ti}^{3+} \), \( \text{Ti}^{2+} \) ion activity in the molten salt. This diagram was used to describe the electrolytic reduction pathway to producing titanium from rutile. It was suggested this could only occur at high \( \text{O}^{2-} \) activities there is a high probability that rutile would react with \( \text{Ca}^{2+} \) ions to form calcium titanate (\( \text{CaTiO}_3 \)). This could have a delirious effect upon the deoxidation process of rutile as the \( \text{O}^{2-} \) ions may have to diffuse through a solid phase. \( \text{CaTiO}_3 \) could however been further reduced to titanium, but may also increase the \( \text{CaO} \) activity in the molten salt. Also the \( K_{\text{sp}} \) values for \( \text{TiO}_2 \) in molten \( \text{CaCl}_2 \) was shown to be -log 12.5 and -log 10 at 1100ºC and 800ºC respectively [206].

In 2006, Dring et al constructed the predominance diagram for titanium in molten \( \text{CaCl}_2 \) and superimposed the predominance diagram for tungsten at 900ºC, relative to the \( \text{Cl}^-/\text{Cl}_2 \) reduction potential at a metal ion activity of 1. These diagrams demonstrated the stability domains for calcium titanate (\( \text{CaTiO}_3 \)), calcium tetraoxotungstate (\( \text{CaWO}_4 \)), \( \text{Ti}_3\text{O}_2 \), titanium(II) oxide (\( \text{TiO} \)), \( \text{Ti}_2\text{O}_3 \), trititanium pentoxide (\( \text{Ti}_3\text{O}_5 \)), \( \text{TiO}_2 \), tungsten(VI) oxide (\( \text{WO}_3 \)), tungsten dioxychloride (\( \text{WCl}_2\text{O} \)), tungsten trioxochloride (\( \text{WO}_2\text{Cl}_3 \)) and titanium oxychloride (\( \text{TiClO} \)) compounds in the molten salt. These were used to describe the electrolytic reduction pathway of \( \text{WO}_3 \) and \( \text{TiO}_2 \) to W-Ti alloys. It was suggested that tungsten was produced prior to titanium upon reducing the potential at the cathode. At less negative potentials than those required for the electrolytic reduction of \( \text{TiO}_2 \), tungsten oxide (\( \text{WO}_2 \)) could be reduced to tungsten before the onset of \( \text{TiO}_2 \). Also the \( K_{\text{sp}} \) values for \( \text{TiO}_2 \) in molten \( \text{CaCl}_2 \) was shown to be -log 12.5 and -log 10 at 1100ºC and 800ºC respectively [207].

In 2007, Yasuda et al constructed the predominance diagram for silicon in molten \( \text{CaCl}_2 \) at 850ºC, relative to the \( \text{Ca}^{2+}/\text{Ca} \) reduction potential at a metal ion activity of 1. This diagram demonstrated the existence of stability domains for \( \beta-\text{Ca}_2\text{SiO}_4 \), calcium silicate (\( \text{Ca}_3\text{Si}_2\text{O}_7 \)), calcium metasilicate (\( \text{CaSiO}_3 \)), \( \text{SiO}_2 \), silicon tetrachloride (\( \text{SiCl}_4 \)) and calcium silicide (\( \text{CaSi}_2 \)) in the molten salt. The electrolytic reduction pathway of \( \text{SiO}_2 \) to silicon was shown and was suggested an intermediate \( \text{CaSiO}_3 \) phase was
formed. SiO$_2$ was stable at positive potentials, between $-\log 5.2$ and $-\log 10.7$ and reduced to silicon at negative potentials. Also the $K_{sp}$ values for CaO in molten CaCl$_2$ was shown to be $-\log 0.1$ [208].

2.6 Summary of literature review

This chapter introduced previous literature describing the **dissolution of compounds in molten salts**, through **phase diagrams**, $\Delta H_{mix}$ and $K_{sp}$ values, MSS of **compounds** and the **diagrammatic representation of molten salt reactions** (predominance diagrams).

**Phase diagrams in molten salts** have been obtained by measuring liquidus and solidus values of unary/binary/ternary/quaternary systems, using a DSC, under different atmospheres and/or calculated directly from thermodynamic data using computer programs (such as FactSage and MTDATA and many others) [270] [209-210]. These programs use mathematical models to represent the thermodynamic potentials (Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$), entropy ($\Delta S$) and heat capacity ($\Delta C_p$)) for each phase within the phase diagram. These potentials are used in an optimization method (CALPHAD coupled with a Gibbs free energy minimization routine) to obtain the equilibrium compositions of mixtures of phases to plot liquidus and solidus points of unary/binary/ternary/quaternary systems as a function of temperature [208-210]. Often the potentials include $\Delta H_{mix}$ values from drop calorimetry experiments which have proven to affect the liquidus lines on a phase diagram. Phase diagrams in molten salts will be useful for our investigation as they can help describe dissolution reactions and hence suggest whether the MSS of cementitious compounds are possible in industry.

**$\Delta H_{mix}$ values in molten salts** have been obtained from drop calorimetry experiments or existing phase diagrams in literature using FactSage or MTDATA and many others [270] [209-210]. These values can either be positive or negative, depending upon choice of cations and anions in the system [53]. The author has found values reported as high as $\pm 20$ kJ mol$^{-1}$ which have suggested the formation of complex ions or or as low as $\pm 200$-$180$ J mol$^{-1}$ for ideal systems. $\Delta H_{mix}$ values in molten salts will be
useful for our investigation as they can help describe dissolution reactions and hence suggest whether the MSS of cementitious compounds are possible in industry.

**K\text{sp} values in molten salts** have been obtained from using potentiometry or isothermal saturation experiments. These values are dependent upon dependent upon the cation and anion activity in the molten salt and the author has found values as high as -log 1.1 or as low as 25.7 in molten salts. A wide range of molten salt systems have been investigated, and been proven that values in molten chlorides are lower in comparison to other molten salts (where precipitation generally occurs) [209-210]. K\text{sp} values in molten salts will be useful for our investigation as they can help describe dissolution reactions and hence suggest whether the MSS of cementitious compounds are possible in industry.

**MSS** is a proven alternative route to the synthesis of a wide range of compounds (such as TiO\textsubscript{2}, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}). To the authors knowledge, TiO\textsubscript{2} has been produced from the reactants; TiOSO\textsubscript{4}, H\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}TiF\textsubscript{6}, TiOSO\textsubscript{4} in molten LiNO\textsubscript{3}-KNO\textsubscript{3}, LiCl, KNO\textsubscript{3}, LiNO\textsubscript{3}, NaNO\textsubscript{3}, HF, NaOH, NaCl, H\textsubscript{2}O\textsubscript{2} and NaCl-Na\textsubscript{2}HPO. m-ZrO\textsubscript{2} and t-ZrO\textsubscript{2} has been produced from the reactants; Zr(SO\textsubscript{4})\textsubscript{2}, ZrOCl\textsubscript{2}.8H\textsubscript{2}O and ZrO(NO\textsubscript{3})\textsubscript{2}.2H\textsubscript{2}O in molten NaNO\textsubscript{3}, LiNO\textsubscript{3}-KNO\textsubscript{3}, NaNO\textsubscript{3}-KNO\textsubscript{3}, NaNO\textsubscript{2}-KNO\textsubscript{2} and LiF-NaF. α-Al\textsubscript{2}O\textsubscript{3} and γ-Al\textsubscript{2}O\textsubscript{3} has been produced from the reactants; AlCl\textsubscript{3}, Al(OH)\textsubscript{3}, Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}, NaAlO\textsubscript{2} and additives; TiOSO\textsubscript{4}, Na\textsubscript{3}PO\textsubscript{4}.12H\textsubscript{2}O, α-Al\textsubscript{2}O\textsubscript{3} in molten LiNO\textsubscript{3}-KNO\textsubscript{3}, NaNO\textsubscript{3}, NaNO\textsubscript{3}-KNO\textsubscript{3}, NaNO\textsubscript{2}-KNO\textsubscript{2}, Na\textsubscript{2}SO\textsubscript{4}, NaCl-KCl, Na\textsubscript{2}SO\textsubscript{4}-K\textsubscript{2}SO\textsubscript{4} and K\textsubscript{2}SO\textsubscript{4} [161-184]. The final crystallites sizes of these compounds were a function of various heating and cooling rates and the basicity of the molten salt. Upon increasing this basicity, reaction temperatures have been lowered and in some cases produced undesirable products (such as titanates instead of TiO\textsubscript{2}) [183-184]. MSS will be useful for our investigation as they can be used to obtain the cementitious compounds considered in this thesis.

**Predominance diagrams** are a useful tool to depict molten salt reactions, K\text{f} and K\text{sp} values and stability areas for ions, complex ions and precipitated compounds in molten salts [189-208]. These are plotted mainly relative to the Cl\textsubscript{2}/Cl\textsubscript{2} reduction potential, at metal ion activities between 1-10\textsuperscript{-8} at reaction temperatures. Their calculation requires reduction potentials of electrochemical reactions, thermodynamic
data and stability constants of the species considered. The uses of these diagrams are limited to the choice of thermodynamic data as often compounds dissolved in molten salts are subjected to the effects of complexation and thus requires an activity coefficient term. They also require knowledge of the species and molten salt reactions, which can only be confirmed using other analytical techniques. Predominance diagrams will be useful to our investigation as they can help determine molten salt conditions required for the MSS of cementitious compounds.
Chapter 3

Characterization, electroanalytical, calorimetric techniques & experimental setup

3.1 Introduction

This chapter describes the characterization, electroanalytical and calorimetric techniques used in this thesis, to investigate the structures and purities of the reactants in the molten salt, behaviour of the molten salt at the reaction conditions, dissolution of the reactants in the molten salt and the MSS of cementitious compounds, which includes XRD, SEM, potentiometry, CV, drop calorimetry and DSC. It also provides a description of the setup for each experiment.

3.2 X-ray diffraction

XRD was used to investigate the structures and purities of the reactants in the molten salt, dissolution of the reactants in the molten salt and MSS of cementitious compounds. The equipment used was a STOE STADI-P and a PANalytical X’pert PRO powder diffractometer (figure 3.1).
Each system was equipped with a cobalt X-ray tube to provide cobalt X-rays. A typical operating condition was a 2θ scan range of 5-110° with 150 seconds per steps. XRD involved illuminating a crystalline sample with X-rays, between wavelengths of 0.5-22 Å, which caused radiation to be diffracted by adjacent planes in the sample. When path differences between the diffracted waves are equal to an integer number of wavelengths (γ), constructive interference occurs [212-214]. i.e. if AB + BC are equal to γ, a wave with a larger amplitude is produced (figure 3.2).
The intensity of the diffracted radiation was recorded at various detector angles, between 0-180º which were plotted as a function of the scattering angle to provide an XRD pattern. Each XRD pattern was indicative of a crystalline sample’s inter-atomic spacing and used to identify phase(s) of a particular material, after comparing the patterns against a database for possible matches. In these studies, the phases were identified using “The International Centre for Diffraction Data database (ICDD)” [215].

\[ \lambda = 2d\sin\theta \]

Equation 3.1 expresses Bragg’s law, used to relate the X-ray scattering angle with the X-ray wavelength, where \( \lambda \) is the X-ray wavelength, \( \theta \) is the scattering angle and \( d \) is the d-spacing between the adjacent planes in the crystalline sample [212]. From this equation, it was possible to determine peak positions on an XRD pattern theoretically (on a 2θ scale) providing the X-ray wavelength and lattice parameters are known (i.e. 1.78 Å for cobalt, Kα1 radiation).

X-rays were produced by passing a current through a tungsten (cathode) filament causing electrons to be released. These electrons are accelerated over a voltage and attracted to a cobalt target (anode), generating cobalt X-rays of wavelength Kα1 (6930.3 eV), Kα2 (6915.3 eV) and Kβ (7649.4 eV). These were then passed through an iron or germanium filter to remove unwanted Kα2 and Kβ radiation, which would cause unwanted peaks in an XRD pattern (figure 3.3) [212-214].
The analysis of the XRD patterns was performed upon the principle that the inter-atomic spacings of crystalline samples can be described in terms of a unit cell (figure 3.4) [212]. These unit cells are stacked in three dimensional spaces and represented by the lattice parameters; x, y and z, describing the dimensions of the unit cell, a, b and c, describing the axis length, α, β, and γ, describing the angles between the axes and h, k and l, describing the planes of direction. The perpendicular spacing between the planes is the d-spacing [214]. These parameters are determined directly from an XRD pattern, and provide information upon the axis system of the crystalline sample, and ultimately its crystal structure (table 3.1).
### 3.3 Scanning Electron Microscopy

An SEM was used to investigate the *dissolution of the reactants in the molten salt* and *MSS of cementitious compounds*. The SEM equipment was a Jeol JSM 6480LV and Jeol JSM 35CF SEM, each with secondary electron imaging (SEI) and back scattered electron analysis (BSE) detection modes (figure 3.5).

![Figure 3.5: Image of the Jeol JSM 6480LV (left) and Jeol JSM 35CF (right) SEM systems.](image)

SEM involved illuminating a sample with high energy electrons which interacted with its surface, to produce secondary electrons or X-ray’s depending upon the choice of detection mode. These signals were used to determine a sample’s topography, morphology, composition and size which use both SEI and BSE detection modes [216-218].

---

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Axis system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>a = b = c</td>
</tr>
<tr>
<td></td>
<td>α = β = γ = 90°</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>a = b ≠ c</td>
</tr>
<tr>
<td></td>
<td>α = β = γ = 90°</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>a = b ≠ c</td>
</tr>
<tr>
<td></td>
<td>α = β = 90°, γ = 120°</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>a = b = c</td>
</tr>
<tr>
<td></td>
<td>α = β = γ ≠ 90°</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>a = b = c</td>
</tr>
<tr>
<td></td>
<td>α = β = γ ≠ 90°</td>
</tr>
<tr>
<td>Tetrabromic</td>
<td>a = b ≠ c</td>
</tr>
<tr>
<td></td>
<td>α = β = γ ≠ 90°</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>a = b ≠ c</td>
</tr>
<tr>
<td></td>
<td>α ≠ β ≠ γ ≠ 90°</td>
</tr>
</tbody>
</table>

*Table 3.1: Crystal structure and axis system, a, b and α, β, γ cell parameters (reproduced by author) [214].*
During the SEI detection mode, secondary electrons (with energies < 50 eV) in valence orbitals of a sample’s surface are released by inelastic scattering. The number of electrons and projection angle was dependent upon the angle of the incoming beam and sample surface topography, therefore steeper surfaces appeared brighter than flatter surfaces. This resulted in a variation of electron intensity and image contrast, which was used to produce high-resolution images of a sample’s surface (between ~1-5 nm) [216-218].

During the BSE detection mode, a fraction of electrons from the incident beam entered a sample (up to 20 nm below the surface) and became scattered by the electromagnetic field of the nucleus. If the scattering angle was greater than 180°, backscattered electrons (with energies > 50eV) were diffracted out of valence orbitals from the surface by elastic scattering. This caused higher energy electrons to fill the valence orbitals, causing X-rays to be released. The X-ray wavelength was then related to the energy level differences in different orbitals for a given element, and used for EDS analysis. The higher the atomic number of the sample, the more electrons are scattered, leading to a sharper image contrast (up to ~5.5 nm) [216-218].

SEM electrons are produced (~0.0025 nm in wavelength) by passing a current through a tungsten (cathode) filament and accelerating it across a voltage (between 1-300 kV), similar to X-ray production (figure 3.6). The electron beam is passed through a grid cap (an electrostatic lens) and magnetic plate (anode) which focuses the electrons onto a small area (between 50-100 Å in diameter), causing electrons to be produced [218].

![Figure 3.6: Tungsten (cathode) filament for SEM [219].](image)

The interaction of the incident beam within a sample forms a limiting interaction volume, dependent upon the energy of the electron incident beam and density of the
sample. This limiting interaction volume varies throughout the sample, being greatest at the beam impact point [218].

\[
R = \frac{0.0276A^{0.67}}{Z^{0.9} \rho}
\]  

Equation 3.2

Equation 3.2 expresses the radius of the limiting interaction volume of a sample, where \(Z\) is the atomic number of the sample, \(\rho\) is the density of the sample (in g cm\(^{-3}\)), \(E_0\) is the incident beam energy (in kV) and \(A\) is the atomic weight (in g mol\(^{-1}\)) [218]. This demonstrates the interaction volume increases with increasing incident beam energy and decreases as the atomic number of the sample rises.

### 3.4 Drop calorimetry

An isoperibolic drop calorimeter was used to investigate the **dissolution of the reactants in the molten salt**. The calorimeter was constructed in-house with a temperature range up to 930°C however the author used reaction temperatures of 830°C. This temperature was selected previously by the author and the drop calorimeter was allowed to stabilze for at least 3 days prior to measurements. A schematic of the drop calorimeter is shown in figure 3.7 [220].

![Figure 3.7: Drop calorimeter schematic (left) and image of the drop calorimeter (right).](image)
The drop calorimeter contained an Al₂O₃ block, in a cylindrical furnace, surrounded by a steel enclosure. The Al₂O₃ block contained two cylindrical wells placed in parallel to each other, surrounded by thermopiles [220]. A thermopile is a series of thermocouples connected together in a radial arrangement, their purpose being to measure the temperature at a specific location within a tube. The radial arrangement of the thermopiles ensured the complete integration of heat within the tube, allowing the signal to be independent of localised temperature distributions [221]. Each thermopile was constructed from a platinum-rhodium (Pt-Rd) alloy, ~17 mm in diameter, ~80 mm in height containing 22 hollow alumina support discs. These were connected electrically in opposition to compensate for any irregular heat effects. The temperature of the calorimeter was controlled by an electronic thermostat, connected to a thermocouple in the centre of the Al₂O₃ block [221-223].

Before the experiments, a sample and reference closed-ended calorimetric tube, constructed from SiO₂, was inserted into each well, under argon gas. The sample calorimetric tube contained a glassy carbon crucible, containing the sample under study and the reference calorimetric tube remained empty. These materials were selected due to their high melting temperatures (SiO₂ at 1600°C, glassy carbon at 3550°C) thus suitable for the operational temperatures and conditions required [18]. The purpose of the reference calorimetric tube was to provide a stable and reproducible signal to obtain potential readings from, by closing off the entrance to the drop calorimeter, thus avoiding the interference of gases (such as air).

Drop calorimetry involved measuring the differential temperature between the sample and reference calorimetric tube. During an experiment, pellets and crystals of the sample was dropped into the glassy carbon crucible, at steady-state conditions, causing the temperature of the sample calorimetric tube to lag behind (or ahead) of the reference, and then decay exponentially [221-223]. The potential difference between the thermopiles was recorded as a function of time, to produce a heat flow signal (in mV s⁻¹). This potential difference was interpreted by FlukeView Basic 3.0 and OriginPro 8 Peak Analyzer tool [224-225].

---

11 The procedure for making crystals and pellets is stated in the experimental setup section.
Figure 3.8 shows a typical heat flow signal obtained from the drop calorimeter. The fusion, transitional and mixing enthalpies of the sample were evident as peak areas. To calibrate the peak areas, a calibration was performed on the heat flow signal prior to measurements, using a standard material (such as Al₂O₃, NIST-720), at the reaction conditions [220].

\[
\Delta H_{\text{Total}} = \Delta H_{(298-T_{\text{Reaction}})} + \Delta H_{\text{mix}} + \Delta H_{\text{fusion}}
\]

Equation 3.5 expresses the total drop enthalpy, where \( \Delta H_{\text{Total}} \) is the total drop enthalpy (in kJ mol\(^{-1}\)), \( \Delta H_{\text{mix}} \) is the heat of mixing of a mixture of components A in B (in kJ mol\(^{-1}\)), \( \Delta H_{\text{fusion}} \) is the enthalpy of fusion (in kJ mol\(^{-1}\)) and \( \Delta H_{(298-T_{\text{Reaction}})} \) is the enthalpy change of the sample from 298K to the reaction temperature (in kJ mol\(^{-1}\)) [220-222]. Both \( \Delta H_{\text{fusion}} \) and \( \Delta H_{(298-T_{\text{Reaction}})} \) quantities are available from thermodynamic data [18]. Often a drift of the potential base-line was encountered therefore a separate baseline was taken for each peak (this was probably due to reactions between the calorimetric and sample calorimetric tube).
3.5 Differential Scanning Calorimetry

Two DSCs were used to investigate the behaviour of the molten salt at the reaction conditions and dissolution of the reactants in the molten salt. The equipment used was a Setaram DSC 121 and a Netzsch DSC STA 449 Jupiter, capable of reaching temperatures up to 827°C and 2400°C respectively depending upon the furnace type (figure 3.9) [220] [226-227].

The Setaram DSC 121 consisted of two ceramic tubes mounted in parallel, embedded with heating elements. Both tubes had Inconel™ 600 internal liners preinstalled from Setaram to protect the heating elements from molten salt leakages [220] [227-228]. These heating elements had a thermal resistivity of 100 Ω each and generated up to 200 mW every 200 seconds. The heat flow signal was measured by
thermopiles, made from a Pt-Rd alloy which was placed around each tube. Each thermopile was connected electrically in opposition to compensate for any irregular heat effects [220]. The integration of the peaks was performed by Calisto Thermal Analysis software provided by Setaram [227-228].

The Netzsch DSC STA 449 Jupiter consisted of two ceramic tubes mounted in parallel, embedded with heating elements, with a DSC resolution of 1 µW. The heat flow signal was measured by thermopiles, made from a Pt-Rd alloy which was placed around each tube. The machine had a mass balance to measure differences in weight of the sample as a function of time, with a TG resolution of 0.1 µg. The integration of the peaks was performed by Proteus Thermal Analysis software provided by Netzsch [226] [229].

The procedure involved placing identical sample and reference crucibles in the DSC in calorimetric tubes, connected electrically in the furnace. The differential temperature between the containers was recorded by the thermopiles as a function of time. This arrangement produced a heat flow signal (in mW) and was dependent upon the heat flow path within the unit [220]. When both crucibles were subjected to similar heating/cooling rates, the temperature of the sample crucible lagged behind (or ahead) of the reference and then decayed exponentially. To eliminate any heat effects from the surroundings to the sample, a high thermal resistance (ceramic) was placed between the container and surrounding enclosure to allow heat effects associated solely from the sample to be measured [220-223].

*Figure 3.10: DSC heat flow signal (reproduced by author) [220].*
Figure 3.10 shows a typical heat flow signal obtained from the DSC’s. Heat effects associated with fusion/transitional enthalpies are evident as peaks areas and peak onsets can be used to obtain fusion/transitional temperatures, providing a temperature and calorimetric calibration is performed.

\[ \Delta T_C = k \Delta T_D \]  \hspace{1cm} \text{Equation 3.3}

Equation 3.3 expresses the relationship used for the temperature calibration, where \( T_C \) is the differential temperature between the containers (in °C), \( \Delta T_D \) is the differential temperature of the sample (in °C) and \( k \) is a constant [224]. The temperature calibration was performed at specific scan rates, prior to measurements, using a standard material (such as \( \text{Al}_2\text{O}_3 \), NIST-720) over the temperature range of the DSC [224]. This resulted in a differential temperature between the crucibles which was related to the actual differential temperature of the DSC.

\[ K = \frac{m \Delta H}{A} \]  \hspace{1cm} \text{Equation 3.4}

Equation 3.4 expresses the relationship used to calibrate the DSC, where \( K \) is a constant (in J cm\(^{-2}\)), \( A \) is the peak area (in cm\(^2\)), \( \Delta H \) is the enthalpy change of the sample (in J g\(^{-1}\)) and \( m \) is the mass of the sample (in g) [224]. The calibration was performed at a specific scan rate, prior to measurements, using a standard material (such as \( \text{Al}_2\text{O}_3 \), NIST-720) over the temperature range of the DSC. This allowed the peak area to be related to the \( \Delta H_f \) or \( \Delta C_p \) of the sample.

### 3.6 Potentiometry

Potentiometry was used to investigate the dissolution of the reactants in the molten salt. The technique required the construction of a galvanic cell capable of achieving 830°C. The galvanic cell contained an ISE and reference electrode immersed in the molten salt. These electrodes were connected to a high-resistance voltmeter/potentiostat (Uni-trend), and connected together with leads of similar lengths. The construction of the cell underwent at the Centre for CO\(_2\) Technology, University College London.
materials. This ensured no unwanted junction potentials were present from other thermoelectric forces. The electrode designs were based upon previous versions reported by Gale and Lovering, 1991, which have demonstrated a stable and reproducible signal [230]. A schematic of the galvanic cell is shown in figure 3.11.

Figure 3.11: Galvanic cell schematic.
The reference electrode contained an aluminium silicate (Al₆Si₂O₁₃) membrane, denoted “mullite”. This material was selected due to its high melting temperature (at 1840°C) and sodium ion (Na⁺) conductive properties [18] [51]. The membrane contained a silver wire immersed in molten NaCl-AgCl and capped with a silicon cap. This allowed the reference electrode potential to be a function of the silver wire in contact with Ag⁺ ions in molten AgCl-NaCl (Ag/AgCl redox couple) and the Na⁺ ions in the molten salt on both sides of the Al₆Si₂O₁₃ membrane (junction potential).

The ISE contained an YSZ membrane, containing a silver wire, immersed in molten NaCl-AgCl-Na₂CO₃ and capped with a silicon cap. This material was selected due to it containing oxygen vacancies within its lattice structure, which arose when Zr⁴⁺ ions of ZrO₂ were substituted with slightly larger Y³⁺ ions (ionic radius of 0.82 Å to 0.96 Å) [231]. These oxygen vacancies allow O²⁻ ions in to pass through, thus allowing the ISE electrode potential to be a function of the boundary between the silver wire in contact Ag⁺ ions in molten AgCl-NaCl-Na₂CO₃ (Ag/AgCl redox couple), and O²⁻ ions in the molten salt on both sides of the YSZ membrane [51] [230-233]. The arrangement produced a signal which was a function of one sole variable; the O²⁻ ion activity in the molten salt. ZrO₂ was not used as a membrane material as it undergoes a phase transition, from monoclinic to tetragonal (at ~1000°C), which results in a 5% volume change. This induces stresses upon ZrO₂, during heating/cooling cycles, causing it to crack. However when ZrO₂ is stabilized with Y₂O₃ (at 8 mol %), the cubic polymorph is stabilized and phase transitions can be avoided, and consequently also increases its ionic conduction capabilities [232].

The melt was placed in platinum, Al₂O₃ or glassy carbon crucibles. These materials were selected due to their high melting temperatures (Al₂O₃ at ~2072°C, platinum at ~1769°C, glassy carbon at ~3500°C) and virtually no solubility in molten chlorides which is the general consensus in literature [18] [133]. It has also been reported that platinum reacts with molten chlorides (such as LiCl) to form platinate species (such as lithium platinate (Li₂PtO₃)) at low O²⁻ ion activities, therefore it was expected that similar species could also form in other melts (such as disodium hexachloroplatinate.

13 NaCl was selected as a suitable salt for MSS, thus a suitable material for the mullite membrane.
14 The mixtures are named according to A-B-C where A is the initial salt, B is the secondary compound in A and C is the tertiary compound in A.
15 The salt selected for this investigation was NaCl due to it being a liquid at the reaction conditions.
(Na$_2$PtCl$_6$) in molten NaCl) [234-235]. It was also reported that platinum reacts with O$_2$ to produce a thin transparent film on its surface (probably PtO$_2$), and platinum oxide (Pt$_3$O$_4$) however at higher temperatures exceeding ~600°C the film disappears, probably due to the high vapour pressure of these species [234-235]. However as platinum is a frequently used material by previous authors, it was selected for use in our experiments [133].

The cell envelope was constructed from two types of alloys; Stainless steel 316L and Inconel$^{TM}$ 600, selected due to their high operational service, (Stainless steel 316L at ~800°C, Inconel$^{TM}$ 600 at ~1100°C) and high melting temperatures (Stainless steel 316L at ~1400°C, Inconel$^{TM}$ 600 at ~1370°C) [18] [236-239]. These alloys have a high resistance to oxidation due to the presence of chromium, nickel and iron (table 3.2). These elements oxidise to chromium(III) oxide (Cr$_2$O$_3$), chromium (IV) oxide (CrO$_2$), iron(II) oxide (FeO), iron(III) oxide (Fe$_2$O$_3$) and NiO at elevated temperatures, which provide a barrier to further oxidation [238]. However at elevated temperatures (816°C for Stainless Steel 316L), the CrO$_3$ Ce$_2$O$_3$ compounds are selectively removed, thus exposing Fe$_2$O$_3$ and FeO, which results in their removal. This can be greatly improved by increasing the nickel content in the alloy, using Inconel$^{TM}$ 600, as reported by Davis, 1954 [238]. This particular alloy has been reported to have a lower thermal expansion differential between the base metal and oxide film during heating and cooling, which greatly improves its corrosion resistance [238].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Element (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chromium</td>
</tr>
<tr>
<td>Stainless steel 316L</td>
<td>16-18.5</td>
</tr>
<tr>
<td>Inconel$^{TM}$ 600</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Table 3.2: Composition of Inconel$^{TM}$ 600 and Stainless Steel 316L (reproduced by author) [234-235].

The cell envelope was filled with argon, to remove O$_2$ and moisture which could have detrimental effects to compounds sensitive to humidity. It has been reported that O$_2$ and moisture interact with molten salts to produce O$^{2-}$ and OH$^-$ ions in the melt. These ionic species have proven to accelerate the corrosion of metals in contact with the molten salt and cause hydrolysis of the molten salt [51] [240]. It has also been reported that O$_2$ and moisture greatly accelerate the oxidation of Stainless Steel 316L.
and Inconel\textsuperscript{TM} 600 due to the higher diffusion rates of the ionic species (Fe\textsuperscript{2+}, Ni\textsuperscript{2+} and Cr\textsuperscript{2+}), therefore should be avoided [238-239]. An Al\textsubscript{2}O\textsubscript{3} disc was also placed between the crucible and cell envelope to reduce stray potentials that could affect the potential between the ISE and reference electrode. The temperature of the molten salt was also recorded by an N-type thermocouple inserted into the molten salt, sheathed by an Al\textsubscript{6}Si\textsubscript{2}O\textsubscript{13} membrane to avoid any reaction between the alloy and the molten salt. A mullite drop tube was also inserted into the cell, to guide pellets of samples into the molten salt. The galvanic cell was connected to a H\textsubscript{2}O bath (at 2°C) to cool the top portion of the cell below 100°C, for ease of user handling.

The potentiometric method involved measuring the potential difference (in mV), between the ISE and reference electrode, immersed in the molten salt [230]. At steady-state conditions, the potential difference was ∼0, which increased/decreased upon changes to the O\textsuperscript{2-} activity in the molten salt and temperature. These changes were shown on a potentiometric plot (figure 3.12).

![Figure 3.12: Potentiometric plot (reproduced by author).](image)

Figure 3.12 shows a typical potentiometric plot from the galvanic cell. The incline section was created due to the dissolution of compounds (with an O\textsuperscript{2-} ion) below the saturation limit of the molten salt. This section was used to deduce the number of electrons taking part in the electrochemical reactions, at the YSZ membrane surface, using the Nernst relationship [230] [232].
\[ \Delta E = E^0 + \frac{2.3RT}{nF} \text{pO}^2^- \]  \hspace{1cm} \text{Equation 3.6}

Equation 3.6 expresses the Nernst relationship, where \( E^0 \) is the standard redox potential of the electrochemical reaction, \( R \) is the universal gas constant, \( F \) is the Faradays constant and \( T \) is the temperature. The horizontal section is due to the saturation limit of the molten salt, which often results in the precipitation of compounds. The \( K_{sp} \) values for compounds (such as oxides) can be deduced using the following relationships [130] [241].

\[ \sum S_{\text{MeO}} = [\text{Me}^{2+}][\text{O}^{2-}] = K_{sp}^{1/2} \]  \hspace{1cm} \text{Equation 3.7}

or

\[ \sum S_{\text{Me}_2\text{O}} = [2\text{Me}^{2+}]^2[\text{O}^{2-}] = \frac{1}{4}K_{sp}^{1/3} \]  \hspace{1cm} \text{Equation 3.8}

Equation 3.7-3.8 expresses the relationships between the \( K_{sp} \) value and complete oxide solubility, neglecting the non-dissociated oxide term, where \( \sum S_{\text{MeO}} \) and \( \sum S_{\text{Me}_2\text{O}} \) is the complete oxide solubility. Often the horizontal section has shown to contain a bend towards the \(-\log[\text{O}^{2-}]\) axis, caused by the partial dissolution and existence of a non-dissociated compounds [130].

### 3.7 Cyclic voltammetry

CV was used to investigate the \textbf{structures and purities of the reactants in the molten salt}. This required the construction of an electrolytic cell, with an operational temperature up to 830°C. The cell consisted of working, counter and reference electrodes immersed in the molten salt, connected to a potentiostat. The reference electrode was made from an \( \text{Al}_6\text{Si}_2\text{O}_{13} \) membrane, containing a silver wire immersed in molten \( \text{AgCl-NaCl} \) and capped with a silicon cap (similar to the galvanic cell). The working and counter electrodes were made from a platinum wire, selected due to their high melting temperature (at \( \sim 1769^\circ \text{C} \)) and high electrical conductivity, as described by Gale and Lovering, 1991 [18] [230]. The \( \text{Al}_2\text{O}_3 \) crucible was selected due to its high melting temperature (at \( \sim 2072^\circ \text{C} \)) and limited solubility in molten chlorides, as shown by previous authors [18] [50]. A schematic of the electrolytic cell is shown in figure 3.13.
Figure 3.13: Electrolytic cell schematic.
The electrolytic cell was filled with argon to remove significant quantities of $O_2$ and moisture and an $Al_2O_3$ disc was placed between the crucible and cell envelope due to the same reasons described previously (in the potentiometry section). The temperature of the molten salt was recorded by an N-type thermocouple, sheathed by an $Al_6Si_2O_{13}$ tube before inserting into the molten salt to avoid the interaction of the molten salt. The electrolytic cell was connected a $H_2O$ bath (Huber), which cooled the top portion of the cell to temperatures below 100ºC, with running water at 2ºC, for ease of user handling.

Voltammetry involved measuring the potential difference (in mV) and current (in mA) between the working, counter and reference electrode whilst immersed in the molten salt [242]. The working and counter electrodes coupled with the power supply/potentiostat provided electrical energy to the molten salt to facilitate electrochemical reactions using cyclic voltammetry sweeps. These sweeps were both cathodic or anodic depending upon their connection to the working, counter and reference electrode, and power supply/potentiostat. The potential changes of the working electrode and current produced across the electrodes were plotted on a voltammogram (figure 3.14).

![Figure 3.14: Voltammogram (reproduced by author).](image)

Figure 3.14 shows a voltammogram illustrating a typical CV curve from the electrolytic cell containing a molten salt (such as a molten chloride). The
decomposition potential \( (E_d) \) of the molten salt can be obtained between the difference between the oxidation and reduction potential. This is evident when the current begins to increase exponentially upon increasing the potential. The theoretical \( E_d \) of the molten salt can also be determined using thermodynamic data, using the following reaction [208].

\[
\Delta G^\circ = -nF E_d
\]  

Equation 3.9 expresses the relationship between decomposition potential and Gibbs free energy of the dissociation reaction of the molten salt, where \( E_d \) is the decomposition potential, \( F \) is the Faradays constant, \( n \) is the number of electrons in the dissociation reaction and \( \Delta G^\circ \) is the Gibbs free energy of the dissociation reaction of the molten salt [256].

### 3.8 Experimental setup

This section describes the experimental setup for the feasibility of the synthesis of cementitious compounds, structures and purities of the reactants in the molten salt, behaviour of the molten salt at the reaction conditions, dissolution of the reactants in the molten salt and the MSS of cementitious compounds.

#### 3.8.1 Feasibility of the synthesis of cementitious compounds

The first stage of the investigation determined the feasibility of the synthesis of cementitious compounds; \( \beta-\text{Ca}_2\text{SiO}_4 \), \( \text{Ca}_3\text{SiO}_5 \), \( \alpha-\text{Na}_2\text{SiO}_3 \) and \( \beta-\text{Na}_4\text{SiO}_4 \) using thermodynamic data. This was performed using the reaction equation and chemical equilibrium module in HSC-Chemistry 6.1, developed by Outec [18]. The reaction equation module contains a list of mathematical functions for thermodynamic data, compiled by Barin et al, 2008 [19]. The chemical equilibrium module uses the Gibbs free energy optimization method, developed by Eriksson et al, to generate chemical equilibrium calculations for multi-component systems [19]. This method works upon the principle that reactions proceed spontaneously if changes in the total Gibbs free energy (\( \Delta G \)) of the system is negative, at constant temperature and pressure [210].
3.8.2 Structures and purities of the reactants in the molten salt

The second stage of the investigation determined the structures and purities of the reactants; CaCO₃ (≥ 99%), SiO₂ (≥ 99%) and NaCl (≥ 99%) (Sigma-Aldrich) using XRD, CV and thermodynamic data. These studies were performed using the H, S, C and G, Diagrams module in HSC-Chemistry 6.1, developed by Outec which is described earlier [18]. A list of selected experiments that were performed by the author is shown in table 3.4. Prior to all these experiments, the reactants were dried at ~200°C at atmospheric pressure for ~72 hours in an evaporating furnace (Carbolite).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Temperature (°C)</th>
<th>Reactant(s)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Structure and purity of CaCO₃</td>
<td>25</td>
<td>CaCO₃</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Structure and purity of NaCl</td>
<td>25</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Structure and purity of SiO₂</td>
<td>25</td>
<td>SiO₂</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>Purity of NaCl</td>
<td>25</td>
<td>NaCl</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 3.3: Structures and purities of the reactants in the molten salt experiments.

Experiments 1-3 were taken directly to an XRD machine (STOE, PANalytical).

Experiment 4 was placed in a round bottom sintered Al₂O₃ crucible (Dynamic ceramic) of dimensions 50 mm OD x 44 mm ID x 75 mm high, 110 ml capacity, previously dried for ~72 hours [18]. The crucible was placed inside a high-temperature tubular furnace (Vecstar) under argon (≥ 99.9%) (at 0.010 l/s) (BOC). The furnace temperature was controlled by a temperature programmer (Eurotherm 315) (± 2°C) and the internal cell temperature was measured by an N-type thermocouple (RS Components). The furnace was then heated (at 2°C min⁻¹) to 830°C, and two platinum wires (serving as anodes and cathodes) in Al₆Si₂O₁₃ tubes (Dynamic ceramic) and a reference electrode was immersed in the molten salt, at a depth of 1 cm. Then cyclic voltammetry sweeps were performed using a potentiostat (Autolab) controlled by GPES 4.9 software [243].

---

16 The salt was NaCl.
3.8.3 Behaviour of the molten salt at the reaction conditions

The third stage of the investigation determined the **behaviour of the molten salt at the reaction conditions** using a DSC and thermodynamic data. These studies were performed using NaCl (≥ 99%) (Sigma-Aldrich), and CaCl$_2$ (from calcium chloride hexahydrate ((CaCl$_2$.6H$_2$O)) (≥ 99%) (Sigma-Aldrich)). A list of selected experiments performed by the author is shown in table 3.5. Prior to all experiments, NaCl was dried at ~200ºC at atmospheric pressure for ~72 hours in an evaporating furnace (Carbolite) and CaCl$_2$.6H$_2$O was taken directly as received.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Temperature (ºC)</th>
<th>Reactant(s)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Melting point (open crucible)</td>
<td>25-850</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>Melting point (closed crucible)</td>
<td>25-850</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>Melting point (closed crucible)</td>
<td>25-850</td>
<td>CaCl$_2$</td>
<td>100</td>
</tr>
</tbody>
</table>

*Table 3.4: Behaviour of the molten salt at the reaction conditions experiments.*

**Experiment 5** involved placing NaCl (Sigma-Aldrich) in an open Al$_2$O$_3$ crucible (Dynamic ceramic) alongside an empty reference crucible, in a DSC (Setaram) [227].

**Experiment 6** involved placing NaCl (Sigma-Aldrich) in an Inconel$^\text{TM}$ 600 crucible. This was hermetically sealed and heated in a furnace (Vecstar Ltd) to ~860ºC, to ensure the container was airtight. The Inconel$^\text{TM}$ 600 crucible was then placed alongside an empty reference crucible, in a DSC (Setaram) [227].

**Experiment 7** involved placing CaCl$_2$.6H$_2$O in an Al$_2$O$_3$ crucible (Dynamic ceramic) of dimensions 50 mm OD x 48 mm ID x 50 mm height and fusing under argon (≥ 99.9%) in a furnace (Vecstar) to ~860ºC, at atmospheric pressure (BOC), to dehydrate the CaCl$_2$.6H$_2$O to CaCl$_2$. The mixture was then broken into several pieces in a glove box under argon (≥ 99.9%) and placed in an empty Inconel$^\text{TM}$ 600 crucible. The crucible was then hermetically sealed and heated in a furnace (Vecstar) for 15 minutes and placed alongside an empty reference crucible, in a DSC (Setaram) [227]. All samples were then subjected to a heating rate of 2ºC min$^{-1}$ between 25-850ºC.
3.8.4 Dissolution of the reactants in the molten salt

The fourth stage of the investigation determined the dissolution of the reactants; Na$_2$CO$_3$ ($\geq 99\%$), CaCO$_3$ ($\geq 99\%$) and SiO$_2$ ($\geq 99\%$) in molten NaCl ($\geq 99\%$) (Sigma-Aldrich) at 830°C, using XRD, SEM, drop calorimetry, predominance diagrams, thermodynamic data and a DSC, which subsequently led to obtaining the phase diagram for molten NaCl-Na$_2$CO$_3$, $\Delta H_{\text{mix}}$ values for molten NaCl-Na$_2$CO$_3$ and $K_{\text{sp}}$ values for CaO and Na$_2$O in NaCl at 830°C. The solubilities of CaCO$_3$ and SiO$_2$ are well-known to be low, as described by Yasuda, 2007 and Cherginets, 2005, therefore it was not possible to investigate these at this stage [130] [208]. A list of selected experiments performed by the author is shown in tables 3.6-3.9. Prior to these experiments, the reactants were dried at ~200°C at atmospheric pressure for ~72 hours in an evaporating furnace (Carbolite).

3.8.4.1 Phases of the reactants in the molten salt

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Temperature (°C)</th>
<th>Reactant(s)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Phases of CaCO$_3$ in NaCl</td>
<td>830</td>
<td>CaCO$_3$, NaCl</td>
<td>20, 80</td>
</tr>
<tr>
<td>9</td>
<td>Phases of Na$_2$CO$_3$ in NaCl</td>
<td>830</td>
<td>Na$_2$CO$_3$, NaCl</td>
<td>20, 80</td>
</tr>
<tr>
<td>10</td>
<td>Phases of CaCO$_3$ in NaCl</td>
<td>830</td>
<td>CaCO$_3$, NaCl</td>
<td>20, 80</td>
</tr>
<tr>
<td>11</td>
<td>Phases of CaCO$_3$ in NaCl</td>
<td>830</td>
<td>CaCO$_3$, NaCl</td>
<td>20, 80</td>
</tr>
<tr>
<td>12</td>
<td>Phases of CaCO$_3$ in NaCl</td>
<td>830</td>
<td>CaCO$_3$, NaCl</td>
<td>20, 80</td>
</tr>
<tr>
<td>13</td>
<td>Phases of CaCO$_3$ in NaCl</td>
<td>830</td>
<td>CaCO$_3$, NaCl</td>
<td>20, 80</td>
</tr>
<tr>
<td>14</td>
<td>Phases of Na$_2$CO$_3$ in NaCl</td>
<td>830</td>
<td>Na$_2$CO$_3$, NaCl</td>
<td>20, 80</td>
</tr>
<tr>
<td>15</td>
<td>Phases of SiO$_2$ in NaCl</td>
<td>830</td>
<td>SiO$_2$, NaCl</td>
<td>20, 80</td>
</tr>
</tbody>
</table>

*Table 3.5: Phases of the reactants in the molten salt experiments.*

Experiments 8-15 involved placing the reactants in a round bottom sintered Al$_2$O$_3$ crucible (Dynamic ceramic) of dimensions 50 mm OD x 44 mm ID x 75 mm high, 110 ml capacity, also previously dried for ~72 hours. The crucible and contents were then placed in a muffle furnace (Vecstar) with an air atmosphere and open exhaust, and temperature was raised over ~5 hours to 830°C. After ~3 hours, the furnace was switched off and allowed to cool naturally for ~24 hours. The final product was fused to the crucible, and required a screwdriver and hammer to remove the pieces. These
pieces were then taken to an XRD machine (STOE, PANalytical) and an SEM machine (Jeol). The experimental layout for these experiments is shown in figure 3.15.

![Experimental Layout](image)

*Figure 3.15: Phases of the reactants in the molten salt experimental layout.*

### 3.8.4.2 Phase diagrams of the reactants in the molten salt

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Temperature (°C)</th>
<th>Reactant(s)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Molten NaCl-Na₂CO₃</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>Molten NaCl-Na₂CO₃</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>Molten NaCl-Na₂CO₃</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>Molten NaCl-Na₂CO₃</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>Molten NaCl-Na₂CO₃</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
</tbody>
</table>

*Table 3.6: Phase diagrams of the reactants in the molten salt experiments.*

Experiments 16-20 involved placing the reactants in an Inconel™ 600 crucible which was hermetically sealed and heated in a muffle furnace (Vecstar) to ~860°C to ensure the container was airtight. The crucible was then placed alongside an empty reference crucible, in a DSC (Setaram) [227]. All samples were subjected to a heating rate of 2°C min⁻¹ between 25-850°C and all peaks on the heat flow curves were analyzed from heating curves, to avoid any effects of super cooling which can cause shifts in peak temperature. The experimental layout for these experiments is shown in figure 3.16.
3.8.4.3 Heats of mixing of the reactants in the molten salt

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Temperature (°C)</th>
<th>Reactant(s)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Signal stabilization</td>
<td>830</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>22</td>
<td>Signal stabilization</td>
<td>830</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>23</td>
<td>$\Delta H_f$ of Na$_2$CO$_3$ (pellets)</td>
<td>830</td>
<td>Na$_2$CO$_3$</td>
<td>100</td>
</tr>
<tr>
<td>24</td>
<td>$\Delta H_f$ of Na$_2$CO$_3$ (pellets)</td>
<td>830</td>
<td>Na$_2$CO$_3$</td>
<td>100</td>
</tr>
<tr>
<td>25</td>
<td>$\Delta H_f$ of Na$_2$CO$_3$ (crystals)</td>
<td>830</td>
<td>Na$_2$CO$_3$</td>
<td>100</td>
</tr>
<tr>
<td>26</td>
<td>$\Delta H_f$ of Na$_2$CO$_3$ (crystals)</td>
<td>830</td>
<td>Na$_2$CO$_3$</td>
<td>100</td>
</tr>
<tr>
<td>27</td>
<td>$\Delta H_f$ of NaCl (pellets)</td>
<td>830</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>28</td>
<td>$\Delta H_{mix}$ of molten NaCl-Na$_2$CO$_3$ (pellets)</td>
<td>830</td>
<td>Na$_2$CO$_3$, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>$\Delta H_{mix}$ of molten NaCl-Na$_2$CO$_3$ (pellets)</td>
<td>830</td>
<td>Na$_2$CO$_3$, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>$\Delta H_{mix}$ of molten NaCl-Na$_2$CO$_3$ (crystals)</td>
<td>830</td>
<td>Na$_2$CO$_3$, NaCl</td>
<td>-</td>
</tr>
</tbody>
</table>

*Table 3.7: $\Delta H_{mix}$ and $\Delta H_f$ values of the reactants in the molten salt experiments.*
Experiments 21-22 involved filling a glassy carbon crucible (Alfa Aesar) with NaCl and then placing inside a SiO$_2$ calorimetric tube. The tube was then inserted into the drop calorimeter well at ~830°C under argon (≥ 99.9%), (BOC) at a flowrate of 0.1 l min$^{-1}$ to prevent its oxidation, along with a reference tube for 15 minutes.

Experiments 23-26 involved placing Na$_2$CO$_3$ in an Al$_2$O$_3$ crucible (Dynamic ceramic) of dimensions; 50 mm OD x 48 mm ID x 50 mm high, in a furnace at 860°C at atmospheric pressure, and fusing under argon (≥ 99.9%) for 15 minutes (BOC). The crucible was then broken into several pieces in a glove box to produce crystals of Na$_2$CO$_3$. Then Na$_2$CO$_3$ and NaCl were placed into an evacuable pellet die (Specac) and a 5 mm plunger (Specac) placed ontop of the pellet die. These materials were then placed into a manual press, where a pressure was applied by the user for ~10 minutes to produce pellets of Na$_2$CO$_3$ and NaCl (figure 3.17). The exact pressure quantity was unknown due to the limitations of the press.

Figure 3.17: Manual press with pellet die.

Figure 3.18: Pellets (left) and crystals (right) of Na$_2$CO$_3$. 
Figure 3.18 shows the pellets and crystals of Na$_2$CO$_3$ which were ~5 mm in diameter and of irregular shape. The pellets of Na$_2$CO$_3$ were reasonably held together however it was suspected each pellet contained irregular voids due to the limitations of the press. This may have resulted in a slightly different surface area exposed to the atmosphere, which may cause the effects of moisture to play a role (forming sodium carbonate hydate (Na$_2$CO$_3$·nH$_2$O)). It is for this reason that crystals of Na$_2$CO$_3$ were also produced for purposes of comparison. This should result in voids being within the tens to hundreds of nanometres, corresponding to a minute and consistent porosity. These crystals and pellets were both kept in an evaporating oven prior to the experiments to minimize the effects of moisture in the atmosphere. Then an empty crucible was placed into the sample calorimetric tube, which was placed into the drop calorimeter well, at ~830ºC, under an argon flowrate of 0.1 l min$^{-1}$. The drop calorimeter was then stabilized for ~3 hours before each experiment before the addition of pellets or crystals of Na$_2$CO$_3$ and pellets of platinum (between 0.7-1.4 g) for calibration.

**Experiments 27-30** involved placing Na$_2$CO$_3$ in an Al$_2$O$_3$ crucible (Dynamic ceramic) of dimensions; 50 mm OD x 48 mm ID x 50 mm high, in a furnace at 860ºC, at atmospheric pressure and fusing under argon (≥ 99.9%) (BOC) for ~15 minutes. The crucible was then broken into several pieces in a glove box under argon (≥ 99.9%), prior to the experiments to produce crystals of Na$_2$CO$_3$. Then Na$_2$CO$_3$ and NaCl were placed into an evacuable pellet die (Specac) and a 5 mm plunger (Specac) placed onto the die. These materials were placed into the manual press, where a pressure was applied by the user for ~15 minutes, to produce pellets of Na$_2$CO$_3$ and NaCl. Then a glassy carbon crucible (Alfa Aesar) was filled with NaCl and placed inside a SiO$_2$ calorimetric tube. This tube was then inserted into the drop calorimeter well at ~830ºC under argon at a flowrate of 0.1 l min$^{-1}$ (BOC). The drop calorimeter was stabilized for ~3 hours before each measurement before the addition of pellets or crystals Na$_2$CO$_3$, pellets of NaCl and pellets of platinum (between 0.7-1.4 g) for calibration.
3.8.4.4 Solubility products of the reactants in the molten salt

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Temperature (°C)</th>
<th>Reactant(s)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>Signal stabilization (Al₂O₃ crucible)</td>
<td>830</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>32</td>
<td>Signal stabilization (Al₂O₃ crucible)</td>
<td>830</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>33</td>
<td>Signal stabilization (Al₂O₃ crucible)</td>
<td>830</td>
<td>NaCl</td>
<td>100</td>
</tr>
<tr>
<td>34</td>
<td>CaCO₃ in NaCl (Al₂O₃ crucible)</td>
<td>830</td>
<td>CaCO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>Na₂CO₃ in NaCl (Al₂O₃ crucible)</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>36</td>
<td>Na₂CO₃ in NaCl (glassy carbon crucible)</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>37</td>
<td>Na₂CO₃ in NaCl (glassy carbon crucible)</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>38</td>
<td>CaCO₃ in NaCl (glassy carbon crucible)</td>
<td>830</td>
<td>CaCO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>39</td>
<td>Na₂CO₃ in NaCl (glassy carbon crucible)</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>Na₂CO₃ in NaCl (platinum crucible)</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>41</td>
<td>Na₂CO₃ in NaCl (platinum crucible)</td>
<td>830</td>
<td>Na₂CO₃, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>42</td>
<td>NaCl</td>
<td>830</td>
<td>NaCl</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.8: Ksp values of the reactants in the molten salt experiments.

Potentiometry involved constructing a cell envelope, an ISE and a Ag/Ag⁺ reference electrode. The ISE was constructed from a closed ended YSZ (8 mol% Y₂O₃, 92 mol% ZrO₂) membrane of dimensions 6 mm OD, 4 mm ID containing Na₂CO₃ (0.1 mol kg⁻¹), molten AgCl-NaCl (0.75 mol kg⁻¹) and NaCl (0.1 mol kg⁻¹) with a silver wire (≥ 99.9%, 2 mm OD) and silicon cap. The Ag/Ag⁺ reference electrode was constructed from a closed-ended mullite (Al₆Si₂O₁₃) membrane of dimensions 6 mm OD, 4 mm ID, containing molten AgCl-NaCl (0.75 mol kg⁻¹) with a silver wire (≥ 99.9%, 2 mm OD) and silicon cap. The cell envelope was constructed from Inconel™ 600 or Stainless Steel 316L (Philip Cornes, Berkley Stainless Steel).

Experiments 31-33 involved placing NaCl inside an Al₂O₃, platinum and glassy or carbon crucible (Dynamic Ceramic, Alfa Aesar, Johnson Matthew) and placing inside a cell. The cell was then placed inside a high-temperature tubular furnace (Vecstar)
under an argon atmosphere (≥ 99.9%) (BOC) at 0.010 l/s. The furnace temperature was controlled by a Eurotherm 315 programmer (± 2°C) and the internal cell temperature measured with an N-type thermocouple (RS Components). The electrodes were inserted into the cell and connected electrically using a voltmeter (Uni-trend) and a drop tube constructed from an Al$_6$Si$_2$O$_{13}$ membrane was also inserted. The furnace temperature was then heated to 830°C at 2°C min$^{-1}$ for ~8 hours prior to the experiments and both the Ag/Ag$^+$ reference electrode and ISE were immersed in the molten salt, at a 1 cm depth.

**Experiments 34-41** involved placing NaCl inside an Al$_2$O$_3$, platinum and glassy carbon crucible (Alfa Aesar) and placing inside a cell, constructed from Inconel$^\text{TM}$ 600 or Stainless Steel 316L. The cell was then placed inside a high-temperature tubular furnace (Vecstar) under argon (≥ 99.9%) at 0.010 l/s. The electrodes were inserted into the cell and connected electrically using a voltmeter (Uni-trend) and a drop tube constructed from Al$_6$Si$_2$O$_{13}$ was also inserted. The furnace temperature was heated to 830°C at 2°C min$^{-1}$ for ~8 hours prior to the experiments, when both reference electrode and ISE were immersed in the molten salt, at a depth of 1 cm. Then pellets of Na$_2$CO$_3$ and CaCO$_3$ were added to the molten salt, using the drop tube and the potentiometric signal recorded using Uni-Trend software. The pellets of Na$_2$CO$_3$ and CaCO$_3$ were produced using a similar procedure to that described previously in the $\Delta H_{\text{mix}}$ and $\Delta H_f$ experiments however in this case an exact pressure of ~2 tonnes was applied to the pellet press (Specac). Upon the addition of pellets, time frames of between 10 minutes to 5 hours were allowed between each experiment and an argon gas bubbler inserted into the molten salt to ensure the complete dissolution and decomposition of the pellet.

**Experiment 42** involved removing a sample of evaporated powder on the cell envelope walls and taking to an SEM (Joel) machine. The experimental layout for the potentiometric cell and the cell envelope materials are shown in figure 3.19-3.20.
Figure 3.19 Image of the galvanic cell layout (top view).

Figure 3.20: Image of cell envelope materials; Inconel™ 600 (top) and Stainless Steel 316L (bottom).
3.3.5 Molten salt synthesis of cementitious compounds

The fifth stage of the investigation investigated the **MSS for cementitious compounds**: α-Na$_2$SiO$_3$, β-Na$_4$SiO$_4$, Ca$_3$SiO$_5$ and β-Ca$_2$SiO$_4$, from the reactants; SiO$_2$ (≥ 99%) CaCO$_3$ (≥ 99%) Na$_2$CO$_3$ (≥ 99%), to 830°C and 1100°C, using XRD and SEM. The cementitious compounds were also depicted on predominance diagrams for the molten salt systems considered. A list of selected experiments that were performed by the author is shown in table 3.10. Prior to all experiments the reactants were dried at ~200°C at atmospheric pressure for ~72 hours in an evaporating furnace (Carbolite).

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Description</th>
<th>Temperature (°C)</th>
<th>Reactant (s)</th>
<th>Composition (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>MSS of Ca$_2$SiO$_4$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>10, 5, 85</td>
</tr>
<tr>
<td>44</td>
<td>MSS of Ca$_2$SiO$_4$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>10, 5, 85</td>
</tr>
<tr>
<td>45</td>
<td>MSS of Ca$_2$SiO$_4$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>10, 5, 85</td>
</tr>
<tr>
<td>46</td>
<td>MSS of Ca$_2$SiO$_4$ (Al$_2$O$_3$ crucible)</td>
<td>1100</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>11.25, 3.75, 85</td>
</tr>
<tr>
<td>47</td>
<td>Separation of Ca$_2$SiO$_4$ (MgO cupel)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>48</td>
<td>Separation of Ca$_2$SiO$_4$ (MgO cupel)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>49</td>
<td>Separation of Ca$_2$SiO$_4$ (MgO cupel)</td>
<td>1100</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>MSS of Na$_2$SiO$_3$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>Na$_2$CO$_3$, SiO$_2$, NaCl</td>
<td>1.25, 3.75, 85</td>
</tr>
<tr>
<td>51</td>
<td>MSS of Na$_2$SiO$_3$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>Na$_2$CO$_3$, SiO$_2$, NaCl</td>
<td>1.25, 3.75, 85</td>
</tr>
<tr>
<td>52</td>
<td>MSS of Na$_2$SiO$_3$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>Na$_2$CO$_3$, SiO$_2$, NaCl</td>
<td>10, 5, 85</td>
</tr>
<tr>
<td>53</td>
<td>MSS of Na$_2$SiO$_3$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>10, 5, 85</td>
</tr>
<tr>
<td>54</td>
<td>MSS of Na$_2$SiO$_3$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>10, 5, 85</td>
</tr>
<tr>
<td>55</td>
<td>Separation of Ca$_2$SiO$_4$ (MgO cupel)</td>
<td>830</td>
<td>CaCO$_3$, SiO$_2$, NaCl</td>
<td>-</td>
</tr>
<tr>
<td>56</td>
<td>MSS of Na$_2$SiO$_3$ (Al$_2$O$_3$ crucible)</td>
<td>830</td>
<td>Na$_2$CO$_3$, SiO$_2$, NaCl</td>
<td>10, 5, 85</td>
</tr>
<tr>
<td>57</td>
<td>Separation of Na$_2$SiO$_3$ (MgO cupel)</td>
<td>830</td>
<td>Na$_2$CO$_3$, SiO$_2$, NaCl</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3.9: MSS of cementitious compounds experiments.**
Experiments 43-46 involved placing the reactants in an Al$_2$O$_3$ crucible (Dynamic ceramic). The crucible and contents were then placed in a muffle furnace (Vecstar) in an air atmosphere and open exhaust, and furnace temperature raised over ~5 hours to 830$^\circ$C and 1100$^\circ$C. After ~3 hours, the furnace was switched off and allowed to cool naturally for ~24 hours. The final samples were fused to the crucible, therefore a screwdriver and hammer was used to remove the pieces, before being taken for XRD (STOE, PANalytical).

Experiments 47-49 involved placing the products from Experiment 42, 43 and 45 and in an MgO cupel (Cerex Ltd) also previously dried at ~200$^\circ$C. This was selected due to its high melting temperature (at 1800$^\circ$C) and porosity to liquids. The cupel and contents were placed in a muffle furnace and the furnace temperature raised to ~1000$^\circ$C for ~6 hours. During this period, molten NaCl was absorbed by the cupel and a small quantity lost by evaporation. The furnace was then switched off and allowed to cool for ~1 hour. The samples were then removed using a screwdriver and hammer and taken for XRD (STOE, PANalytical).

Experiments 50-54 and 56 involved placing the reactants in an Al$_2$O$_3$ crucible (Dynamic ceramic). The crucible and contents were then placed in a muffle furnace with an air atmosphere and open exhaust, and temperature was raised over ~5 hours to 830$^\circ$C and 1100$^\circ$C. After ~3 hours, the furnace was switched off and allowed to cool naturally for ~24 hours. The samples were then removed using a screwdriver and hammer and taken for XRD (STOE, PANalytical).

Experiments 55 and 57 involved taking the products from Experiment 54 and 56 in an Al$_2$O$_3$ crucible (Dynamic Ceramic) and placing the contents in an MgO cupel (Cerex Ltd) - also previously dried at ~200$^\circ$C. The cupel and contents were placed in a muffle furnace (Vecstar) and the temperature was raised to ~1000$^\circ$C for ~6 hours. During this period, molten NaCl was absorbed by the cupel and a small quantity lost by evaporation. The furnace was then switched off and allowed to cool for ~1 hour and samples removed using a screwdriver and hammer and taken to an SEM (Joel). The experimental layout for these experiments is shown in figure 3.21.
Figure 3.21: MSS of cementitious compounds experimental layout.
Chapter 4

Results & discussion

4.1 Introduction

This chapter describes an investigation into the MSS of cementitious compounds. Initially the feasibility of the synthesis of cementitious compounds will be investigated using thermodynamic data. This will be used to suggest the reaction temperatures required to produce cementitious compounds, useful for the selection of a salt for MSS. Then the structures and purities of the reactants in the molten salt will be investigated using XRD and CV. This will be used to suggest the purity and phase transitions of the reactants at the reaction conditions, useful for analyzing XRD and SEM patterns. Then, the behaviour of the molten salt at the reaction conditions will be investigated using a DSC and the chemical equilibrium module in HSC-Chemistry 6.1, useful for describing the effects of vapour pressure upon the salt, and reaction conditions required for the experiments. Then, the dissolution of the reactants in the molten salt will be investigated, using a DSC, drop calorimetry, potentiometry and thermodynamic data, and will subsequently lead to obtaining $K_{sp}$, $\Delta H_{mix}$ values and phase diagrams, useful for determining whether MSS of cementitious compounds are possible. Then the MSS of cementitious compounds will be investigated using XRD and SEM and depicted on predominance diagrams, useful for determining which other compounds can be produced in this manner.
4.2 Feasibility of the synthesis of cementitious compounds

The initial stage of the investigation was to determine the feasibility of the synthesis of cementitious compounds; β-Ca$_2$SiO$_4$, Ca$_3$SiO$_5$, α-Na$_2$SiO$_3$ and β-Na$_4$SiO$_4$ from the reactants; CaCO$_3$, Na$_2$CO$_3$ and SiO$_2$, using thermodynamic data. This information will be used to select a salt for investigation.

![Diagram showing ΔH$_R$ and ΔG$_R$ data for the synthesis as a function of temperature.](image)

*Figure 4.1: ΔH$_R$ (bottom) and ΔG$_R$ (top) data for the synthesis as a function of temperature, 1 atm (HSC-Chemistry 6.1) [18-19].*

The reaction temperatures for the synthesis of β-Ca$_2$SiO$_4$, Ca$_3$SiO$_5$, α-Na$_2$SiO$_3$ and β-Na$_4$SiO$_4$ was investigated using the reaction equation module in HSC-Chemistry 6.1 [18]. This module plotted the Gibbs free energies (ΔG$_R$) and enthalpies of reaction (H$_R$) data for α-Na$_2$SiO$_3$, β-Na$_4$SiO$_4$, β-Ca$_2$SiO$_4$ and Ca$_3$SiO$_5$ from the reactants; CaCO$_3$, Na$_2$CO$_3$ and SiO$_2$, as a function of temperature respectively (figure 4.1).

The ΔH$_R$ data shows these reactions are highly exothermic, producing between ~100-400 kJ mol$^{-1}$ of energy over this temperature range. The ΔG$_R$ data shows these reactions occur at 330ºC, 450ºC, 600ºC and 750ºC respectively (shown by negative ΔG$_R$ values above these temperatures). This information is similar to previous reviews by Taylor, 1990 and synthesis studies by Wesselsky and Jensen, 2009, and the Na$_2$O-
SiO$_2$ phase diagram generated by Ryś and Müller, 2010 and Halter et al, 2004, whom state that $\beta$-Ca$_2$SiO$_4$, $\alpha$-Na$_2$SiO$_3$ and $\beta$-Na$_4$SiO$_4$ require reaction temperatures exceeding 680°C, 577.8°C and 750°C to be produced [14] [49] [246-247]. However the synthesis studies performed by Wesselsky and Jensen, 2009 state that Ca$_3$SiO$_5$ requires reaction temperatures exceeding 1250°C to be produced, and below which CaO and $\beta$-Ca$_2$SiO$_4$ is produced [14] [49]. This difference of ~500°C suggests there maybe an intermediate reaction which takes place before this compound is produced, probably $\beta$-Ca$_2$SiO$_4$. This intermediate reaction has also been reported on the CaO-SiO$_2$ phase diagram generated in the Bale et al, 2002, FactSage thermochemical database [209].

![Figure 4.2: Chemical equilibrium calculations for the synthesis of $\beta$-Ca$_2$SiO$_4$ (top) and Ca$_3$SiO$_5$ (bottom) as a function of temperature, 1 atm (HSC-Chemistry 6.1) [18-19].](image)

The reaction temperatures for the synthesis of $\beta$-Ca$_2$SiO$_4$ and Ca$_3$SiO$_5$ were also obtained using the chemical equilibrium module in HSC-Chemistry 6.1 [18]. This module plotted the equilibrium conditions for these reactions as a function of temperature (figure 4.2).

The diagram shows the synthesis of $\beta$-Ca$_2$SiO$_4$ and Ca$_3$SiO$_5$ occurs at ~820°C and ~1250°C. The information supports previous experimental studies by Wesselsky and Jensen, 2009, the $\Delta G_R$ data for $\beta$-Ca$_2$SiO$_4$ in the reaction equation module in HSC-
Chemistry 6.1, however disagrees with the $\Delta G_R$ data for $\text{Ca}_3\text{SiO}_5$ [14] [49]. This also supports the conclusion that $\beta$-$\text{Ca}_2\text{SiO}_4$ is an intermediate compound which forms before the formation of $\text{Ca}_3\text{SiO}_5$, and can be supported by the previous experimental synthesis studies by Wesselsky and Jensen, 2009 [49]. These authors also produced $\beta$-$\text{Ca}_2\text{SiO}_4$ and $\text{Ca}_3\text{SiO}_5$ in solid-state reactions at 680ºC, which required quenching and stabilization with foreign ions and at 1250ºC respectively [49]. It is the authors opinion however that these solid-state reactions are difficult to incorporate in an industrial process as this requires the presence of a liquid flux (melting the reactant with the lowest melting temperature (i.e. $\text{CaCO}_3$ (at 1339ºC))), making such reactions extremely energy-intensive [18]. MSS could potentially lower these reaction temperatures, and hence the energy requirement as suggested by Kimura, 1991 [50].

![Chemical equilibrium calculations](image_url)

*Figure 4.3: Chemical equilibrium calculations for the synthesis of $\beta$-$\text{Na}_4\text{SiO}_4$ (bottom) and $\alpha$-$\text{Na}_2\text{SiO}_3$ (top) as a function of temperature, 1 atm (HSC-Chemistry 6.1) [18-19].*

The reaction temperatures for the synthesis of $\beta$-$\text{Na}_4\text{SiO}_4$ and $\alpha$-$\text{Na}_2\text{SiO}_3$ were obtained using the chemical equilibrium module in HSC-Chemistry 6.1 [18]. This module plotted the equilibrium conditions of the reactions considered as a function of temperature (figure 4.3).

The diagram shows the synthesis of $\alpha$-$\text{Na}_2\text{SiO}_3$ and $\beta$-$\text{Na}_4\text{SiO}_4$ occurs at ~200ºC and ~750ºC respectively. This information agrees with the previous $\Delta G_R$ data shown earlier and demonstrates the synthesis of these compounds do not have an
intermediate compound. The information also supports the Na₂O-SiO₂ phase diagrams generated by authors such as Halter et al, 2004, Ryš and Müller, 2010 that β-Na₄SiO₄ and α-Na₂SiO₃ require reaction temperatures of ~800°C to be produced (using Na₂O instead of Na₂CO₃) [245-249]. This information also coupled with previous reports from Mersen Group, 2016 that state that these compounds are produced at reaction temperatures exceeding ~900°C, in a solid-liquid reaction (by melting Na₂CO₃ and reacting with SiO₂) [264]. This information suggests there is potential to lower the reaction temperatures in industry using MSS, and hence the overall energy requirement.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reaction temperature (°C)</th>
<th>ΔG_R data</th>
<th>Chemical equilibrium module</th>
<th>Solid-state synthesis studies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SiO₃(s)</td>
<td>330</td>
<td>200</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>Na₄SiO₄(s)</td>
<td>450</td>
<td>750</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>Ca₂SiO₄(s)</td>
<td>600</td>
<td>820</td>
<td>680</td>
<td></td>
</tr>
<tr>
<td>Ca₃SiO₅(s)</td>
<td>750</td>
<td>1250</td>
<td>1250</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Reaction temperatures for the synthesis of cementitious compounds; β-Na₄SiO₄(s), Na₂SiO₃(s), β-Ca₂SiO₄(s) and Ca₃SiO₅(s) [18-19].

The reaction temperatures from various sources were tabulated for comparison (table 4.1). It can be noted the reaction temperatures from ΔG_R data are often lower than the chemical equilibrium module in HSC-Chemistry 6.1, which can be attributed to the possible presence of intermediate compounds before the reaction which affects the calculation. The reaction temperatures from ΔG_R data and chemical equilibrium module were also different from previous synthesis studies, which can be attributed to differences in reaction conditions (such as the flow of gases affecting the pressure of the system).

This section has shown it maybe possible to synthesise α-Na₂SiO₃, β-Ca₂SiO₄, Ca₃SiO₅ and β-Na₄SiO₄ at reaction temperatures between 200-1250°C and hence MSS. This suggests a suitable molten salt for this investigation could be NaCl, which has a stability range between ~801-1413°C (the same range as the reactions investigated in this thesis) [56]. Also the viscosity of NaCl (1.03 Pa.s at 810°C) is in the same magnitude of H₂O (0.874 Pa.s at 25°C) which allows for a reasonable separation from an insoluble product and the vapour pressure of NaCl (0.302 mmHg °C⁻¹ at 801°C)
was lower than \( \text{H}_2\text{O} \) (26.5 mmHg °C\(^{-1}\) at 25°C) indicating minimal loss of the reactants at 830°C [56].

4.3 Structures and purities of the reactants in the molten salt

The second stage of this investigation was to investigate the structures and purities of the reactants: \( \text{Na}_2\text{CO}_3 \), \( \text{SiO}_2 \), \( \text{CaCO}_3 \) and \( \text{NaCl} \), using XRD and CV. This will be used to deduce any phase transitional temperatures at room temperature and pressure (25°C, 1 atm) and at 830°C, useful for analysing XRD and SEM data at a later stage.

![XRD pattern for CaCO\(_3\), NaCl and SiO\(_2\) powders (as received) at room temperature and pressure (25°C, 1 atm), typical operating conditions; 2θ scan range of 5-110° with 150 seconds per steps.](image)

The purities of the reactants were investigated by taking samples of \( \text{SiO}_2 \), \( \text{CaCO}_3 \) and \( \text{NaCl} \) directly from their containers (as received) at room temperature and pressure (25°C, 1 atm) and recording their XRD patterns (figure 4.4).

The structure for \( \text{Na}_2\text{CO}_3 \) was stated as \( \lambda \)-\( \text{Na}_2\text{CO}_3 \) (a monoclinic structure) on the packet, therefore no XRD studies were performed. However previous structural studies for \( \lambda \)-\( \text{Na}_2\text{CO}_3 \) have shown it undergoes polymorphic phase transitions at \( \approx\)332°C and \( \approx\)478°C to \( \beta \)-\( \text{Na}_2\text{CO}_3 \) (monoclinic structure) and \( \alpha \)-\( \text{Na}_2\text{CO}_3 \) (hexagonal...
structure) respectively, which is stable up to its melting temperature of 851ºC [246]. This suggests that Na$_2$CO$_3$ will be in its $\beta$-Na$_2$CO$_3$ phase (hexagonal structure) at 830ºC and 1100ºC. There is also evidence of the Na$_2$CO$_3$.nH$_2$O compound in literature, suggesting one should dry this reactant prior to experiments [215].

The XRD pattern for SiO$_2$ demonstrates the existence of $\alpha$-quartz (silica) its most natural form found in nature. There was no significant interaction with air/O$_2$ or H$_2$O vapour under these conditions, shown by the absence of SiO$_2$.nH$_2$O phases (hydrates) which can exist under these conditions, however previous reports by Monroe et al, 1969 suggests one should dry this reactant prior to experiments [253]. Previous structural studies by Kuskov and Fabrichnaya, 1987 and information stored on the ICCD suggest for $\alpha$-quartz (monoclinic structure) suggests it exhibits four polymorphic transitions at 573ºC, 870ºC and 1470ºC to $\beta$-quartz (hexagonal structure), $\beta$-tridymite (monoclinic structure) and $\beta$-cristobalite (cubic structure) up to its melting point of 1607ºC (including many other metastable structures still under investigation) [116] [215]. This suggests that SiO$_2$ ($\alpha$-quartz) is likely to exist in its $\beta$-quartz (hexagonal structure) at 830ºC and 1100ºC.

The XRD pattern for NaCl shows the existence of halite. The XRD pattern demonstrates no significant interaction with air/O$_2$ or H$_2$O vapour which can exist under these conditions and has been reported by Kotiranta and Roine 2009 [18]. Previous structural studies for NaCl by Stern 2001 and information stored on the ICCD have shown it exhibits a single cubic structure up to its melting temperature of 801ºC, which is its most natural phase found in nature [215] [254]. This suggests that halite is most likely to be found at 830ºC and 1100ºC.

The XRD pattern for CaCO$_3$ shows the existence of calcite. Previous structural studies for CaCO$_3$ by Clifford and Chen, 1998 have shown it exhibits three anhydrous polymorphs namely; Vaterite (hexagonal structure), Aragonite (orthorhombic structure) and calcite (monoclinic structure) [255]. These polymorphic transitions occur at $\sim$60ºC and $\sim$400ºC of which the last two are metastable structures as shown on the Na$_2$O-SiO$_2$ phase diagram [247]. This suggests that CaCO$_3$ will probably remain in its calcite phase (monoclinic structure) at 830ºC and 1100ºC. There is also
evidence of the CaCO$_3$.nH$_2$O compound in literature and on the ICCD which suggests one should dry this reactant prior to experiments [215] [255].

![Figure 4.5: ΔC$_p$ data for the reactants; Na$_2$CO$_3$, CaCO$_3$, SiO$_2$ and NaCl as a function of temperature, 1 atm (HSC Chemistry 6.1) [18-19].](image)

The temperatures of the phase transitions of the reactants were shown by plotting the ΔC$_p$ data for Na$_2$CO$_3$, CaCO$_3$, SiO$_2$ and NaCl, as a function of temperature respectively at 1 atm. This was plotted using the “H, S, C and G, Diagrams” module in HSC-Chemistry 6.1, which contains a list of mathematical functions for the thermodynamic data, compiled by Barin et al, 2008 (figure 4.5) [18-19].

The ΔC$_p$ data for SiO$_2$ lies between 40-60 J mol$^{-1}$ °C$^{-1}$, exhibiting a directional change at ~570°C, which can be attributed to its phase transitional temperature from α-quartz (monoclinic structure) to β-quartz (hexagonal structure). It also shows that the other transitional temperatures are not that significant in terms of energy being released from the bonds. This agrees with previous structural studies for SiO$_2$ by Kuskov and Fabrichnaya, confirming that it is most likely to be found in its β-quartz phase at 830°C and 1100°C [18-19] [116].

The ΔC$_p$ data for NaCl lies between 40-55 J mol$^{-1}$ °C$^{-1}$, exhibiting a directional change at ~800°C which can be attributed to its melting temperature at 801°C. This can be
attributed to being a single halite phase (monoclinic structure) throughout the temperature range. This agrees with previous structural studies for NaCl, stored on the ICCD and thermodynamic tables, confirming that it is most likely to remain in this state at 830ºC and 1100ºC [18-19] [215].

The $\Delta C_p$ data for CaCO$_3$ lies between 80-150 J mol$^{-1}$ C$^{-1}$, exhibiting a directional change at 1300ºC, which can be attributed to its melting temperature at 1336ºC. This shows that the transitional temperatures are not that significant in terms of energy being released from the bonds. This agrees with previous structural studies for CaCO$_3$ by Clifford and Chen, 1998 and thermodynamic tables, confirming that it is most likely to remain in its calcite phase at 830ºC and 1100ºC [18-19] [215].

The $\Delta C_p$ data for Na$_2$CO$_3$ lies between 50-190 J mol$^{-1}$ C$^{-1}$, exhibiting two directional changes at 470ºC and 851ºC, which can be attributed to its phase transitional temperature from $\beta$-Na$_2$CO$_3$ (monoclinic structure) to $\alpha$-Na$_2$CO$_3$ (hexagonal structure) and its melting temperature of 851ºC. It also shows the other transitional temperatures are not that significant in terms of energy being released from the bonds. This agrees with previous structural studies for Na$_2$CO$_3$, thermodynamic tables and the ICCD, confirming it is most likely to remain as $\alpha$-Na$_2$CO$_3$ (monoclinic structure) at 830ºC and 1100ºC [18-19] [215].
Figure 4.6: CV curve using platinum working and counter electrodes and Ag/Ag\(^{+}\) reference electrode in NaCl at 830°C (scan rate 0.1 V s\(^{-1}\), electrode surface area 0.05 cm\(^2\)).

The purity of NaCl at the reaction conditions, was also investigated by immersing two platinum wires (sheathed in hollow Al\(_6\)Si\(_2\)O\(_{13}\) tubes) in molten NaCl and connecting to a silver-silver chloride (Ag/Ag\(^{+}\)) reference electrode and potentiostat. These wires behaved as counter and working electrodes, and the potentiostat supplied electrical charge (electrons) for the facilitation of non-spontaneous electrochemical reactions in the molten salt (and measure the current across the electrodes). The electrodes were immersed in molten NaCl, at a depth of 1 cm, at 830°C and the CV curve recorded (figure 4.6).

The CV curve shows an increase in current at 0.7 V/Ag/Ag\(^{+}\) (E4a) which is presumed to be due to a compound forming at the anode (probably sodium ions (Na\(^{+}\)) converting to sodium liquid (Na (l))) and a decrease in current at -1.8 V/Ag/Ag\(^{+}\) (E4b) which is presumed to be due to a gas forming at the cathode (probably chlorine ions (Cl\(^{-}\)) converting to chlorine (Cl\(_2\) (g))). These are shown by the following electrochemical reactions.

\[
\text{Na}^{+} + \text{e} = \text{Na (l)} \quad \text{Equation 4.1}
\]
The difference between these values is presumed to be the decomposition potential \( \Delta V_d \) of \( \text{NaCl} \) at \( \sim 3.1 \text{ V} \), which is in good agreement with values calculated using the Gibbs energy of the dissociation reaction \( \Delta G^\circ \);

\[
E_{\text{Na/Na}^+} = -\frac{\Delta G^\circ}{F} = -3.2 \text{ V}
\]  

Equation 4.3  

Equation 4.3 describes the reduction potential for the \( \text{Na/Na}^+ \) reduction potential where \( \Delta G^\circ \) is the Gibbs free energy for the dissociation reaction and \( F \) is the Faraday's constant \([256]\). There is a difference of 0.1 V between the theoretical and actual value which can be attributed towards reaction inefficiencies (common for reactions involving gases) or a temperature gradient across the molten salt. The shape of the CV curve at the cathode is characteristic of a substance dissolving in the molten salt, which suggests good solubility of the presumed compound (\( \text{Na (l)} \)). This CV curve also confirms the high purity of molten \( \text{NaCl} \) shown by no further reduction peaks for electrochemical reactions, such as \( \text{O}^{2-} \) ions.

\[ \Delta G^\circ \text{ NaCl at } 830^\circ \text{C} = 312.4 \text{ kJ mol}^{-1}. \]

Faraday's constant = 96485.3 C mol\(^{-1}\).
The decomposition potential of NaCl can be represented on a fundamental predominance diagram for the Na-O-Cl system at 830°C, 1 atm (figure 4.7). This diagram utilizes the calculation method described by Littlewood and Trémillon [189-191]. The diagram displays O\textsuperscript{2-} ion activity (in logarithmic scale) on the x-axis and reduction potentials for electrochemical reactions on the y-axis, relative to the Cl\textsubscript{2}/Cl\textsuperscript{-} reduction potential and reduction potentials on the z-axis, relative to the Ag\textsuperscript{+}/Ag reduction potential for comparison. The Cl\textsubscript{2}/Cl\textsuperscript{-} reduction potential is frequently set as zero in a pure halide melt which has a difference of ~0.8 V relative to the Ag\textsuperscript{+}/Ag reduction potential, which has also been confirmed by experimental measurements by Plambeck (molten NaCl-KCl at 800°C) [257]. The reduction potential for O\textsubscript{2}/O\textsuperscript{2-} was calculated using the ΔG\textsubscript{f} of the O\textsuperscript{2-} ion, which was calculated using ΔG\textsubscript{f} for Na\textsubscript{2}O (l) from HSC-Chemistry 6.1 using the following equations [18]:

\begin{align*}
\text{Na}^+ + \text{e} &= \text{Na} \text{ (l)} \\
2\text{Na} + \frac{1}{2}\text{O}_2 &\rightarrow 2\text{Na}^+ + \text{O}^{2-} \quad \text{Equation 4.4}^{18} \\
2\text{e} + \frac{1}{2}\text{O}_2 &\rightarrow \text{O}^{2-} \quad \text{Equation 4.5}^{19} \\
\end{align*}

\begin{align*}
\Delta G\textsubscript{f}^{\text{NaCl at 830°C}} &= 312.5 \text{ kJ mol}^{-1}[18-19] \\
\Delta G\textsubscript{f}^{\text{Na}_2\text{O (l) at 830°C}} &= -255.4 \text{ kJ mol}^{-1}[18-19] \\
\end{align*}
Equations 4.4-4.6 describe the relationships used to obtain the \( \Delta G_f \) of the O\(^{2-}\) ion in molten NaCl. This allows the \( \Delta G_f \) of the O\(^{2-}\) ion to be different according to the electrolyte chosen. The reduction potential for the O\(_2\)/O\(^{2-}\) redox system is shown by the broken line at -1.8 V for infinite O\(^{2-}\) activities which then decreases for low O\(^{2-}\) activities. The \( \Delta V_d \) for molten NaCl was obtained using the relationship described previously (equation 4.3). At the anodic and cathodic limits, sodium liquid (Na (l)) and Cl\(_2\) are produced which is in agreement with the CV curve of molten NaCl. A difference of 3.2 V exists between these limits, which is the \( \Delta V_d \) of NaCl [190]. Between these limits, molten NaCl is partially dissociated into Na\(^+\) and Cl\(^-\) ions. This diagram provides a framework to superimpose further electrochemical and chemical reactions occurring in the molten salt. The molten salt reactions depicted on this diagram can be found in table A5 (Appendix).

This section has shown the reactants were pure with no significant interaction with air or moisture. Also these compounds are expected to exhibit phase transitions at the reaction temperatures, therefore all phases should be considered upon examining XRD patterns.

### 4.4 Behaviour of the molten salt at the reaction conditions

The third stage of this investigation was to investigate the **behaviour of the molten salt at the reaction conditions** to determine the effects of vapour pressure of NaCl at 830°C, using thermodynamic data and a DSC. This was to select suitable reaction conditions required for the dissolution of the reactants and MSS of cementitious compounds.

\[ \Delta G_f \text{ at } 830°C = 365.6 \text{ kJ mol}^{-1} \]
The behaviour of molten NaCl exposed to the atmosphere at the reaction conditions (830°C, 1100°C) was investigated by filling an Al₂O₃ crucible with NaCl and placing in a DSC under N₂ (experiment 5). The crucible was then heated at 5°C min⁻¹ to 1200°C and the heat flow and mass signal was recorded (figure 4.8).

The diagram shows a strong endothermic peak (at ~801°C), which can be attributed towards the fusion temperature of NaCl. This agrees with previous experimental studies by Ye et al, 2014 on the melting point of NaCl (at 801°C) [128]. A sharp decrease in mass was observed after 801°C, which can be attributed towards the effects of increasing vapour pressure of the molten salt and the effect of a flow of gas coupled with colder surfaces in the DSC equipment. There is also sufficient evidence to suggest that pressurized vessels cause increase of partial pressure of gases inside the cell, however these results suggest this probably wouldn’t affect the outcome of the melting temperatures.
The behaviour of NaCl in a closed environment at 830°C and 1100°C, was investigated using a DSC. The procedure involved filling an Inconel™ 600 crucible with NaCl and CaCl₂ and hermetically sealing it. The Inconel™ 600 crucibles were selected due to their proven stability in molten chlorides [220]. To serve as a suitable comparison, CaCl₂ was prepared from CaCl₂.6H₂O, which was dehydrated according to the procedure described earlier. The crucible was then placed in a DSC under argon and the heat flow signal recorded (figure 4.9).

The diagram shows strong exothermic peaks at 801°C and 770°C which can be attributed towards the fusion temperatures of NaCl and CaCl₂ respectively. These are in agreement with the previous studies by Ye et al, 2014 and thermodynamic tables for the melting temperatures of NaCl and CaCl₂ (at 801°C and 772°C respectively) [18] [220]. The shape of the peaks can be attributed to the liquidus temperatures for high purity substances as reported by Brown and Gallagher, 2008 [222]. The heat flow signal for CaCl₂ showed a gradient change at 260°C, which can be attributed to the decomposition of CaCl₂.6H₂O to CaCl₂, suggesting the purification procedures could be improved and/or the atmosphere of the glove box may have had minute amounts of moisture.
The behaviour of molten NaCl was also investigated using the chemical equilibrium module in HSC-Chemistry 6.1, by plotting the equilibrium conditions for NaCl as a function of temperature (figure 4.10) [18]. The diagram shows these compounds are subjected to the increasing effects of vapour pressure as shown by the changes in composition below the boiling temperature. It is expected the flow of gases above the molten salt coupled with temperature gradients in reaction vessels can cause the evaporation of the molten salt, therefore it is expected that some mass loss may be present during the experiments.

This section has shown it is possible to utilize molten NaCl at these reaction temperatures; however the thermodynamic data suggests the salt is likely to evaporate beyond its melting temperature, probably due to the increasing effects of vapour pressure. This could also in turn have delirious effects upon the experiments performed, such as in the presence of a temperature gradient across the reaction vessel will likely drive the evaporation process. It is the author’s opinion that the reaction vessels that will be used should be sealed where possible to minimize this occurring.
4.5 Dissolution of the reactants in the molten salt

The fourth stage of this investigation was to investigate the dissolution of the reactants; Na$_2$CO$_3$, CaCO$_3$ and SiO$_2$ in NaCl at 830ºC, using XRD, SEM, drop calorimetry and a DSC (which will subsequently lead to obtaining K$_{sp}$, $\Delta H_{mix}$ values and phase diagrams). This was to determine whether the MSS of cementitious compounds are possible.

4.5.1 Phases of the reactants in the molten salt

This section investigates the dissolution reactions of the reactants; Na$_2$CO$_3$, CaCO$_3$ and SiO$_2$ in molten NaCl at the reaction conditions (830 ºC, 1 atm), using XRD and SEM.

Initially, the dissolution of the reactants: Na$_2$CO$_3$ and CaCO$_3$ in NaCl were investigated at 830ºC, using XRD and SEM, by filling an Al$_2$O$_3$ crucible with the reactants and raising the temperature to 830ºC for ~3 hours (experiment 8-9). The
Al₂O₃ crucible was then cooled and samples removed (using the procedure described earlier) and taken to record their XRD patterns (figure 4.11).

The XRD pattern shows multiple low intensity peaks of Na₂O probably produced during the decomposition of Na₂CO₃. The XRD pattern shows multiple peaks for Na₂CO₃, indicating the extent of the decomposition reaction for Na₂CO₃ was low. It is suspected this decomposition reaction occurred at the melting temperature of NaCl (at 801°C) which can be probably attributed to a lower eutectic melting temperature of the mixture [258].

The XRD pattern also shows strong multiple peaks of CaO, which were probably produced due to the decomposition of CaCO₃. This suggests a ~3 hour reaction time was sufficient to complete the reaction and the reaction kinetics for the decomposition of CaCO₃ were sufficiently high, in comparison to other carbonates such as Na₂CO₃, as reported by Hills, 1968 and Kim and Lee. 2001 [259-260]. This also confirms that reactions in molten salts can occur more rapidly in comparison to solid-state reactions (probably due to the dissolution of the compounds in the molten salt), as reported by Kimura, 1991 and Trémillon and Inman, 1997 [50-51]. In both cases, no other significant peaks for additional compounds were observed (CaCl₂ or Al₂O₃) before separation stage, which indicates the dissolution of the Al₂O₃ crucible or interaction of molten NaCl with the reactants were not that significant.

The decomposition temperatures for CaCO₃ and Na₂CO₃ were lower than those reported by previous solid-state reactions (at 900°C and 851°C respectively), reported by Motzfeldt 1955 and Hills, 1968, from thermodynamic data (825°C for CaCO₃) and the chemical equilibrium module (860°C for CaCO₃) [18-19] [258-259]. This was probably attributed to the exhaust above our muffle furnace, which drove the decomposition reactions to completion.
The effect of reaction time upon the dissolution of CaCO$_3$ in molten NaCl was investigated by filling an Al$_2$O$_3$ crucible with the reactants and heating to 830°C, for ~2 hours (experiment 11) and ~3 hours (experiment 10, 12). Then samples were removed from the crucible using the procedure described earlier and their XRD patterns recorded (figure 4.12).

The XRD pattern shows strong multiple peaks for CaCO$_3$ (experiment 11) after a reaction time of ~2 hours. This suggests this molten salt reaction did not go to completion. Strong multiple peaks for CaO were observed after ~3 hours (experiment 10, 12) which indicates a high extent of reaction for the decomposition of CaCO$_3$ in molten NaCl and demonstrates good data reproducibility. In both cases, no other peaks were observed for additional compounds (CaCl$_2$ or Al$_2$O$_3$), indicating no significant dissolution of the Al$_2$O$_3$ crucible or the molten salt itself with the reactants.
The phases produced during the dissolution of CaCO$_3$ and Na$_2$CO$_3$ in molten NaCl (experiments 13-14), were investigated by removing samples from the Al$_2$O$_3$ crucible, using the procedure described earlier and taking to an SEM for particle size and EDS analysis (figure 4.13).

The EDS analysis suggested the phases; Na$_2$O (experiment 13), CaO (experiment 14) NaCl and/or their constituent ions (O$^{2-}$ and CO$_3^{2-}$ ions) were possibly present. Na$_2$O was probably produced during the decomposition of Na$_2$CO$_3$ and CaO during the decomposition of CaCO$_3$. The O$^{2-}$ ion could also have been caused by the dissolution
of O\textsubscript{2} from the atmosphere in molten NaCl however the solubility of this gas has been reported to be generally low, as shown by Hefter and Tomkins, 2004 [261].

The amount of calcium (experiment 14) was also reported to be extremely low, which can be attributed to a low K\textsubscript{sp} value of CaO in molten NaCl. No other elements were observed such as glassy carbon or aluminium, indicating no significant dissolution of the Al\textsubscript{2}O\textsubscript{3} crucible in molten NaCl and in agreement with previous authors whom used similar crucibles [50]. It also demonstrates the decomposition of CaCO\textsubscript{3} was driven to completion in both cases, due to presence of CO\textsubscript{2}. The agglomerated particle sizes for experiment 14 (~200 µm) was lower than experiment 13 (~2 mm) which also suggests that Na\textsubscript{2}O has higher physical solubility in molten NaCl than CaO and/or K\textsubscript{d} value which can correspond to higher particle sizes. No hydrolysis of NaCl was observed, at the reaction conditions which can be attributed to low humidity levels in the atmosphere.

![Figure 4.14: ΔH\textsubscript{R} (bottom) and ΔG\textsubscript{R} (top) data for the decomposition of Na\textsubscript{2}CO\textsubscript{3} and CaCO\textsubscript{3} as a function of temperature, 1 atm (HSC-Chemistry 6.1).](image)

The decomposition of Na\textsubscript{2}CO\textsubscript{3} and CaCO\textsubscript{3} was also investigated using the reaction equation module in HSC-Chemistry 6.1 [18]. This module contained a list of
The ΔG<sub>R</sub> data for the decomposition of Na<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub> indicates these reactions are highly endothermic, and require between ~200-300 kJ mol<sup>-1</sup> of energy over this temperature range. This indicates these reactions won’t proceed unless an external source of energy is applied.

The ΔG<sub>R</sub> data for the decomposition of CaCO<sub>3</sub> shows this reaction occurs above ~890ºC, shown by negative ΔG<sub>R</sub> values above this temperature. This supports previous decomposition studies by Motzfeldt, 1955 and Hills, 1968 whom show that CaCO<sub>3</sub> decomposes at ~840ºC [258-259]. This reaction has also proven to be reversible and upon cooling will react with CO<sub>2</sub> in the atmosphere to revert back to CaCO<sub>3</sub>.

The ΔG<sub>R</sub> data for the decomposition of Na<sub>2</sub>CO<sub>3</sub> shows this reaction is unfeasible up to 1500ºC, due to positive ΔG<sub>R</sub> values throughout this temperature range. However, this doesn’t agree with previous decomposition studies by Kim and Lee, 2001, and Motzfeldt, 1955, whom show that Na<sub>2</sub>CO<sub>3</sub> decomposes slowly upon melting at 851ºC, however the amount of Na<sub>2</sub>O produced is ~1 mass % in comparison to Na<sub>2</sub>CO<sub>3</sub> [258] [260]. This was probably due to different reaction conditions being used, such as the presence of an inert gas to increase the partial pressure of CO<sub>2</sub> or the fact that ΔG<sub>R</sub> data can only serve as a useful “guide” to solving reaction feasibility problems and requires improved thermodynamic data (ΔG<sub>f</sub> function) for Na<sub>2</sub>CO<sub>3</sub> (s).
The decomposition of CaCO$_3$ and Na$_2$CO$_3$ was also investigated using the chemical equilibrium module in HSC-Chemistry 6.1 [18]. The module plotted the equilibrium conditions of species as a function of temperature respectively (figure 4.15).

The chemical equilibrium module shows that CaCO$_3$ (s) decomposes to CaO (s) and CO$_2$ (g) at ~840°C, which supports previous decomposition studies by Motzfeldt, 1955 and Hills, 1968 and our dissolution experiments [259-260]. The diagram also shows that Na$_2$CO$_3$ (s) only transforms to Na$_2$CO$_3$ (l) and doesn’t decompose, which doesn’t agree with the current dissolution results or literature, probably due to the pressure of the system being different to 1 atm which could have been caused by the flow of argon gas over molten NaCl.
The **dissolution of the reactant**; SiO$_2$ in NaCl at 830°C was investigated by filling an Al$_2$O$_3$ crucible with SiO$_2$ and NaCl and heating to 830°C over ~3 hours and leaving at the reaction temperature for ~3 hours. Upon cooling to room temperature, a sample was removed from the crucible using the procedure described earlier, and taken to an SEM for particle size and EDS analysis (figure 4.16).

The EDS analysis suggested the phases; SiO$_2$, Na$_2$O, NaCl and/or their constituent ions (O$^{2-}$ or Si$^{4+}$ ions) were possibly present (experiment 15). This could have been either caused by the solubility of SiO$_2$ in molten NaCl or the dissolution of O$_2$ in molten NaCl from the atmosphere, however as the solubility of O$_2$ in molten NaCl has been reported to be low, it was deemed to be the latter [261]. Solid particles were evident in molten NaCl which were visually evident, which also suggested a low solubility in the melt. No other elements were present, such as glassy carbon or aluminium indicating no significant dissolution of the Al$_2$O$_3$ crucible.

![Figure 4.16: SEM image and EDS analysis of SiO$_2$ in NaCl at 830°C, for 3 hours.](image)
This section has shown that Na$_2$CO$_3$ and CaCO$_3$ decompose in molten NaCl to Na$_2$O, CaO and CO$_2$ and have some solubility in the melt. This is in agreement with previous decomposition studies by Motzfeldt, 1955, Hills, 1968 and Kim and Lee. 2001 and the $\Delta$G$_R$ data for the decomposition of CaCO$_3$ [258-260]. These compounds probably form CO$_3^{2-}$ and O$_2^-$ ions in molten NaCl, and produce CO$_2$ in the process. SiO$_2$ also dissolves in molten NaCl but with a limited solubility in comparison to other oxides (such as CaO) and no other phases were detected. In all cases, the Al$_2$O$_3$ crucible had a limited interaction with the reactants, as no compounds containing the Al$^{3+}$ ion were detected on the XRD patterns. The next stage is to attempt to describe the dissolution reactions that probably take place. This can be performed using previous dissolution and decomposition studies of carbonates by Cherginets, 2005 and Combes et al, 1977 [130] [263]. Using the same analogy, the dissolution and decomposition of Na$_2$CO$_3$ in molten NaCl can be described using the following equations;

\[ \text{Na}_2\text{CO}_3 (s) = \text{Na}_2\text{CO}_3 (l) \]  \hspace{1cm} \text{Equation 4.7}

\[ \text{Na}_2\text{CO}_3 (l) = 2\text{Na}^+ + \text{CO}_3^{2-} \]  \hspace{1cm} \text{Equation 4.8}

\[ \text{CO}_3^{2-} = \text{CO}_2(g) + \text{O}^2^- \]  \hspace{1cm} \text{Equation 4.9}

\[ 2\text{Na}^+ + \text{O}^2^- = \text{Na}_2\text{O} (l) \]  \hspace{1cm} \text{Equation 4.10}

\[ \text{Na}_2\text{O} (l) = \text{Na}_2\text{O} (s) \]  \hspace{1cm} \text{Equation 4.11}

Equation 4.7-4.11 describes the dissolution and decomposition of Na$_2$CO$_3$ (s) in molten NaCl, to produce Na$^+$, CO$_3^{2-}$, O$_2^-$ ions and CO$_2$. The O$_2^-$ ions then react with Na$^+$ ions in molten NaCl to form Na$_2$O (l), which possibly precipitates out of the molten salt. These reactions can be summarised using the following equation;

\[ \text{Na}_2\text{CO}_3 (l) = \text{Na}_2\text{O} (l) + \text{CO}_2 (g) \]  \hspace{1cm} \text{Equation 4.12}

Equation 4.12 describes the dissolution and decomposition of Na$_2$CO$_3$ (s) in molten NaCl, to produce Na$_2$O (l) and CO$_2$ (g). Using a similar analogy, the dissolution and decomposition of CaCO$_3$ in molten NaCl can be described using the following equations;

\[ \text{CaCO}_3 (s) = \text{CaCO}_3 (l) \]  \hspace{1cm} \text{Equation 4.13}

\[ \text{CaCO}_3 (l) = \text{Ca}^{2+} + \text{CO}_3^{2-} \]  \hspace{1cm} \text{Equation 4.14}
Equation 4.13-4.17 describes the dissolution and decomposition of CaCO$_3$ (s) in molten NaCl to produce Ca$^{2+}$, CO$_3^{2-}$, O$^{2-}$ ions and CO$_2$. The O$^{2-}$ ions then react with Ca$^{2+}$ ions to form CaO (l), which possibly precipitates out of the molten salt. These reactions can also be summarised using the following equation:

\[
\text{CaCO}_3 (s) = \text{CaO} (s) + \text{CO}_2 (g)
\]  

Equation 4.18 describes the dissolution and decomposition of CaCO$_3$ (s) in molten NaCl, to produce CaO (l) and CO$_2$ (g). Using a similar analogy, the dissolution of SiO$_2$ in molten NaCl can be written in the following equation.

\[
\text{SiO}_2 (s) = \text{Si}^{4+} + 2\text{O}^{2-}
\]  

Equation 4.19 describes the dissolution of SiO$_2$ (s) in the molten salt, to produce Si$^{4+}$ and O$^{2-}$ ions. As the solubility of SiO$_2$ (s) in molten NaCl was deemed to be low in our case, only the solid phase was considered. However the author didn’t consider the possibility of SiO$_3^{2-}$ complex ions which can also form when SiO$_2$ (s) reacts with O$^{2-}$ ions in molten NaCl, as described by Yasuda 2007, and further experimental studies should be performed to investigate this [208]. The agglomerated particle sizes for SiO$_2$ (~100 µm) suggests a low solubility in molten NaCl and/or K$_d$ value which can correspond with higher particle sizes. No hydrolysis of NaCl was observed at 830ºC, as described by Hanf and Sole, 1970, which can be attributed to low humidity levels in the atmosphere [240].
4.5.2 Phase diagrams of the reactants in the molten salt

The dissolution of the reactant; Na\textsubscript{2}CO\textsubscript{3} in molten NaCl was investigated by obtaining the liquidus and solidus points of molten NaCl-Na\textsubscript{2}CO\textsubscript{3}, using a DSC. \textsuperscript{21} However the dissolution of the reactants; SiO\textsubscript{2} and CaCO\textsubscript{3} in molten NaCl were not investigated however due to their low solubilities in the melt, which have been described previously by Yasuda, 2007 and Cherginets, 2005 \cite{130} \cite{208}.

Initially, an Al\textsubscript{2}O\textsubscript{3} crucible was filled with Na\textsubscript{2}CO\textsubscript{3} and NaCl and heated in a furnace to \textasciitilde900°C and leaving at the reaction temperature for \textasciitilde30 minutes. Then samples were removed from the crucible, using the procedure described earlier and placed in an Inconel\textsuperscript{TM} 600 crucible. This material was selected due to its high melting temperature

\textsuperscript{21} These experiments were performed at the Wrocław University of Technology, in Poland with the support of Dr. J. Kapala and Dr. L. Rycerz.
(-1100°C) and proven stability in molten chlorides [220]. The Inconel™ 600 crucible was then placed in a DSC, alongside an empty reference crucible (experiment 16-20). The DSC was then heated at a temperature ramp rate of 5°C min⁻¹ over ~5 hours and the heat flow signal recorded (figure 4.17).

The diagram shows multiple peaks occurring in the same experiment, which are characteristic of liquidus and solidus points of mixtures [222]. This confirms that heat effects associated with fusion/transitional temperatures of our samples were greater than any interaction of the sample with the Inconel™ 600 crucible, which is good for our investigation. The onset temperatures for the peaks from the cooling curves were used to plot the phase diagram for molten NaCl-Na₂CO₃. The enthalpies of fusion for the samples were determined by integrating the peaks and using the Calisto Thermal Analysis Software by Setaram [228]. The values were; -88.3 J g⁻¹ (20 mol% of Na₂CO₃), -488.51 J g⁻¹ (50 mol% of Na₂CO₃) -255.6 J g⁻¹ (30 mol% of Na₂CO₃) and -144.1 J g⁻¹ (60 mol% of Na₂CO₃). This information suggests the mixture had a eutectic point between 40-60 mol% of Na₂CO₃.
The liquidus and solidus points from the DSC heat flow signal were plotted as a function of composition, also described as the phase diagram for the NaCl-Na$_2$CO$_3$ binary system (figure 4.18). The literature value for Na$_2$CO$_3$ was obtained from thermodynamic tables compiled by Barin et al., 2008 [19].

This diagram is characteristic of a eutectic phase diagram with a eutectic point at 47 mol% Na$_2$CO$_3$. This point was determined by extrapolating the liquidus lines on the NaCl-rich side. A complete solid phase was also reported below 638°C which was lower than previously thermodynamic calculations performed by Yaokawa et al., 2007, Lindberg et al., 2006 and Iwasawa and Maeda, 2000, whom illustrated a solidus temperature of 634°C [106] [124]. This was attributed to the effects of the decomposition of Na$_2$CO$_3$ to Na$_2$O and CO$_2$ under these conditions. The diagram also confirms that Na$_2$CO$_3$ decomposes in molten NaCl at elevated temperatures, which is in agreement with previous decomposition studies by Motzfeldt, 1955 and Kim and Lee, 2001 [258] [260].

Figure 4.18: Phase diagram for molten NaCl-Na$_2$CO$_3$, under argon.
The author couldn’t locate any transitional points for Na₂CO₃, probably due to the mixture being heated to 860°C prior to measurements to produce β-Na₂CO₃ (hexagonal structure) from its original α-Na₂CO₃ (monoclinic structure). There was also no evidence of mutual solubility of phases, which are often evident by additional peaks on the NaCl or Na₂CO₃ rich-side, which can also be described by thermodynamic calculations performed by Dessureault, 1990 [106].

![Figure 4.19: Phase diagrams of the NaCl-Na₂CO₃ binary system by previous authors and DSC measurements](124-126).

The liquidus and solidus points from previous phase diagrams for molten NaCl-Na₂CO₃ were obtained using Plot Digitizer 2.6.3, and superimposed onto the current experimental phase diagram for analysis (figure 4.19) [125-126]. The liquidus and solidus lines (functions) were obtained by linear extrapolation using Origin Pro 8 [225]. The values for the liquidus and solidus points (experiment 7 and 16-20) can be found in tables A3-A4 (Appendix).
The diagram shows Na₂CO₃ is soluble in molten NaCl with a eutectic point between 40-50 mol% and confirms that Na₂CO₃ is not stable under these conditions. These results are slightly different to those reported in literature, which can be attributed to the decomposition of Na₂CO₃ and evaporation of NaCl occurring in the melt. This was probably due to the presence of argon over our experimental setup in comparison to CO₂ used by Lindberg et al, 2006 and Yaokawa et al, 2007 and/or the use of faster heating times [124-126]. There are also differences in the fusion temperatures of Na₂CO₃ (at 851°C or 858°C) which can be attributed to confusions over the phase transitional temperatures of Na₂CO₃ [106].

![Image of the Inconel™ 600 (left) and Al₂O₃ (right) crucibles after phase diagram experiments.](figure4.20)

Images were taken of the Al₂O₃ crucibles that were used in the preparation of the NaCl-Na₂CO₃ binary mixtures, and the Inconel™ 600 crucible that was used for obtaining the liquidus and solidus points. The images for the Al₂O₃ crucibles were taken after ~1 hour at 900°C and the image of the Inconel™ 600 was taken after ~6 hours reaction temperatures between 25-850°C (figure 4.20).

The diagram shows the surface of the Inconel™ 600 crucible exhibiting a slight discoloration, from silver to grey. These colour changes can be attributed to the oxidation of the crucible at the reaction temperatures with O₂ gas that was possibly present. This suggests O₂ could have entered the atmosphere within the DSC and
reacted with the crucible. A slight expansion of the Inconel™ 600 crucible was also observed, which can be attributed to CO₂ being released during the decomposition of Na₂CO₃ and modifying the shape of the crucible. Therefore to avoid any breakages of the DSC from their expansion, each Inconel™ 600 crucible was heated to ~900°C in a furnace for 15 minutes, prior to our experiments as a safety measure. After heating, the author found that molten NaCl-Na₂CO₃ had condensed upon the inner walls of the Al₂O₃ crucible. This was attributed to the walls of the crucible being cooler than the temperature of the mixture (at 830°C). The final mixture was stuck to the sides of crucible and required a chisel to remove the salt. This suggests there was a slight solubility of the Al₂O₃ crucible in molten NaCl otherwise the mixture would have easily been removed. Both Inconel™ 600 and Al₂O₃ crucibles were disused after each experiment.

This section has shown that Na₂CO₃ is not stable in molten NaCl and decomposes to produce CO₂ and Na₂O in a reaction with slow kinetics. These observations support previous experimental studies by Kim and Lee, 2001, and ΔGR data for the decomposition of Na₂CO₃ [260]. The diagram is also different to previous calculated phase diagram studies by Yaokawa et al, 2007 and Lindberg et al, 2006, which can be attributed to the presence of an inert argon gas over molten NaCl and slower heating times [125-126].
4.5.3 Heats of mixing of the reactant in the molten salt

The **dissolution of the reactant**; Na$_2$CO$_3$ in NaCl at 830°C was investigated by obtaining the $\Delta H_{\text{mix}}$ values for molten NaCl-Na$_2$CO$_3$ and $\Delta H_f$ values for Na$_2$CO$_3$ and NaCl, using drop calorimetry. However the dissolution of CaCO$_3$ and SiO$_2$ in molten NaCl was not obtained due to their low solubilities, as described by Yasuda, 2007 and Cherginets, 2005 [130] [208]. These experiments were performed using a glassy carbon crucible, selected due to its slow oxidation rate at high temperatures than conventional carbon [264]. Initially, the procedure involved placing an empty glassy carbon crucible in two locations in a calorimetric tube; Position A (experiment 21) and B (experiment 22) (figure 4.22).

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**Figure 4.21**: Position of the crucible in the calorimetric tube in the drop calorimeter.

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22 The experiments were performed at the Wrocław University of Technology, in Poland with the support of Dr. J. Kapala and Dr. L. Ryczew.
The calorimetric tube was then placed into the well of the drop calorimeter alongside an additional empty reference tube. Then the heat flow signal was recorded between these two tubes for ~15 minutes until the temperature stabilized to its set point value (figure 4.22).

The diagram illustrates that Position B had the lowest potential change (~1 mV) in comparison to Position A (~6 mV). This can be attributed to the glassy carbon crucible being a shorter distance away from the thermopiles (temperature sensors) and therefore selected for every experiment. The relatively long time duration for the heat flow signal to stabilize was attributed to the large mass of the drop calorimeter.
Then an empty glassy carbon crucible was filled with NaCl and placed at Position B in the calorimetric tube. The calorimetric tube was then placed inside the drop calorimeter and the heat flow signal recorded for ~15 minutes until the temperature of the calorimeter stabilized. Then pellets and crystals of Na₂CO₃ were added to the empty glassy carbon crucible and ~30 minutes allowed for the temperature of the calorimeter to reach its initial set point (experiment 23-26), as evident from the heat flow data. Upon every few additions, a pellet of platinum was added to the glassy carbon crucible to provide a suitable calibration point for calculating the Δ₇ values (figure 4.23).

The diagram shows the heat flow signal for both crystals and pellets of Na₂CO₃ rising and falling slowly, which can be attributed to the thermal energy from the drop calorimeter being used to heat the compounds to the reaction temperature. The Δ₇ values for both crystals and pellets of Na₂CO₃ were obtained from the heat flow signal by integrating each peak and subtracting the base-line using OriginPro 8 Peak Analyzer tool.
The typical $\Delta H_f$ values for both pellets and crystals of Na$_2$CO$_3$ with the least scatter were compared against its theoretical $\Delta H_f$ value of $\text{-}127$ kJ mol$^{-1}$ at 830°C (table 4.2). The average $\Delta H_f$ value for the pellets of Na$_2$CO$_3$ was $\sim90.2$ kJ mol$^{-1}$ over three pellet drops, which was $\sim30\%$ lower than its theoretical value. The average $\Delta H_f$ value for crystals of Na$_2$CO$_3$ was $\sim129$ kJ mol$^{-1}$ over three pellet drops, which was 1.57% higher than its theoretical value. In both cases, these values were fairly consistent over the experiments. However, the $\Delta H_f$ value for pellets of Na$_2$CO$_3$ beyond the third drop was $\sim46.8\%$ lower than expected and the $\Delta H_f$ value for crystals of Na$_2$CO$_3$ beyond the fourth drop was $\sim31\%$ lower than expected.

This data suggests Na$_2$CO$_3$ was probably decomposing under these conditions to produce Na$_2$O and CO$_2$, as described by Motzfeldt, 1955 and Kim and Lee, 2001 [258] [260]. However, the decomposition temperature was lower than at 851°C, which is probably caused by the lowering of partial pressure of CO$_2$ due to the flow of argon gas over the melt. This was confirmed by Trémillon and Inman, 1997, whom state that the dissociation constant of the carbonate ion is large enough that lowering the partial pressure of CO$_2$ leads to its complete dissociation [190]. The data also suggests the $\Delta H_f$ values for pellets and crystals of Na$_2$CO$_3$ were fairly consistent over the first three drops. There were however small discrepancies between the pellets and crystals of Na$_2$CO$_3$, probably due to their geometry, which could affect their distance away from the thermopiles.

Table 4.2: $\Delta H_f$ data for pellets and crystals of Na$_2$CO$_3$ at 830 °C.

<table>
<thead>
<tr>
<th>Experiment 23-26 (left to right)</th>
<th>Na$_2$CO$_3$ of $\Delta H_f$ (kJ mol$^{-1}$)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pellets</td>
<td>Crystals</td>
</tr>
<tr>
<td>Theoretical</td>
<td>-127</td>
<td></td>
</tr>
<tr>
<td>Drop 1</td>
<td>-108</td>
<td>-108</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>14.9</td>
</tr>
<tr>
<td>Drop 2</td>
<td>-89.3</td>
<td>-95.2</td>
</tr>
<tr>
<td></td>
<td>29.7</td>
<td>25.0</td>
</tr>
<tr>
<td>Drop 3</td>
<td>-68.7</td>
<td>-71.8</td>
</tr>
<tr>
<td></td>
<td>45.9</td>
<td>43.5</td>
</tr>
<tr>
<td>Drop 4</td>
<td>-64.7</td>
<td>-67.6</td>
</tr>
<tr>
<td></td>
<td>49.1</td>
<td>46.8</td>
</tr>
<tr>
<td>Drop 5</td>
<td>-43.2</td>
<td>-117</td>
</tr>
<tr>
<td></td>
<td>66.0</td>
<td>7.87</td>
</tr>
<tr>
<td>Drop 6</td>
<td>-28.2</td>
<td>-81.2</td>
</tr>
<tr>
<td></td>
<td>77.8</td>
<td>-</td>
</tr>
</tbody>
</table>
The $\Delta H_f$ data also suggests the decomposition was more significant at the later stages of the experiment, probably due to the flow of gas over the melt. It was unlikely that additional reactions of the platinum pellets with $O_2$ to produce $PtO_2$ or $Pt_3O_4$ films affected the calibration of the drop calorimeter as the mass of pellets of platinum remained consistent throughout the experiments [234-235]. It was also unlikely the effects of moisture played a role as this would have contributed to higher $\Delta H_f$ values. It is the author’s recommendation that if one performs these experiments again, a $CO_2$ gas above the melt should be utilized, to avoid the decomposition of $Na_2CO_3$ and thus yield closer $\Delta H_f$ values to the theoretical.

![Figure 4.24: Drop calorimeter heat flow signal for NaCl, molten NaCl-Na$_2$CO$_3$ at 830ºC, under argon.](image)

Then an empty glassy carbon crucible was filled with NaCl and placed at Position B in the calorimetric tube. The calorimetric tube was then placed inside the drop calorimeter and the heat flow signal recorded for $\sim$15 minutes until the temperature of the calorimeter stabilized. Then pellets of NaCl and Na$_2$CO$_3$ were added to the empty glassy carbon crucible and a time period of $\sim$30 minutes was allowed between each drop, to allow the temperature of the calorimeter to stabilize to its initial set point, as evident from the heat flow signal. Upon every third addition, a pellet of platinum was added to the glassy carbon crucible to provide a suitable calibration point for calculating the heat of formation ($\Delta H_f$) and $\Delta H_{mix}$ values (figure 4.24).
The diagram shows the heat flow signal for NaCl and molten NaCl-Na$_2$CO$_3$ rising and falling slowly, which can be attributed to the thermal energy from the drop calorimeter used to heat the compounds to the reaction temperature. In all cases, a minimum baseline of ±1 mV was observed, which can be attributed to the decomposition of Na$_2$CO$_3$, as suggested by Kim and Lee, 2001, evaporation of NaCl, and corrosion reactions of the calorimetric tube with NaCl [18] [260]. For this reason, no more than ~6 hours was allowed for each experiment to avoid the deterioration of the drop calorimeter. The ΔH$_f$ values for NaCl and ΔH$_{mix}$ for molten NaCl-Na$_2$CO$_3$, was obtained by integrating each peak and subtracting the base-line using OriginPro 8 Peak Analyzer tool.

<table>
<thead>
<tr>
<th>Experiment 27</th>
<th>Experiment 28-30 (left to right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH$_f$ of NaCl (kJ mol$^{-1}$)</td>
<td>ΔH$_{mix}$ of NaCl-Na$_2$CO$_3$ (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>% Difference</td>
<td>Pellets</td>
</tr>
<tr>
<td>Pellets</td>
<td></td>
</tr>
<tr>
<td>Theoretical</td>
<td>-74.7</td>
</tr>
<tr>
<td>Drop 1</td>
<td>-73.2</td>
</tr>
<tr>
<td>Drop 2</td>
<td>-74.9</td>
</tr>
<tr>
<td>Drop 3</td>
<td>-71.8</td>
</tr>
<tr>
<td>Drop 4</td>
<td>-72.2</td>
</tr>
<tr>
<td>Drop 5</td>
<td>-69.9</td>
</tr>
<tr>
<td>Drop 6</td>
<td>-69.4</td>
</tr>
<tr>
<td>Pellets</td>
<td>0.364</td>
</tr>
<tr>
<td>Crystals</td>
<td>1.55</td>
</tr>
<tr>
<td>Crystals</td>
<td>-0.471</td>
</tr>
</tbody>
</table>

Table 4.3: ΔH$_f$ data for NaCl and ΔH$_{mix}$ data for molten NaCl-Na$_2$CO$_3$, at 830ºC.

The typical ΔH$_f$ values for both pellets of NaCl were compared against its theoretical value of ~74.7 kJ mol$^{-1}$, and typical ΔH$_{mix}$ values for both crystals and pellets of molten NaCl-Na$_2$CO$_3$, with the least scattering (R$^2$ values) were compared against each other at 830ºC (table 4.3). The average ΔH$_f$ value for the pellets of NaCl was ~72.9 kJ mol$^{-1}$ over three pellet additions, which was ~0.4% lower than expected. The average ΔH$_{mix}$ values for molten NaCl-Na$_2$CO$_3$, were ~2 kJ mol$^{-1}$, which were in the same range as other ΔH$_{mix}$ values in literature, with the differences between crystals and pellets of Na$_2$CO$_3$ being ~1%.

The table suggests Na$_2$CO$_3$ was probably decomposing under these conditions to produce Na$_2$O and CO$_2$ as described by Motzfeldt, 1955 and Kim and Lee, 2001, and NaCl was probably evaporating under these conditions [258] [260]. This
decomposition temperature was higher than at 851°C, as reported previously, which was also contributed by the lowering of the partial pressure of CO₂, due to a flow of argon gas over molten NaCl. It was unlikely the corrosion of the SiO₂ calorimetric tube with NaCl contributed to these results as the base-line was omitted before analysis. There was also no significant difference between the shape of the pellets and crystals of Na₂CO₃, which suggests the effects of moisture in the atmosphere, can be neglected. However the author cannot confirm whether the pellets and crystals had completely dissolved in the melt due to the limitations of the experiment, however when the calorimetric tube was removed and the molten salt was cooled, the molten NaCl-Na₂CO₃ mixture appeared to be a consistent white solution. Also the ΔHₘᵢₓ values were obtained below the saturation limit of the melt and at least ~30 minutes had been allowed between each drop.

![Figure 4.25](image)

*Figure 4.25 ΔHₘᵢₓ data for molten NaCl-Na₂CO₃ at 830°C under argon.*

The ΔHₘᵢₓ data for crystals and pellets of molten NaCl-Na₂CO₃ at 830°C were plotted as a function of composition, and the sub-regular solution model was fitted (experiment 28-30). The ΔHₘᵢₓ data for the crystals of molten NaCl-Na₂CO₃ at 830°C were then fitted to the regular solution model over initial three drops, and extrapolated over the entire composition range, under the assumption that the decomposition of Na₂CO₃ was less significant at the initial stages of the experiment (figure 4.25).
The diagram represents two S-shaped curves, with a positive contribution ≤50 mol% Na₂CO₃ and a negative contribution ≥50 mol% Na₂CO₃. The positive contribution can be attributed towards the intermolecular interactions of Na₂CO₃ and NaCl, being greater than the energy required for the dissolution of Na₂CO₃. The negative contribution can be attributed towards the decomposition of Na₂CO₃ to CO₂ and Na₂O, coupled with its slow reaction kinetics. This probably arose due to the fact that as the concentration of Na₂CO₃ increases in the molten salt, the amount of CO₂ evolved also increases, which could have contributed towards the evaporation rate of NaCl. It was unlikely the corrosion reactions of the calorimetric tube didn’t affect these functions, as the base-line had been substracted.

![Diagram of S-shaped curves](image)

**Figure 4.26**: Literature and experimental ΔHₘᵢₓ data for binary chloride, carbonate and their mixtures. ²³

The average ΔHₘᵢₓ regular solution model for crystals of molten NaCl-Na₂CO₃ was plotted against previous chloride, carbonate and chloride-carbonate binary systems in literature. The general consensus in literature is the dependence of the ΔHₘᵢₓ functions

²³ A is the initial salt and B is the secondary compound that dissolves in A
i.e. for NaCl = A and Na₂CO₃ = B
upon temperature is minimal at high temperatures, therefore values taken at different temperatures can be compared (figure 4.26) [120-128].

The diagram demonstrates the $\Delta H_{\text{mix}}$ functions can be positive or negative, and become larger as the size difference between the solute and solvent ions increases. The relatively large positive $\Delta H_{\text{mix}}$ function for molten NaCl-Na$_2$CO$_3$ ($\sim$2 kJ mol$^{-1}$) at 830ºC was attributed to the decomposition of Na$_2$CO$_3$ to CO$_2$ and Na$_2$O, as described by Kim and Lee, 2001, and agrees with the previous phase diagram studies by the author [260]. If the experiment was performed again, the author would use a CO$_2$ above the molten salt to avoid the decomposition of Na$_2$CO$_3$ and yield the true values of $\Delta H_{\text{mix}}$ function for molten NaCl-Na$_2$CO$_3$. Also, the author would also use a different NIST calibration material, such as Al$_2$O$_3$, as this would confirm that the effect of PtO$_2$ or Pt$_3$O$_4$ layers had no affect upon the $\Delta H_{\text{mix}}$ or $\Delta H_f$ values. An Inconel$^\text{TM}$ 600 calorimetric tube could also be used to avoid the deterioration of the calorimetric tube and ensure the duration of the experiments can be extended.

![Figure 4.27: Image of the calorimetric tube after 1 (left) and 5 (right) $\Delta H_f$ and $\Delta H_{\text{mix}}$ experiments at 830ºC.](image)

The calorimetric tubes were removed from the drop calorimeter and examined after 1 and 5 experiments and images were taken (figure 4.27). The diagram shows a significant colour change was evident upon the inner walls. This colour change was
attributed towards the formation of sodium silicates such as $\alpha$-Na$_2$SiO$_3$ or $\beta$-Na$_4$SiO$_4$ as described by Kracek, 1930, Ryś and Müller, 2010, Halter et al, 2004 and Kracek, 1930 and Zhang et al, 2013 [240-249]. It is likely the decomposition of Na$_2$CO$_3$ to Na$_2$O and CO$_2$ coupled with the evaporation of NaCl, caused sufficient contact with the inner walls for these reactions to occur. The author also found the strength of the calorimetric tubes weakened over the course of the experiments, which can be attributed to changes in its composition. Therefore each tube was replaced after ~5 experiments and the time frame of a single experiment was shortened to less than 6 hours. It is the author’s recommendation if these experiments were performed again, the calorimetric tubes should be constructed from Inconel$^\text{TM}$ 600, due to its proven stability in molten chlorides, and a CO$_2$ gas above the molten salt to inhibit the decomposition of Na$_2$CO$_3$ [261-262].

This section has shown that Na$_2$CO$_3$ is not stable in NaCl at 830°C, and decomposes to CO$_2$ and Na$_2$O, with slow reaction kinetics, as described by Kim and Lee, 2001 [254]. This was confirmed by a positive (endothermic) $\Delta H_{\text{mix}}$ contribution and lower $\Delta H_f$ values for Na$_2$CO$_3$, thus supporting the dissolution studies described earlier.

4.5.4 Solubility products of the reactants in the molten salt

The dissolution of the reactants: CaCO$_3$ and Na$_2$CO$_3$ in NaCl at 830°C was investigated using potentiometry, which subsequently led to obtaining $K_{sp}$ values of CaO and Na$_2$O in NaCl, using an argon gas bubbler (Al$_6$Si$_2$O$_{13}$). The $K_{sp}$ value for SiO$_2$ in molten NaCl however was not obtained, due to its low solubility, as shown by Yasuda, 2007 [208]. The potentiometric technique required the construction of an electrochemical cell, consisting of a tubular cell envelope (Stainless Steel 316L and/or Inconel$^\text{TM}$ 600), a circular lid (Stainless Steel 316L) containing several apertures for the insertion of electrodes, a drop tube (Al$_6$Si$_2$O$_{13}$), argon gas bubbler (Al$_6$Si$_2$O$_{13}$) and inert gas inlet and outlet tubes (Stainless steel 316L) [195-198]. The electrodes consisted of an $\text{Ag}^+/\text{Ag}$ reference electrode (Al$_6$Si$_2$O$_{13}$), and ISE (YSZ), based upon the design by Cherginets, 2005 [130] (figure 4.28).
Figure 4.28: Diagram of electrochemical cell (left) and electrodes (right).
Initially, the ISE and Ag/Ag\textsuperscript{+} reference electrode were immersed in molten NaCl, to produce a potentiometric signal (E\textsubscript{Total}) (figure 4.29). This signal was the sum of several junction and interface potentials within the cell, which arose due to the separation of charge. This allowed the potentiometric signal (E\textsubscript{Total}) to be dependent upon changes in O\textsuperscript{2-} activity in molten NaCl within the crucible, thus suitable for our solubility measurements and following molten salt reactions. Upon the addition of Na\textsubscript{2}CO\textsubscript{3} or CaCO\textsubscript{3} to the melt, produced CO\textsubscript{3}\textsuperscript{2-} and Na\textsuperscript{+} ions which dissociated to O\textsuperscript{2-} ions (as the dissociation constant of CO\textsubscript{3}\textsuperscript{2-} is extremely large) and CO\textsubscript{2}.

The diagram shows junction potentials were present between the silver wires in contact with Ag\textsuperscript{+} ions in molten NaCl (the Ag/Ag\textsuperscript{+} redox couple) in the ISE and reference electrodes (E\textsubscript{Reference 1}, E\textsubscript{ISE 1}). It also shows a membrane potential was present between O\textsuperscript{2-} ions in molten NaCl in the ISE (E\textsubscript{ISE 2}) and crucible, introduced from the dissolution of Na\textsubscript{2}CO\textsubscript{3}. This potential existed due to the YSZ membrane containing oxygen vacancies within its lattice structure [231]. Such vacancies arose when Zr\textsuperscript{4+} ions of ZrO\textsubscript{2} were substituted with slightly larger Y\textsuperscript{3+} ions (ionic radius of 0.82 Å to 0.96 Å), therefore when O\textsuperscript{2-} ions were present upon both sides of the YSZ membrane, a concentration gradient was established. This concentration gradient would cause O\textsuperscript{2-} ions to selectively migrate through the oxygen vacancies and...
establish a charge separation [231-233]. Finally it shows a membrane potential (E_{Reference 2}) was present between Na\(^+\) ions in molten NaCl in the Ag/Ag\(^+\) reference electrode and crucible, due to the \(\text{Al}_6\text{Si}_2\text{O}_{13}\) membrane containing vacancies for Na\(^+\) ions. As Na\(^+\) ions were present in molten NaCl in the crucible and the reference electrode in excess quantities, a constant and reproducible potential was established [230].

The author made several modifications to the electrochemical cell to produce the potentiometric signal, for example an \(\text{Al}_2\text{O}_3\) disc was placed between the crucible and cell envelope and place the crucible away from the inner walls of the cell envelope. This removed electrical contact between the crucible and cell envelope and ensured changes in the potentiometric signal were solely due to the dissolution of the reactants in molten NaCl. This is because when dissimilar metals are exposed to electrolytes such as molten salts, junction potentials are created between metals and metal ions in molten NaCl (denoted redox couples) which contribute towards producing a potentiometric signal, as described by Back, 2001 and Ray, 2006 [53] [265]. Also, when dissimilar metals are in contact with one another at elevated temperatures, junction potentials are created due to a phenomenon called the thermoelectric effect [53]. The author also increased the length of the inert gas inlet and outlet tubes (to at least ~5 cm) into the cell to improve the circulation of inert gas over the molten NaCl to remove unwanted moisture in the cell.
The author also made several improvements to improve the stability and reproducibility of the potentiometric signal (figure 4.30). The author found that the signal often becoming sensitive to changes in the environment instead of O$_2^-$ ions in molten NaCl (experiment 31). This was attributed to the silver wire in the ISE breaking into two pieces, thus causing the membrane potential between the silver wire and Ag$^+$ ions in molten NaCl in the ISE to be lost. To reproduce this signal, the author replaced the silver wire in the ISE in-situ and restarted the experiment.

The author also found the potentiometric signal often became unresponsive to O$_2^-$ ions in molten NaCl, which was due to the YSZ membrane breaking into two separate pieces. This phenomena occured during heating and cooling cycles of the furnace thus attributed to the expansion in volume of the YSZ membrane from its tetragonal phase to monoclinic. It was the author’s opinion this phenomena shouldn’t have occurred due to the composition of YSZ (8 mol% Y$_2$O$_3$, 92 mol% Y$_2$O$_3$). This was attributed to insufficient doping from the manufacturer or the effects of thermal shock. To avoid the YSZ membrane breaking again, the heating and cooling cycles were reduced from 10°C to 2°C min$^{-1}$ thus extending the experimental time to ~24 hours. This lead to

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24 Thermal shock is when thermal gradients cause various parts of an object to expand by different amounts.
safety concerns by our department, as 24 hour experiments weren’t part of the health and regulations. To meet these safety regulations, a switch was incorporated into the furnace to cut the power supply if the temperature rose above a set point value (950°C).

The author also produced a secondary ISE design, using pieces of the broken YSZ membrane (experiment 31). This produced an unstable potentiometric signal (experiment 32) which was attributed to air and moisture entering the ISE which could have interacted with molten NaCl and affect the dissociation of the \( \text{CO}_3^{2-} \) complex ion to \( \text{CO}_2 \) and \( \text{O}^{2-} \) ions.

![Figure 4.31: Images of Stainless steel 316L and Inconel™ 600 cell envelopes at 830ºC (top) and 900ºC (bottom).](image)

Images of the internal and external surfaces of the Stainless Steel 316L and Inconel™ 600 cell envelopes were taken after exposure to ~900ºC and molten NaCl (figure 4.31). These images illustrate a change in colour and surface finish of the Stainless Steel 316L which was attributed to changes in the composition of the alloy. This probably occurred due to \( \text{CrO}_3 \) \( \text{Ce}_2\text{O}_3 \) compounds selectively removed (above 816ºC).
to expose Fe$_2$O$_3$ and FeO to the effects of oxygen and moisture and produce their hydrated forms [238-239].

These compounds were probably produced due to Intergranular Attack (IGA), which occurs when carbon and chromium in the alloy react to form chromium carbides, as described by Davis, 1954 and Indacochea et al, 2000 [238-239]. These chromium carbide compounds precipitate out at grain boundaries which result in chromium depleted zones adjacent to the grain boundaries and a discontinuous oxide layer. This discontinuous oxide layer exposes iron to O$_2$ and moisture in the air to produce Fe$_2$O$_3$ and FeO compounds before disintegrating. The chromium depleted zones also allow the molten salt to enter the alloy to produce galvanic couples between the interface of the salt and alloy to cause corrosion reactions. The author found the performance of Inconel$^{TM}$ 600 was found to be better than Stainless Steel 316L which has probably due to the higher nickel content of Inconel$^{TM}$ 600 [237-238]. The higher nickel content probably causes a lower thermal expansion differential between iron and the oxide layer during heating and cooling cycles, thus greatly improving its corrosion resistance.

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25 A grain boundary is the interface between two grains (crystallites) in a polycrystalline material.
Figure 4.32: Potentiometric signal and $O^{2-}$ ion activity of CaCO$_3$ in NaCl at 830°C, under argon.

The dissolution of the reactant; CaCO$_3$ in NaCl was investigated by filling an Al$_2$O$_3$ crucible with NaCl, and heating to 830°C over ~10 hours at 2°C min$^{-1}$. The Ag/Ag$^+$ reference electrode and ISE were then immersed in molten NaCl in the crucible and the potentiometric signal was recorded. Then ~5 pellets of CaCO$_3$ were added to molten NaCl and at least 10 minutes allowed between each drop. This time period was selected to allow the dissolution and decomposition of CaCO$_3$ in molten NaCl to
occur. The experiment was then discontinued by removing the Ag/Ag\(^+\) reference electrode and ISE from the molten NaCl and cooling the furnace to \(\sim 50^\circ\text{C}\) over \(\sim 18\) hours. Then the potential values when pellets of CaCO\(_3\) equilibrated in the melt were obtained directly from the signal using Uni-trend software and plotted as a function of the negative logarithm of \(O^{2-}\) ion activity (-log [O\(^2\)]) in molten NaCl. The \(O^{2-}\) activity in molten NaCl was calculated from the weighed amounts of CaCO\(_3\) added to molten NaCl under the assumption that CaCO\(_3\) completely dissociated and dissolved to produce CO\(_2\) and CaO, CaO completely dissolved to produce \(O^{2-}\) and Ca\(^{2+}\) ions and the \(O^{2-}\) ion had no deviations from ideality. The total amount of \(O^{2-}\) ions in molten NaCl were assumed to have accumulated from previous additions and no additional reactions had occurred (figure 4.32).

The diagram shows the potentiometric signal was initially sensitive to changes in \(O^{2-}\) ion activity in molten NaCl, prior to the addition of pellets of CaCO\(_3\). This was attributed to minute quantities of \(O^{2-}\) ions being present in molten NaCl, probably due to small quantities of O\(_2\) dissolved in molten NaCl. The signal also didn’t stabilize over \(\sim 2\) hours upon immersion of the electrodes, which was attributed to changes in the partial pressure of O\(_2\) and its dissolution in molten NaCl. It was unlikely the solubility of the Al\(_2\)O\(_3\) crucible and Al\(_6\)Si\(_2\)O\(_{13}\) membrane in molten NaCl affected this to a large degree, as these were probably extremely small [266]. Upon the addition of pellets of CaCO\(_3\) to molten NaCl, the potentiometric signal changed from its initial base-line before reverting back (E34 a-c). This was attributed to the decomposition of CaCO\(_3\) to CaO and CO\(_2\), and the dissolution of \(O^{2-}\) ions in molten NaCl. It was found that additional pellets (E34 b) didn’t affect the potentiometric signal in the same way as previous pellets, which were attributed to molten NaCl becoming saturated from previous additions. The regression line through the potential values and -log [O\(^2\)] in molten NaCl didn’t match a complete electron value (n, 1, 2, 3) from the Nernst equation. This suggests other processes were taking place that could have affected the potentiometric signal or \(O^{2-}\) ion activity. These could have been the pellets not dissolving completely and/or the evaporation of molten NaCl which was probably aided by CO\(_2\) leaving the cell and/or its incomplete decomposition to CO\(_2\). The evaporation of molten NaCl was also supported by a mass change of \(\sim 5\) wt\% of the crucible. These observations however support the fact that CaCO\(_3\) decomposes at 830\(^\circ\text{C}\) to produce \(O^{2-}\) ions and CO\(_2\).
Figure 4.33: Potentiometric signal and O$_2^-$ ion activity of Na$_2$CO$_3$ in NaCl at 830ºC, under argon, with an argon gas bubbler.

The dissolution of the reactant; Na$_2$CO$_3$ in NaCl was investigated by filling an Al$_2$O$_3$ crucible and glassy carbon crucible with NaCl and heating to 830ºC over ~10 hours at 2ºC min$^{-1}$. Then the Ag/Ag$^+$ reference electrode and ISE were immersed into the molten NaCl and the potentiometric signal recorded. Then ~11 pellets of Na$_2$CO$_3$ were added to molten NaCl and at least ~30 minutes allowed between each drop. The experiment was then discontinued by removing the Ag/Ag$^+$ reference electrode and ISE from the molten NaCl in the crucible and cooling the furnace to ~50ºC over ~18 hours. The potential values when pellets of Na$_2$CO$_3$ equilibrated in molten NaCl were
obtained directly from the potentiometric signal, using Uni-trend software and plotted as a function of the negative logarithm of $O^{2-}$ ion activity ($-\log [O^{2-}]$) in molten NaCl. The $O^{2-}$ activity in molten NaCl was calculated from the weighed amounts of Na$_2$CO$_3$ added to molten NaCl under the assumption that Na$_2$CO$_3$ completely dissociated and dissolved to produce CO$_2$ and Na$_2$O, Na$_2$O completely dissolved to produce $O^{2-}$ and Na$^+$ ions and the $O^{2-}$ ion had no deviations from ideality. The total amount of $O^{2-}$ ions in molten NaCl were assumed to have accumulated from previous additions and no additional reactions had occurred (figure 4.33).

The diagram shows the potentiometric signal was initially sensitive to changes in $O^{2-}$ ion activity in molten NaCl, before the addition of pellets of Na$_2$CO$_3$. This can be attributed to minute quantities of $O^{2-}$ ions being present in molten NaCl, probably due to small quantities of O$_2$ dissolved in the melt. The potentiometric signal didn’t stabilize over ~2 hours, upon immersion of the electrodes, which can be attributed to changes in the partial pressure of O$_2$ and its dissolution in molten NaCl. It was unlikely this was affected by the solubility of the Al$_2$O$_3$ crucible and Al$_6$Si$_2$O$_{13}$ membrane, which was probably extremely small [266] [269]. Upon the addition of pellets of Na$_2$CO$_3$ to molten NaCl, the potentiometric signal changed from its initial base-line before reverting back (E35-37 a-f). This was attributed to their decomposition to Na$_2$O and CO$_2$ and the dissolution of $O^{2-}$ and Na$^+$ ions in molten NaCl. It was found that additional pellets affected the potentiometric signal in similar ways to previous additions, which suggested that molten NaCl was not saturated. The regression line through the potential values and $-\log [O^{2-}]$ in molten NaCl didn’t match a complete electron value ($n$, 1, 2, 3) from the Nernst equation. This suggests other processes were taking place that affected the potentiometric signal or $O^{2-}$ ion activity. These could have been the pellets not dissolving completely and/or evaporation of molten NaCl which was probably aided by CO$_2$ leaving the cell and/or its incomplete decomposition to CO$_2$. The evaporation of molten NaCl was also supported by a mass change of ~5 wt% of the crucible. These observations however support the fact that Na$_2$CO$_3$ decomposes at 830°C to produce $O^{2-}$ ions and CO$_2$. 

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Figure 4.34: Potentiometric signal and \( O^2^- \) ion activity of \( CaCO_3 \) in \( NaCl \), at 830°C, under argon, with an argon gas bubbler.

The **dissolution of the reactant**; CaO in NaCl was investigated by filling an glassy carbon crucible with NaCl and heating to 830°C over ~10 hours at 2°C min\(^{-1}\). Then the Ag/Ag\(^+\) reference electrode, ISE and argon gas bubbler (\( Al_6Si_2O_13 \)) immersed into molten NaCl in the crucible and the potentiometric signal recorded. Then ~4 pellets of \( CaCO_3 \) were added to molten NaCl in the crucible and ~5 hours allowed between each drop. This time period was selected to ensure the complete decomposition and dissolution of \( CaCO_3 \) which was aided by the argon gas bubbler. The experiment was then discontinued by removing the Ag/Ag\(^+\) reference electrode and ISE from the...
molten NaCl in the crucible and cooling the furnace to ~50°C over ~18 hours occurred.

The potential values when pellets of CaCO$_3$ equilibrated in molten NaCl were obtained directly from the potentiometric signal using Uni-trend software and plotted as a function of the negative logarithm of O$^{2-}$ ion activity (-log [O$^{2-}$]) in molten NaCl. The O$^{2-}$ activity in molten NaCl was calculated from the weighed amounts of CaCO$_3$ added to molten NaCl, assuming CaCO$_3$ completely dissociated and dissolved to produce CO$_2$ and CaO, CaO completely dissolved to produce O$^{2-}$ and Ca$^{2+}$ ions and the O$^{2-}$ ion had no deviations from ideality. The total amount of O$^{2-}$ ions in molten NaCl were assumed to have accumulated from previous additions and no additional reactions had occurred (figure 4.34).

The diagram shows the potentiometric signal was initially sensitive to changes in O$^{2-}$ ion activity in molten NaCl, before the addition of pellets of CaCO$_3$. This can be attributed to minute quantities of O$^{2-}$ ions being present in molten NaCl, probably from minute quantities of O$_2$ dissolved in the melt. It was found the signal didn’t stabilize over ~2 hours upon immersing the electrodes, which can be attributed to changes in partial pressure of O$_2$ and its dissolution in molten NaCl. The signal did however stabilize over ~5 hours, which can be attributed to a consistent partial pressure of O$_2$ being achieved. It was unlikely this was affected by the solubility of the Al$_6$Si$_2$O$_{13}$ membrane, which was probably extremely small. Upon the addition of pellets of CaCO$_3$, the potentiometric signal changed from its initial base-line before reverting back (E38 a-f). This was attributed to their decomposition to CaO and CO$_2$, and the dissolution of O$^{2-}$ and Ca$^{2+}$ ions in molten NaCl. It was found that additional pellets (E38 b) didn’t affect the potentiometric signal in the same way as previous pellets. This was attributed to molten NaCl being saturated from previous additions.

The regression line through the potential values and -log [O$^{2-}$] in molten NaCl didn’t match a complete electron value (n, 1, 2, 3) from the Nernst equation, which suggests other processes were taking place that affected the potentiometric signal or O$^{2-}$ ion activity. These could have been attributed to the evaporation of molten NaCl which was probably aided by CO$_2$ leaving the cell. It was also most likely the pellets of CaCO$_3$ had completely decomposed, due to the effects of the argon gas bubbler. The evaporation of molten NaCl was supported by a mass change of ~25 wt% of the crucible. This increase in weight loss from previous experiments was attributed to the argon gas bubbler aiding the evaporation process. The K$_{sp}$ value for CaO in molten
NaCl was calculated from the saturation limit on the potentiometric signal and the calculated amounts of CaO in molten NaCl to be \( \sim 1.1 \text{ mol kg}^{-1} \).

![Potentiometric signal and \( \text{O}^{2-} \) ion activity of \( \text{Na}_2\text{CO}_3 \) ini NaCl at 830ºC, under argon, with an argon gas bubbler.]

Figure 4.35: Potentiometric signal and \( \text{O}^{2-} \) ion activity of \( \text{Na}_2\text{CO}_3 \) ini NaCl at 830ºC, under argon, with an argon gas bubbler.

The **dissolution of the reactant;** \( \text{Na}_2\text{O} \) in molten NaCl was investigated by filling a glassy carbon and platinum crucible with NaCl and heating to 830ºC at 2ºC min\(^{-1}\) over \( \sim 10 \) hours. Then the Ag/Ag\(^+\) reference electrode and ISE were immersed in molten NaCl at 830ºC, under argon, with an argon gas bubbler.
NaCl in the crucible and the potentiometric signal was recorded. Then ~13 pellets of Na$_2$CO$_3$ were added to molten NaCl in the crucible and ~5 hours allowed between each drop. This time period was selected to allow the complete dissolution and decomposition of Na$_2$CO$_3$ in molten NaCl which was aided by the argon gas bubbler. The potential values when pellets of Na$_2$CO$_3$ equilibrated in molten NaCl were obtained directly from the potentiometric signal using Uni-trend software and plotted as a function of the negative logarithm of O$^{2-}$ ion activity (-log [O$^{2-}$]) in molten NaCl. The O$^{2-}$ activity in molten NaCl in the crucible was calculated from the weighed amounts of Na$_2$CO$_3$ added to molten NaCl, assuming Na$_2$CO$_3$ had completely dissociated and dissolved to produce CO$_2$ and Na$_2$O, Na$_2$O had completely dissolved to produce O$^{2-}$ and Na$^+$ ions and and the O$^{2-}$ ion had no deviations from ideality. The total amount of O$^{2-}$ ions in molten NaCl were assumed to have accumulated from previous additions and no additional reactions had occurred. Upon the addition of pellets of Na$_2$CO$_3$, the potentiometric signal changed from its initial base-line before reverting back (E39-41 a-f). This was attributed to their decomposition to Na$_2$O and CO$_2$, and the dissolution of O$^{2-}$ ions in molten NaCl. It was found that additional pellets (E40 p) didn’t affect the potentiometric signal in the same way as previous pellets. This was attributed to molten NaCl being saturated with the previous additions (figure 4.35).

The diagram shows the potentiometric signal was initially sensitive to changes in O$^{2-}$ ion activity in molten NaCl, before the addition of pellets of Na$_2$CO$_3$. This can be attributed to minute quantities of O$^{2-}$ ions being present in molten NaCl, probably from quantities of O$_2$ dissolved in the melt. It was found the signal didn’t stabilize over ~2 hours upon immersion of the electrodes, which can be attributed to changes in partial pressure of O$_2$ and its dissolution in molten NaCl. The signal did however stabilize over ~5 hours, which can be attributed to a consistent partial pressure of O$_2$ being achieved. It was unlikely this was affected by the solubility of the Al$_6$Si$_2$O$_{13}$ membrane which was probably extremely small. The regression line through the potential values and -log [O$^{2-}$] in molten NaCl didn’t match a complete electron value (n, 1, 2, 3) from the Nernst equation, which suggests other processes were taking place that affected the potentiometric signal or O$^{2-}$ ion activity. These could have been attributed the evaporation of molten NaCl which was probably aided by CO$_2$ leaving the cell. The evaporation of molten NaCl was also supported by a mass change of ~25 wt% of the crucible. This increase in weight loss from previous experiments was
attributed to the argon gas bubbler aiding the evaporation process. There was no evidence of Na$_2$O$_2$ compounds forming on the platinum crucible as evident by no point of inflection on the potentiometric signal, as described by Cherginets, 2005 [130]. Also it was most likely the pellets of Na$_2$CO$_3$ had completely decomposed, due to the effects of the argon gas bubbler. The author was able to dissolve 0.337 moles of Na$_2$O in 0.966 moles of NaCl therefore the $K_{sp}$ value for Na$_2$O in molten NaCl was calculated to be -log 1.58 (using equation 3.8).

![SEM image and EDS analysis of NaCl at 830°C.](image)

During the investigation, condensed particles were observed ~2 thirds of the way up the cell, which appeared to have risen from molten NaCl. These condensed particles were taken to an SEM for particle size and EDS analysis (figure 4.36). The EDS analysis suggested the phases; Na$_2$O, NaCl, K$_2$O and CaO and/or their constituent ions (O$^{2-}$ ions) were possibly present (experiment 42), in molten NaCl. The presence of Na$_2$O appeared in large quantities, possibly from the decomposition of Na$_2$CO$_3$, coupled with the high vapour pressure of NaCl and release of CO$_2$. The presence of potassium and calcium appeared in minute quantities, suggesting these were present as impurities. The particles were of various shapes (between 2-10 µm) suggesting the molten salt condensed at various cooling rates across the cell envelope (attributed to
the temperature gradient across the cell). The EDS analysis also suggested there was no interaction of the Inconel™ 600 cell envelope with the melt.

The $K_{sp}$ values for Na$_2$O (log 1.58) and CaO (log 1.1) in molten NaCl at 830°C, obtained from potentiometry, were compared with previous reported $K_{sp}$ values in literature (figure 4.37) [130] [144-145] [150] [154]. The $K_{sp}$ value for CaO was found to be higher than those previously reported in literature (log 3.77) at similar temperatures. This was probably due to the use of the potentiometric titration method over SAM, which is deemed to provide more accurate readings due to the detection of minute O$^{2-}$ ion activities (in the $10^{-3}$ range). The $K_{sp}$ value for Na$_2$O was the first reported value according to the author’s knowledge, however cannot yet be published due to the significant evaporation of NaCl during the experiments. If these experiments were performed again, the author would insert pellets of Na$_2$CO$_3$ and CaCO$_3$ into the cell without opening, which would probably avoid the evaporation of molten NaCl.

![Figure 4.37: $K_{sp}$ values for CaO and Na$_2$O as a function of temperature [130] [144-145] [150] [154]](image-url)
Images of the platinum, carbon and Al₂O₃ crucibles were taken after being exposed to NaCl at 830°C from the potentiometric measurements (figure 4.38). Upon examination of the Al₂O₃ crucible, the inner surface walls were white instead of its original yellow colour. This was probably attributed to the dissolution of the Al₂O₃ crucible and the formation of CaO. The Al₂O₃ crucible was also slightly attached to molten NaCl, probably due to the same reason.

\[
\text{Al}_2\text{O}_3(s) = 2\text{Al}^{3+} + 3\text{O}^{2-}
\]  

**Equation 4.20**

Equation 4.20 describes the dissolution of Al₂O₃ in molten NaCl, to produce Al³⁺ and O²⁻ ions. As this compound has a low reported solubility in molten chlorides, as described by Inman et al., 1978 thus not expected to cause significant changes to the potentiometric signal or \( K_{sp} \) values. The possibility of aluminate compounds, such as sodium aluminate (NaAlO₂) was also considered, as described by Kotz, 2009, there was no evidence on the Al₂O₃ crucible or potentiometric signal [266-269].

Upon examination of the glassy carbon crucible, small holes (~1 mm) were seen on the walls, which were not evident on the original design. This could have been attributed to the oxidation of the glassy carbon to CO₂ and CO, which has been reported to occur above ~600°C. As these experiments were done under an inert atmosphere, it can be concluded that this was caused by O₂ leaking into the cell. The oxidation of carbon can be described via the following reaction;

\[
\text{C} + \text{O}_2 (g) = \text{CO}_2(g)
\]  

**Equation 4.21**
Equation 4.21 describes the oxidation of carbon to CO$_2$, as described by Kotz et al, 2009 [268]. As the solubility of CO$_2$ is low in molten chlorides, it is expected this probably wouldn’t cause significant changes to the potentiometric signal and $K_{sp}$ values [261-262]. The contents of the crucible were easily removed, which suggested no other side reactions occurred between the crucible and molten salt.

Upon examination of the platinum crucible, the surface of the external walls was grey in colour, which was different from its original silver colour from the manufacturer. This was probably attributed to platinum reacting with O$_2$ in the atmosphere caused by O$_2$ leaking into the cell to form PtO$_2$ or Pt$_3$O$_4$ which has been reported to occur above ~600°C. The oxidation of platinum can be described via the following reaction;

$$\text{Pt} + \text{O}_2 (g) = \text{PtO}_2$$  \hspace{1cm} \text{Equation 4.22}

Equation 4.22 describes the oxidation of platinum to produce PtO$_2$, as described by Chaston, 1975 and Jehn, 1984 [234-235]. The contents within the crucible were slightly attached to the melt however easily removed by hand which suggested a slight interaction between the crucible and molten salt. This was probably attributed to the PtO$_2$ film dissolving in molten NaCl, however was just a speculation.
The dissolution of alumina in molten NaCl was depicted on a predominance diagram for the Al-Na-O-Cl system at 830°C (figure 4.39). This diagram was produced using the calculation method previously described by Littlewood and Trémillon, using thermodynamic data and the decomposition potential of molten NaCl from CV [189-191]. The ∆G_f for the O^{2-} ion was calculated using ∆G_f data of Na_2O (l), using the equations described previously. The formation of sodium aluminates were not considered in this calculation as described by Christie et al, 1978, as there was no visual evidence in our experiments [267]. The diagram illustrates Al_2O_3 has a low solubility in molten NaCl, governed by a low K_sp value for Al_2O_3 (at -log 21.2 at 830°C) (in mol fraction). The diagram also illustrates that no further reactions take place in the molten salt at a high O^{2-} ion activity in the molten salt. The molten salt reactions depicted on this diagram can be found in table A6 (Appendix).

This section has shown that CaCO_3 and Na_2CO_3 dissolve in NaCl to produce CaO, Na_2O and CO_2, using the equations described earlier. The K_sp values for Na_2O and CaO were found to be -log 1.58 and -log 1.1 which indicates the MSS of cementitious compounds are suitable for industry, due to the reactants having a reasonably high solubility which is a basic requirement. These values were higher than values reported in literature for similar melts probably attributed to the evaporation of molten NaCl.

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27 K_sp values calculated from thermodynamic data are in mol%
during the experiments and is therefore recommended to that the design of the cell requires improvement. The solubility of SiO$_2$ was low under these conditions, suggesting the limiting factor was probably the decomposition processes of CaCO$_3$ and Na$_2$CO$_3$ in molten NaCl. The Al$_2$O$_3$, glassy carbon crucible, platinum crucibles and SiO$_2$ calorimetric tube was found to interact with NaCl in different ways and affect the dissolution behaviour of the reactants but the Al$_2$O$_3$ crucible was found to be the most stable under our conditions.
4.6 Molten salt synthesis of cementitious compounds

The fifth stage of the investigation was to investigate the **MSS of cementitious compounds**: \(\alpha-\text{Na}_2\text{SiO}_3\), \(\beta-\text{Na}_4\text{SiO}_4\), \(\beta-\text{Ca}_2\text{SiO}_4\) and \(\text{Ca}_3\text{SiO}_5\) from the reactants; \(\text{SiO}_2\), \(\text{CaCO}_3\), \(\text{Na}_2\text{CO}_3\) at 830°C and 1100°C, using an XRD and SEM and to depict them on predominance diagrams. This will help determine which other compounds can be produced in this manner.

![XRD pattern for the MSS of \(\beta-\text{Ca}_2\text{SiO}_4\) and \(\text{Ca}_3\text{SiO}_5\) from \(\text{CaCO}_3\) and \(\text{SiO}_2\) in \(\text{NaCl}\) at 830°C for ~3 hours, typical operating condition; 2θ scan range of 5-110° with 150 seconds per step.](image)

The MSS of \(\beta-\text{Ca}_2\text{SiO}_4\) (experiment 43-46) and \(\text{Ca}_3\text{SiO}_5\) (experiment 45), were investigated by filling an \(\text{Al}_2\text{O}_3\) crucible with the reactants and heating to 830°C, and 1100°C for ~3 hours. A sample was then taken from the fused mixture, using the procedure described previously (Chapter 3) and taken to XRD equipment to identify the phases (figure 4.40).

The diagram shows the presence of metastable \(\beta-\text{Ca}_2\text{SiO}_4\), which is in agreement with the feasibility studies described earlier. The \(\text{Ca}_3\text{SiO}_5\) phase was not possible, indicating much larger temperatures were required (exceeding the limitations of the furnace). The \(\text{CaO}\) phase wasn’t present, indicating a high extent of reaction. The absence of \(\text{Al}_2\text{O}_3\), \(\text{SiCl}_4\), \(\text{CaCl}_2\) and \(\text{Na}_2\text{O}\) phases suggested there were no reactions
with NaCl, Al₂O₃ crucible or O₂ from the atmosphere, which is agreement with previous experimental studies for the solubility of O₂ in molten chlorides [256].

![XRD pattern for the MSS of Ca₃SiO₅ and β-Ca₂SiO₄ (separation) for CaCO₃ and SiO₂ in NaCl at 830-1100°C taken for ~3 hours typical operating condition; 2θ scan range of 5-110° with 150 seconds per step.](image)

Figure 4.41: XRD pattern for the MSS of Ca₃SiO₅ and β-Ca₂SiO₄ (separation) for CaCO₃ and SiO₂ in NaCl at 830-1100°C taken for ~3 hours typical operating condition; 2θ scan range of 5-110° with 150 seconds per step.

The separation of Ca₃SiO₅ (experiment 48) and β-Ca₂SiO₄ (experiment 46-47) were investigated for ~3 hours in an Al₂O₃ crucible at 1100°C. After the experiments, each sample was taken from the fused mixture using the procedure outlined earlier and taken to XRD equipment to identify the phases (figure 4.41).

For experiment 48, the XRD pattern shows the presence of the β-Ca₂SiO₄ and CaO phases, and absence of the Ca₃SiO₅ phase, which confirms this isn’t possible to achieve at 1100°C, however in this case CaO was detected. This suggests the synthesis of Ca₃SiO₅ is a two step reaction, which is in agreement with the feasibility studies described earlier. For experiment 46-47, the XRD patterns shows only the presence of β-Ca₂SiO₄, confirming a high extent of reaction. The absence of Al₂O₃, SiCl₄, and CaCl₂ confirms limited reactions with NaCl or Al₂O₃ crucible and also suggests that CaO is not readily soluble in molten NaCl as the sample was removed from the top layer of the fused melt. No SiO₂ peaks were detected in experiment 48 which could be due to it being an amorphous solid.
Figure 4.42: XRD pattern for the MSS of $\alpha$-Na$_2$SiO$_3$ and $\beta$-Na$_4$SiO$_4$ from Na$_2$CO$_3$ and SiO$_2$ in NaCl for 3 hours, typical operating condition; 2θ scan range of 5-110° with 150 seconds per step, at 830°C.

The MSS for the $\alpha$-Na$_2$SiO$_3$ (experiment 50) and $\beta$-Na$_4$SiO$_4$ (experiment 51) were investigated by reacting Na$_2$CO$_3$ and SiO$_2$ in molten NaCl, for ~3 hours in an Al$_2$O$_3$ crucible. After the experiments, each sample was taken from the fused mixture using the procedure described earlier and taken directly to XRD equipment to identify the phases (figure 4.42).

The XRD pattern shows the presence of $\alpha$-Na$_2$SiO$_3$ in both cases, and absence of Na$_2$O indicating a high extent of reaction. The absence of the $\beta$-Na$_4$SiO$_4$ phase for experiment 51, indicates this reaction is not possible and possibly due to inadequate mixing, although the thermodynamic data supported the fact that it can be produced at 750°C. The absence of Al$_2$O$_3$, SiCl$_4$ and Na$_2$O suggests there was a limited reaction with NaCl, Al$_2$O$_3$ crucible or O$_2$ from the atmosphere, which is agreement with previous experimental studies for the solubility of O$_2$ in molten chlorides [261-262].
The elements and particle sizes produced during the MSS of β-Ca$_2$SiO$_4$ and Ca$_3$SiO$_5$ in NaCl (experiments 45–46), were investigated by removing samples from the Al$_2$O$_3$ crucible using the procedure described earlier and taking them to an SEM for particle size and EDS (figure 4.43).

In both cases, the EDS analysis suggested the phases β-Ca$_2$SiO$_4$, CaO, NaCl and/or their constituent ions (O$^{2-}$ ions) were possibly present. The CaO phase was probably produced during the decomposition of CaCO$_3$ in the molten salt. No additional (hydrolysis) reactions occurred which indicates humidity levels in the laboratory were reasonably low. The particle sizes for β-Ca$_2$SiO$_4$ was reasonably low (~400 µm), which was probably due to it having a low solubility in molten NaCl.
Figure 4.44: SEM image and EDS analysis for the MSS of $\alpha$-Na$_2$SiO$_3$ (top) and $\beta$-Ca$_2$SiO$_4$ (bottom) from Na$_2$CO$_3$ and SiO$_2$ in NaCl for 3 hours at 830ºC.

The EDS analysis and particle sizes were repeated for the MSS of $\alpha$-Na$_2$SiO$_3$ and $\beta$-Na$_4$SiO$_4$ experiments (experiment 52-53) and different samples taken to an SEM for particle size and EDS analysis (figure 4.44).

The EDS analysis suggested the phases; $\alpha$-Na$_2$SiO$_3$, Na$_2$O, NaCl, $\beta$-Ca$_4$SiO$_4$, CaO and/or their constituent ions (O$^{2-}$ ions) were possibly present demonstrating good reproducibility of the data. The presence of Na$_2$O and CaO can be attributed to the decomposition and dissolution of Na$_2$CO$_3$ and CaCO$_3$ in the molten salt, although these may not have been present in the molten salt. The image shows the particle sizes were $\sim$400 µm and $\sim$300 µm for $\alpha$-Na$_2$SiO$_3$ and $\beta$-Ca$_2$SiO$_4$ respectively, indicating a
high solubility in the molten salt. It is also suggests a separation stage is required to separate the products from molten NaCl.

![SEM image and EDS analysis of the separation of β-Ca$_2$SiO$_4$ from NaCl, reacted for 3 hours (top) and separated for 6 hours (bottom) at 1000ºC.](image)

**Figure 4.45:** SEM image and EDS analysis of the separation of β-Ca$_2$SiO$_4$ from NaCl, reacted for 3 hours (top) and separated for 6 hours (bottom) at 1000ºC.

The β-Ca$_2$SiO$_4$ compound was separated from molten NaCl by removing a sample from the Al$_2$O$_3$ crucible (experiment 54) and placing in an MgO crucible for ~6 hours at 1000ºC (experiment 55). These samples were then removed and taken to an SEM for particle size and EDS analysis (figure 4.45).

The EDS analysis confirms that it is possible to separate this product from molten NaCl, due to the removal of large quantities of chlorine and sodium from the final product. This can be attributed to different densities of NaCl and β-Ca$_2$SiO$_4$. There
was also some evidence of aluminium and magnesium not previously seen on the XRD patterns, indicating some dissolution of the Al₂O₃ crucible and MgO cupel. The differences in the cupel weight loss were ~5 wt%, indicating most NaCl was absorbed and some lost by evaporation. The final particle size for β-Ca₂SiO₄ was ~4 mm.

Figure 4.46: SEM image and EDS analysis of the separation of α-Na₂SiO₃ from NaCl, reacted for 3 hours (top) and separated for 6 hours (bottom) at 1000°C.

The separation of α-Na₂SiO₃ from molten NaCl was investigated by removing a sample from the Al₂O₃ crucible (experiment 56) and placing in an MgO crucible for ~6 hours at 1000°C (experiment 57). These samples were then removed and taken to an SEM for particle size and EDS analysis (figure 4.46).
The EDS analysis confirms that it is possible to separate this product from molten NaCl, due to the removal of large quantities of chlorine and sodium from the final product. This can be attributed to different densities of NaCl and α-Na$_2$SiO$_3$. There was no evidence of aluminium and magnesium in the final product although this could be due to the in homogeneity of the molten salt. The image shows agglomerated particles of ~between 300-400 µm. The differences in the MgO cupel weight loss were ~5 wt%, indicating most NaCl was absorbed and some lost by evaporation. The dissolution (and decomposition) of carbonates have been previously described by Cherginets, 2005 and Combes et al, 1977 [130] [263]. Using the same analogy, the MSS of β-Ca$_2$SiO$_4$ and α-Na$_2$SiO$_3$ in molten NaCl can be written in the following form;

$$\text{Si}^{4+} + 2\text{Ca}^+ + 4\text{O}^{2-} = \text{Ca}_2\text{SiO}_4 (s) \quad \text{Equation 4.23}$$

$$\text{Si}^{4+} + 2\text{Na}^+ + 3\text{O}^{2-} = \text{Na}_2\text{SiO}_3 (s) \quad \text{Equation 4.24}$$

Equation 4.23-24 describes the MSS of β-Ca$_2$SiO$_4$ (s) and α-Na$_2$SiO$_3$ (s) in molten NaCl from their constituent ions; Na$^+$, Si$^{4+}$, Ca$^{2+}$ and O$^{2-}$. These arise from the dissolution (and decomposition) of CaCO$_3$ (s) and Na$_2$CO$_3$ (s) in molten NaCl. The solubility of β-Ca$_2$SiO$_4$ (s) and α-Na$_2$SiO$_3$ (s) were assumed to be low in our case, therefore only the solid phases were considered. These reactions can also be summarised in the following form;

$$\text{SiO}_2 (s) + 2\text{CaO} (l) = \text{Ca}_2\text{SiO}_4 (s) \quad \text{Equation 4.25}$$

$$\text{SiO}_2 (s) + 2\text{Na}_2\text{O} (l) = \text{Na}_2\text{SiO}_3 (s) \quad \text{Equation 4.26}$$

Equation 4.25-4.26 describes the MSS of β-Ca$_2$SiO$_4$ (s) and α-Na$_2$SiO$_3$ (s) in molten NaCl from the reactants; SiO$_2$ (s), CaO (l) and Na$_2$O (l). The solubility of SiO$_2$ as assumed to be low in our case, therefore only the solid phase was considered.
The final stage of the investigation was to produce predominance diagrams for the Na-Cl-O and Ca-Si-O systems at 830°C, to illustrate the compounds in a summarising form using MSS. The compounds that can be produced in the Na$_2$O-SiO$_2$ and CaO-SiO$_2$ binary systems (figure 4.47) [14-15] [245-249].

These diagrams suggest that $\beta$-Ca$_2$SiO$_4$, tricalcium disilicate (Ca$_3$Si$_2$O$_7$), CaSiO$_3$, $\beta$-Na$_4$SiO$_4$, hexasodium disilicate (Na$_6$Si$_2$O$_7$), Na$_2$SiO$_3$, and disodium disilicate (Na$_2$Si$_2$O$_5$) can be produced at 830°C.  

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**Figure 4.47: Phase diagrams of the Na$_2$O-SiO$_2$ (bottom) and CaO-SiO$_2$ (top) binary systems [242] [266].**

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$^{28}$ Compounds 1-7 on figure 4.47 respectively.
The reaction temperatures required producing the cementitious compounds; CaSiO$_3$, Ca$_3$Si$_2$O$_7$, Na$_2$Si$_2$O$_5$, and Na$_6$Si$_2$O$_7$, were also found using the reaction equation module in HSC-Chemistry 6.1. This module plotted the $\Delta G_R$ and $\Delta H_R$ data as a function of temperature respectively. As the reaction temperatures for the synthesis of $\beta$-Ca$_2$SiO$_4$, $\alpha$-Na$_2$SiO$_3$ and $\beta$-Na$_4$SiO$_4$ were obtained previously and therefore not required (figure 4.48).

The $\Delta H_R$ data shows these reactions are highly exothermic, producing between $\sim$100-400 kJ mol$^{-1}$ of energy over this temperature range. The $\Delta G_R$ data shows these reactions occur at $\sim$280$^\circ$C, $\sim$280$^\circ$C, $\sim$320$^\circ$C and $\sim$670$^\circ$C respectively (shown by negative $\Delta G_R$ values above these temperatures. This agrees with the phase diagrams provided by other authors that these compounds can be synthesised at 830$^\circ$C [14-15] [245-252].
The MSS reactions of Na₂Si₂O₅, α-Na₂SiO₃, β-Na₄SiO₄ and Na₆Si₂O₇ were depicted on a predominance diagram for the Na-Si-O-Cl system at the reaction conditions (830°C, 1 atm) (figure 4.49). This diagram utilizes the calculation method described previously by Littlewood and Trémillon, using thermodynamic data and the decomposition potential of NaCl at 830°C from CV [189-191].

The diagram suggests that SiO₂ has a low solubility in molten NaCl, governed by a low K_{sp} value, at -log 22 (in mole fraction) under the assumption that SiO₂ dissociates completely to Si⁴⁺ and O²⁻ ions. It also suggests the stability domains for α-Na₂Si₂O₅, Na₂SiO₃, β-Na₄SiO₄, and Na₆Si₂O₇ initiate at O²⁻ ion activities of -log 11.8, -log 10.9, -log 6.59, and -log 5.68 (in mole fraction). Therefore if one was to produce these compounds, one would have to mix these concentrations. The molten salt reactions depicted on this diagram can be found in table A7 (Appendix).
The MSS reactions for Ca$_3$SiO$_5$, Ca$_3$Si$_2$O$_7$, CaSiO$_3$ and β-Ca$_2$SiO$_4$ were depicted on a predominance diagram for the Ca-Na-Si-O-Cl system, at the reaction conditions (830°C, 1 atm). This diagram utilizes the calculation method described previously by Littlewood and Trémillon, using thermodynamic data and the decomposition potential of NaCl from CV [181-191] (figure 4.50). For this case, the $\Delta G_f$ for the O$_{2^{-}}$ ion was calculated using CaO (l) in molten NaCl via the following equations.

$$Ca^{2+} + 2e = Ca (s) \quad \text{Equation 4.27}^{29}$$

$$Ca(s) + \frac{1}{2}O_2(g) = Ca^{2+} + O^{2-} \quad \text{Equation 4.28}^{30}$$

$$2e + \frac{1}{2}O_2(g) = O^{2-} \quad \text{Equation 4.29}^{31}$$

Equations 4.27-4.29 describe the equations used to calculate the $\Delta G_f$ of the O$_{2^{-}}$ ion. The compounds from the Na$_2$O-SiO$_2$ system were not shown under the assumption

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$^{29}\Delta G^*_{CaCl_2}$ at 830°C = 631.9 kJ mol$^{-1}$ [18-19]

$^{30}\Delta G_f$ CaO (l) at 830°C = -470.23 kJ mol$^{-1}$ [18-19]

$^{31}\Delta G_f O^2-$ at 830°C = -159.5 kJ mol$^{-1}$
that the attraction of the Ca$^{2+}$ ion is greater than the Na$^+$ ion. The diagram suggests SiO$_2$ has a low solubility in the molten salt governed by a low K$_{sp}$ value, at -log 12.2 (in mole fraction) but higher than the Na-Si-O-Cl system. It also suggests the stability domains for CaSiO$_3$, Ca$_3$Si$_2$O$_7$, β-Ca$_2$SiO$_4$ initiate at O$^{2-}$ ion activities of -log 6.58, -log 6.16 and -log 3.32 (in mole fraction). Therefore if one was to produce these compounds, one would have to mix these concentrations. The molten salt reactions depicted on this diagram can be found in table A8 (Appendix).

This section confirmed it is possible to synthesise α-Na$_2$SiO$_3$ and β-Ca$_2$SiO$_4$ in NaCl at 830°C and 1100°C. α-Na$_2$SiO$_3$ was produced at lower reaction temperatures than some current industrial process and β-Ca$_2$SiO$_4$ was produced at lower temperatures than previous studies in literature and without the need for quenching or stabilization with foreign ions [49] [14-15]. It was not possible to produce β-Na$_4$SiO$_4$ which may have been due to inadequate mixing of the reactants. It was also not possible to produce Ca$_3$SiO$_5$ probably due to insufficient reaction temperatures at is the author’s suggestion that at least 1250°C is required to achieve this. [14-15]. No peaks for additional compounds (such as CaCl$_2$ or Al$_2$O$_3$) were observed on the XRD patterns which suggested that no significant dissolution of the Al$_2$O$_3$ crucible or reaction of the molten salt with the reactants. Upon separation however there was some evidence of aluminium and magnesium, which suggested some interaction of the Al$_2$O$_3$ crucible and MgO cupel. The complexity of these molten salt systems were described on predominance diagrams at 830°C and 1 atm and suggested that Ca$_3$Si$_2$O$_7$, CaSiO$_3$, β-Na$_4$SiO$_4$, Na$_6$Si$_2$O$_7$ and Na$_2$Si$_2$O$_5$ could be produced using a similar methodology at 830°C.
Conclusions & suggestions for future work

5.1 Introduction

This chapter reports the conclusions to the feasibility of the synthesis of cementitious compounds, structures and purities of the reactants in the molten salt, behaviour of the molten salt at the reaction conditions, dissolution of the reactants in the molten salt and MSS of cementitious compounds. It also describes future work for other researchers in this field.

5.2 Feasibility of the synthesis of cementitious compounds

The first stage of the investigation determined the feasibility of the synthesis reactions of the cementitious compounds; α-Na$_2$SiO$_3$, β-Ca$_2$SiO$_4$, Ca$_3$SiO$_5$ and β-Ca$_2$SiO$_4$, using thermodynamic data and chemical equilibrium diagrams. This was used to suggest the reaction temperatures required to produce cementitious compounds and select a suitable salt for MSS.

The Δ$G_R$ data and chemical equilibrium module suggested it maybe possible to synthesise these compounds between 200-1250°C. On this basis, NaCl was selected as a suitable molten salt solvent due to its stability range between ~801-1413°C, which is in the same range as the reactions investigated in this thesis [56]. The viscosity of NaCl (1.03 Pa.s at 810°C) is also in the same magnitude of H$_2$O (0.874 Pa.s at 25°C), which suggests it can be separated from an insoluble product without requiring additional equipment and the vapour pressure of NaCl (0.302 mmHg °C$^{-1}$ at 801°C) was lower than H$_2$O (26.5 mmHg °C$^{-1}$ at 25°C) suggesting minimal losses of the reactant at 830°C [56].
This section could be improved by investigating the feasibility of other cementitious compounds; Ca$_2$(Al, Fe)$_2$O$_5$, and/or Ca$_2$(Al, Fe)$_2$O$_{12}$ and Ca$_3$Al$_2$O$_6$, which are found in cement ([14-15]. If the $\Delta G_R$ data and chemical equilibrium module suggests these can be formed, this could lead to obtaining the complete cement product in a molten salt solvent.

5.3 Structures and purities of the reactants in the molten salt

The second stage of the investigation determined the structures and purities of the reactants; Na$_2$CO$_3$, CaCO$_3$, SiO$_2$ and NaCl, using XRD and CV techniques. This was used to suggest the purity and phase transitions of the reactants at the reaction conditions, useful for analyzing XRD and SEM patterns at a later stage.

The Na$_2$CO$_3$, CaCO$_3$, SiO$_2$ and NaCl, suggested that all reactants were pure with no significant interaction with air or moisture at room temperature and pressure. The $\Delta C_p$ data suggested SiO$_2$ would be in its $\beta$-quartz phase, NaCl in its halite phase, CaCO$_3$ in its calcite phase and Na$_2$CO$_3$ in its $\alpha$-Na$_2$CO$_3$ phase at 830ºC, and 1100ºC, which was considered upon examining the XRD patterns [18-19]. The purity of NaCl was found to be high at the reaction conditions, due to no significant peaks for electrochemical reactions on the CV curve. In addition, the $\Delta V_d$ for NaCl was found to be $\sim$3.1 V, which was in agreement with values calculated using $\Delta G^\circ$ for NaCl, at 3.2 V, the difference of 0.1 V being attributed to a possible temperature gradient across the cell.

This section can be improved by heating the compounds to 830ºC and 1100ºC and investigating the phases formed using XRD. This can be performed in conjunction with quenching and stabilizing with foreign ions, as often transitional compounds revert back to their most stable phases at lower temperatures. However this information cannot truly represent an accurate scenario of the phases formed at the reaction temperatures in a molten salt solvent, therefore experiments should also accompany this.
5.4 Behaviour of the molten salt at the reaction conditions

The third stage of the investigation determined the **behaviour of the molten salt at the reaction conditions**, using a DSC technique and chemical equilibrium diagrams.\(^{32}\) This was useful for describing the effects of vapour pressure upon the salt, and reaction conditions required for the experiments.

The chemical equilibrium diagram suggested that NaCl evaporates at 830°C due to its high vapour pressure. This high vapour pressure coupled with a temperature gradient across the reaction vessel would probably assist in the evaporation of salt. It was therefore recommended that all reaction vessels containing the molten salt have smaller dimensions to avoid the effects of temperature gradients and sealed to contain the molten salt. However there is some evidence to suggest that pressurized vessels can cause the partial pressure of internal gases produced to increase, however this probably would have a small impact upon the final conclusions drawn from this thesis.

This section can be improved by investigating the effect of various atmospheres (such as moisture, O\(_2\) and N\(_2\)) upon the behaviour of molten NaCl and the effect of various drying procedures for NaCl, using a DSC. This could help the author understand the effects and mechanisms of these variables and minimize the quantity of salt evaporated.

5.5 Dissolution of the reactants in the molten salt

The fourth stage of the investigation determined the **dissolution of the reactants;** CaCO\(_3\), Na\(_2\)CO\(_3\) and SiO\(_2\) in molten NaCl, using potentiometry, calorimetry, XRD and SEM, which subsequently led to obtaining phase diagrams, K\(_{sp}\) and ΔH\(_{mix}\) values, to determine whether MSS of cementitious compounds are possible in industry.

\(^{32}\) The salt was selected to be NaCl
5.5.1 Phases of the reactants in the molten salt

This section determined the dissolution reactions of the reactants; \( \text{Na}_2\text{CO}_3, \text{CaCO}_3 \) and \( \text{SiO}_2 \) in molten \( \text{NaCl} \) at the reaction conditions (830ºC, 1 atm), using XRD, SEM techniques.

The XRD data suggested \( \text{CaCO}_3 \) and \( \text{Na}_2\text{CO}_3 \) dissolved and decomposed in \( \text{NaCl} \) at 830ºC, to produce \( \text{CaO}, \text{Na}_2\text{O}, \text{CO}_2^2-, \text{O}^{2-} \) ions and \( \text{CO}_2 \). The decomposition temperatures for \( \text{CaCO}_3 \) and \( \text{Na}_2\text{CO}_3 \) were similar to those reported by Motzfeldt, 1955, Hills, 1968 and Kim and Lee, 2001 for solid-state reactions (at 840ºC and 851ºC respectively) [258-260]. The decomposition temperature was also similar to that reported by the chemical equilibrium module (860ºC for \( \text{CaCO}_3 \)) and thermodynamic data (825ºC for \( \text{CaCO}_3 \)) [18-19]. The author found the decomposition of \( \text{CaCO}_3 \) occurred to completion, probably due to the presence of an exhaust above our muffle furnace. This suggests the decomposition rate is dependent upon the partial pressure of \( \text{CO}_2 \) in the reaction vessel. The reaction kinetics for the decomposition of \( \text{Na}_2\text{CO}_3 \) was slower than \( \text{CaCO}_3 \). This was probably due to a low extent of reaction for \( \text{Na}_2\text{CO}_3 \) (at 0.41 at 830ºC from HSC-Chemistry 6.1) [18-19]. This information was also confirmed by Motzfield, 1955 and Kim and Lee, 2001 [18-19] [258] [260]. The SEM data suggested \( \text{SiO}_2 \) dissolved in \( \text{NaCl} \) at 830ºC, to produce the constituent species; \( \text{O}^{2-} \) and \( \text{Si}^{4+} \) ions with an extremely low solubility. This was also evident by the appearance of solid particles on the surface of molten \( \text{NaCl} \). This information concludes that all the reactants dissolve in molten \( \text{NaCl} \), according to equations 4.7-4.19 and the \( \text{Al}_2\text{O}_3 \) crucible used had a limited interaction in molten \( \text{NaCl} \). This was due to no significant \( \text{Al}^{3+} \) peaks were detected on the XRD pattern and was not expected to cause significant changes to the final phases formed.

This section can be improved by identifying the phases produced at the reaction conditions in-situ, using other analytical techniques such as neutron diffraction or XRD. These have proven useful for the phase identification in molten salts in literature and could suggest the stability domains where these reactions occur [271]. These stability domains could also be investigated by using various quenching times, reaction times and temperatures, which would probably affect the structure of the final phases formed [18-19] [112].
5.5.2 Phase diagrams of the reactants in the molten salt

This section confirmed the dissolution reactions of the reactant; Na$_2$CO$_3$, by obtaining the phase diagram of the Na$_2$CO$_3$-NaCl binary system, using a DSC technique. The phase diagram for the SiO$_2$-NaCl and CaCO$_3$-NaCl binary systems were unable to be investigated via this technique, due to their low solubilities, as described by Yasuda, 2007 [208].

The DSC data suggested the eutectic point for molten NaCl-Na$_2$CO$_3$ was 638°C, 47 mol% Na$_2$CO$_3$, which was different to values reported by Iwasawa and Maeda, 2000, Yaokawa et al, 2007 and Lindberg et al, 2006 at 643°C, 43 mol% Na$_2$CO$_3$. This suggests that Na$_2$CO$_3$ decomposed above 801°C, probably due to the flow of argon above NaCl, causing the partial pressure of CO$_2$ to decrease. This observation also agrees with studies previously performed by Hills, 1968 and Kim and Lee, 2001 [253] [255]. A slight expansion of the Inconel$^{TM}$ 600 crucible was also observed, which was attributed to CO$_2$ being released from the decomposition reaction and modifying the shape of the crucible. This information concludes that Na$_2$CO$_3$ and CaCO$_3$ decomposes in NaCl at 830°C, and SiO$_2$ only dissolves according to equations 4.7-4.18

This section can be improved by obtaining the phase diagram for molten NaCl-Na$_2$CO$_3$, under CO$_2$. These should inhibit the decomposition of Na$_2$CO$_3$ and allow the true value of the eutectic point to be obtained. This can be compared against other eutectic points to confirm whether the reactant was truly decomposing or due to the affects of other variables. One could also determine the phase diagrams for molten CaCO$_3$-NaCl and SiO$_2$-NaCl using potentiometry, or software packages such as FactSage (Thermfact/CRCT and GTT-Technologies) or MTDATA (National Physical Laboratory (NPL)), which use the CALPHAD (CALculation of PHAse Diagrams) method, to provide further evidence of their dissolution in molten NaCl [210] [270-271].
5.5.3 Heats of mixing of the reactants in the molten salt

This section confirmed the **dissolution reactions of the reactant**; Na$_2$CO$_3$ by obtaining the $\Delta H_{\text{mix}}$ values for the Na$_2$CO$_3$-NaCl binary system, using a drop calorimetry technique. The $\Delta H_{\text{mix}}$ values for the SiO$_2$-NaCl and CaCO$_3$-NaCl binary systems were unable to be investigated via this technique, due to their low solubilities, as described by Yasuda, 2007 and Cherginets, 2005 [130] [208].

The $\Delta H_{\text{mix}}$ values illustrated a positive (endothermic) contribution (~2 kJ mol$^{-1}$), which suggests that Na$_2$CO$_3$ decomposes at 830°C to produce CO$_2$ and Na$_2$O (equations 4.7-4.12). The average $\Delta H_f$ value for pellets of Na$_2$CO$_3$ was ~90.2 kJ mol$^{-1}$ over three pellet drops, which was ~30% lower than its theoretical value. The average $\Delta H_f$ value for crystals of Na$_2$CO$_3$ was ~129 kJ mol$^{-1}$ over three pellet drops, which was 1.57% higher than its theoretical value. In both cases, these values were fairly consistent over the experiments. However the $\Delta H_f$ value for pellets of Na$_2$CO$_3$ beyond the third drop was ~46.8% lower than expected and the $\Delta H_f$ value for crystals of Na$_2$CO$_3$ beyond the fourth drop was ~31% lower than expected. This $\Delta H_f$ data suggests that Na$_2$CO$_3$ decomposes probably and aided by the decrease in partial pressure of CO$_2$ from the flow of argon gas. The SiO$_2$ calorimetric tubes demonstrated significant corrosion in the drop calorimeter, probably due to the formation of sodium silicates, such as α-Na$_2$SiO$_3$. However it was unlikely that affected the $\Delta H_{\text{mix}}$ values as their interaction were mitigated from the data by subtracting the base-line upon analysis.

This section can be improved by obtaining $\Delta H_{\text{mix}}$ values for molten SiO$_2$-NaCl and CaCO$_3$-NaCl, using $K_{sp}$ values in literature as a function of temperature. These values can be implemented into the Vant Hoff’s equation as described by Flengas and Rideal, 1956, to obtain the $\Delta H_{\text{mix}}$ values for the liquid phase of such systems [241]. The $\Delta H_{\text{mix}}$ values can also be obtained from phase diagrams using various thermodynamic software packages such as MTDATA or FactSage, as described earlier [210] [270]. These values would provide further evidence of the dissolution of the reactants in molten NaCl. However as $K_{sp}$ values are also a function of the sizes of the pellets and crystals, these would have to also be taken into account, as reported by Cherginets 2005 [130]. If these experiments were performed again, the SiO$_2$ calorimetric tubes
would be replaced with Inconel™ 600, which has a proven stability in molten chlorides.

5.5.4 Solubility products of the reactants in the molten salt

This section determined the dissolution reactions of the reactants; Na$_2$CO$_3$ and CaCO$_3$ in molten NaCl, using a potentiometric technique, which subsequently lead to obtaining the K$_{sp}$ values for Na$_2$O and CaO in molten NaCl. The K$_{sp}$ value for SiO$_2$ in molten NaCl was unable to be investigated via this technique, due to its low solubility, as described by Yasuda, 2007 [208].

The potentiometry technique required the construction of an electrochemical cell that was capable of producing a stable and reproducible signal at 830°C. However the construction of the cell required several modifications to its design to provide a stable and reproducible signal. These modifications included placing an Al$_2$O$_3$ disc between the crucible and cell envelope, to remove electrical contact between molten NaCl and cell envelope. This also removed the possibility of redox couples forming between the metals and metal ions in molten NaCl (denoted redox couples) which can cause galvanic corrosion and removed the possibility of junction potentials, caused by the thermoelectric effect [53] [265]. The length of the gas inlet and outlet tubes was extended to improve the circulation of argon gas over molten NaCl, and remove moisture in the cell. The Stainless steel 316L cell envelope demonstrated signs of deterioration probably due to it’s interaction with O$_2$ and moisture from the atmosphere [241] [261]. This deterioration probably occurred due to CrO$_3$ Ce$_2$O$_3$ compounds being selectively removed (above 816°C) thus exposing Fe$_2$O$_3$ and FeO to the effects of oxygen and moisture. The performance of Inconel™ 600 was better than Stainless Steel 316L which probably occurred due to its higher nickel content. The higher nickel content probably caused a lower thermal expansion differential between iron and the oxide layer during heating and cooling cycles, thus greatly improving its corrosion resistance [238-239]. The heating and cooling rates of the furnace were also reduced from 10°C min$^{-1}$ to 2°C min$^{-1}$ to avoid the YSZ membrane breaking.

The platinum crucible experienced a grey colour change on its outer surface which was different from its original silver colour from the manufacturer. The contents were
also found to be slightly attached to the crucible, which was attributed to platinum reacting with O$_2$ in the atmosphere, to form PtO$_2$ or Pt$_3$O$_4$. The inner surface of the crucible remained its original silver colour, suggesting if oxide films did form, they probably dissolved in molten NaCl [234-235]. As the platinum crucible didn’t experience any significant mass changes between the experiments, these effects were unlikely to impact the final K$_{sp}$ values. Also no points of inflection on the potentiometric signal were observed, as described by Cherginets, 2003, which suggests no species such as Na$_2$O$_2$ were produced [156]. The glassy carbon crucible experienced significant mass losses between the experiments, suggesting it may have reacted with O$_2$ to produce CO$_2$. It was however unlikely these affected the K$_{sp}$ values, due to the low reported solubility of CO$_2$ in molten NaCl, as reported by Hefter and Tomkins, 2004 [261]. The contents were easily removed from the glassy carbon crucible, suggesting no significant solubility of the glassy carbon crucible. The Al$_2$O$_3$ crucible experienced no mass changes between the experiments and its contents were slightly attached to the Al$_2$O$_3$ crucible. This suggested the Al$_2$O$_3$ crucible had a small solubility in molten NaCl. The dissolution of the Al$_2$O$_3$ crucible in molten NaCl was also described on a predominance diagram for the Al-Na-O-Cl system, at 830ºC. The diagram suggested that Al$_2$O$_3$ has a low solubility in molten NaCl, governed by a low K$_{sp}$ value for Al$_2$O$_3$ (at -log 21.2 at 830ºC) (in mol fraction).

The potentiometric data suggested that Na$_2$CO$_3$ and CaCO$_3$ decomposed in molten NaCl to Na$_2$O and CaO and CO$_2$. The K$_{sp}$ values for Na$_2$O and CaO in NaCl at 830ºC were found by inserting an argon gas bubbler to drive the decomposition reaction to completion and ensure the complete dissolution of the pellets. The K$_{sp}$ values were found to be -log 1.58 and -log 1.1 respectively, suggesting such compounds had high solubilities in molten NaCl in comparison to other oxides in literature [144-155]. However these values didn’t take into account the evaporation of molten NaCl, suggesting their true K$_{sp}$ values were probably slightly higher. This information concludes that Na$_2$CO$_3$ and CaCO$_3$ decompose in NaCl at 830ºC, as described by equations 4.7-4.18, suggesting the MSS of cementitious compounds is possible in industry.

This section can be improved by obtaining the evaporation rate of molten NaCl at 830ºC, using a DSC. The evaporation rate can then be used to calculate the true K$_{sp}$
values for Na$_2$O and CaO in molten NaCl, which takes into account its evaporation. The evaporation of molten NaCl could also be minimized using a ceramic lid to allow the electrochemical cell to be calibrated for low O$^{2-}$ ion activities (in the $10^{-3}$ range). The equilibration times for pellets of NaCO$_3$ and CaCO$_3$ could also be reduced by decreasing the volume of the cell envelope which would reduce the volume of inert gas required to achieve a consistent partial pressure in the cell. The $K_{sp}$ values for Na$_2$O and CaO in molten NaCl could also be obtained directly by heating pellets of Na$_2$CO$_3$ and CaCO$_3$ beyond their decomposition temperatures, and sintering to avoid their decomposition.

5.5 Molten salt synthesis of cementitious compounds

The fifth stage of the investigation determined the **MSS reactions of the cementitious compounds**, $\alpha$-Na$_2$SiO$_3$, $\beta$-Ca$_2$SiO$_4$, Ca$_3$SiO$_5$ and $\beta$-Ca$_2$SiO$_4$, using XRD and SEM techniques at the reaction conditions (830°C 1 atm), which were depicted on predominance diagrams. This was useful to determine whether cementitious compounds can be produced in this manner.

The XRD data reported the successful synthesis of the transitional compound; $\beta$-Ca$_2$SiO$_4$ which was produced without quenching or stabilization with foreign ions, which is often a requirement for transitional compounds [49]. However the reaction temperatures were higher than those reported by previous solid-state synthesis reactions and the chemical equilibrium module, at 680°C and 300°C [49] [18-19]. The XRD data also reported the successful synthesis of $\alpha$-Na$_2$SiO$_3$ without quenching or stabilizing with ions. These reaction temperatures were lower than industry but higher than the chemical equilibrium module, 900°C and 200°C respectively [18-19] [251].

The XRD data also reported the synthesis of Ca$_3$SiO$_5$ was not successful and instead $\beta$-Ca$_2$SiO$_4$ and CaO were produced, probably due to a higher temperature requirement, as reported by Wesselsky and Jensen, 2009 [49]. The XRD data also reported the synthesis of $\beta$-Na$_4$SiO$_4$ was not successful and instead $\alpha$-Na$_2$SiO$_3$ and Na$_2$O were produced, probably due to inadequate mixing of the reactants. The absence of other phases such as CaCl$_2$ in the final product suggested there was limited interaction of NaCl with the reactants and products. There was however a small
presence of aluminium detected by EDS analysis which suggested some interaction of the Al₂O₃ crucible.

The MSS reactions were described on predominance diagrams for the Na-Si-O-Cl and Ca-Na-Si-O-Cl systems at 830°C. The diagrams showed that Na₂Si₂O₅, α-Na₂SiO₃, β-Na₄SiO₄, and Na₆Si₂O₇ could be produced at O²⁻ ion activities of -log 11.8, -log 10.9, -log 6.59, and -log 5.68 (in mole fraction) respectively and CaSiO₃, Ca₅Si₂O₇, β-Ca₂SiO₄ could be produced at O²⁻ ion activities of -log 6.58, -log 6.16 and -log 3.32 (in mole fraction) respectively, at 830°C. This information concludes that Na₂CO₃ and CaCO₃ decompose and dissolve in NaCl at 830°C, as reported by equations 4.7-4.18, which suggests the MSS of cementitious compounds are possible in industry, and results in lower reaction temperatures, a lower energy consumption and hence CO₂ emissions.

This section can be improved by synthesising other cementitious compounds in molten NaCl, such as Na₆Si₂O₇, Na₂Si₂O₅ and Na₆Si₂O₇, at 830°C (from the CaO-SiO₂ and Na₂O-SiO₂ binary systems). Also the CaO-SiO₂-Al₂O₃ and Al₂O₃-Fe₂O₃-Ca₂CO₃ ternary systems could be investigated to produce the additional phases of cement; Ca₂(Al, Fe)₂O₃ and/or Ca₂(Al, Fe)₂O₁₂ and Ca₃Al₂O₆ phases via MSS. This would give an indication whether the complete cement product could be achieved. Also, the predominance diagram calculation procedure could be improved using the Gibbs free energy minimization method (the principle of minimum energy) to provide truly accurate scenarios whether these compounds can be formed [210].
Acknowledgements

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Conferences, publications & awards

My research has been presented at the following conferences:

- Shape of Science Symposium, 5\textsuperscript{th} July 2010, Poster presentation, University of Manchester, Manchester.
- Cement and Concrete Science, 13-15\textsuperscript{th} September 2010, Technical discussion, University of Birmingham, Birmingham.
- Electrochemical Innovation Lab Launch, 16\textsuperscript{th} June 2011. Poster presentation, University College London, London.
- Molten Salts Chemistry and Technology, MS9. 5-9\textsuperscript{th} June 2010. Poster competition, NTNU: Norwegian University of Science and Technology, Trondheim, Norway.
- European Congress and Exhibition on Advanced Materials and Processes (Euromat), 12-15\textsuperscript{th} September 2011. Poster competition. Le Corum conference centre, Montpellier, France.
- 13\textsuperscript{th} International Congress on the Chemistry of Cement Science, 3-8\textsuperscript{th} July 2011, Palacio de Congresos de Madrid. Madrid, Spain.
- Molten Salts Discussion Group, 15\textsuperscript{th} December 2014, Chemistry Centre, Royal Society Chemistry (RSC), Burlington House, London
- Royal Academy of Engineering (RAEng), SET for Britain, Poster Competition, 9\textsuperscript{th} March 2015, Houses of Parliament.

I have the following publications:

I have received the following awards:


- Best poster nominee Molten Salts Chemistry and Technology, MS9. 5-9\textsuperscript{th} June 2010. Poster competition, NTNU: Norwegian University of Science and Technology, Trondheim, Norway.

- The Entente Cordiale Scholarship Scheme, 2011, for a 6 month study period at Aix-Marseille University. French Embassy, London.
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# Appendix

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*Table A1: Lattice parameters for compounds of interest (including polymorphic transitions) [248].*
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<tr>
<td>Nickel wire.</td>
<td>1 mm diameter.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Platinum wire.</td>
<td>1 mm diameter.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcium chloride.</td>
<td>Purity ≥ 99.9%</td>
<td>Sigma-Aldrich.</td>
<td>The Old Brickyard, New Road Gillingham, Dorset, SP8 4XT.</td>
</tr>
<tr>
<td>Calorimetric tube.</td>
<td>Purity ≥ 99%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Graphite crucible.</td>
<td>6 mm diameter.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DSC.</td>
<td>Temperature limit, 830ºC</td>
<td>Setaram.</td>
<td>7, rue de l'Oratoire 69300 Caluire, France.</td>
</tr>
<tr>
<td>BOC.</td>
<td>-</td>
<td>-</td>
<td>10 Priestley Road Surrey Research Park, Guildford Surrey GU2 7XY.</td>
</tr>
<tr>
<td>XRD.</td>
<td>-</td>
<td>Stoe.</td>
<td>Hilperstrasse 10 64295 Darmstadt Germany</td>
</tr>
<tr>
<td>Thermocouple.</td>
<td>N-type.</td>
<td>RS Components.</td>
<td>RS Components, Birchington Road, Corby, Northants, NN17 9RS, UK</td>
</tr>
<tr>
<td>Voltmeter.</td>
<td>-</td>
<td>Uni-trend</td>
<td>83 Baker Street 5th Floor London W1U 6AG</td>
</tr>
</tbody>
</table>

Table A2: Supplier list.
<table>
<thead>
<tr>
<th>NaCl (mol %)</th>
<th>Na₂CO₃ (mol %)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC Ref 124</td>
<td>Ref 125 Ref 126</td>
<td>DSC Ref 124 Ref 125 Ref 126</td>
</tr>
<tr>
<td>100 100 100</td>
<td>100 0 0</td>
<td>801 801 801</td>
</tr>
<tr>
<td>95 98 98</td>
<td>5 2 2</td>
<td>786 792 792</td>
</tr>
<tr>
<td>80 85 92 95</td>
<td>20 15 8 5</td>
<td>729 752 774</td>
</tr>
<tr>
<td>75 87 82</td>
<td>25 13 18</td>
<td>716 755 736</td>
</tr>
<tr>
<td>60 65 78 76</td>
<td>40 35 22 24</td>
<td>698 678 722</td>
</tr>
<tr>
<td>60 67 72</td>
<td>40 33 28</td>
<td>658 680 702</td>
</tr>
<tr>
<td>55 53 68</td>
<td>45 47 32</td>
<td>644 632 686</td>
</tr>
<tr>
<td>45 50 61</td>
<td>55 50 39</td>
<td>705 658 659</td>
</tr>
<tr>
<td>35 32 55</td>
<td>65 68 45</td>
<td>729 737 631</td>
</tr>
<tr>
<td>25 11 49</td>
<td>75 89 51</td>
<td>751 792 659</td>
</tr>
<tr>
<td>15 10 43</td>
<td>85 90 57</td>
<td>806 820 687</td>
</tr>
<tr>
<td>5 3 10</td>
<td>95 97 90</td>
<td>834 848 819</td>
</tr>
<tr>
<td>0 0 0</td>
<td>100 100 100</td>
<td>851 851 858</td>
</tr>
</tbody>
</table>

Table A3: Liquidus points for molten NaCl-Na₂CO₃ [124-126].

<table>
<thead>
<tr>
<th>NaCl (mol %)</th>
<th>Na₂CO₃ (mol %)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC Ref 124</td>
<td>Ref 125 Ref 126</td>
<td>DSC Ref 124 Ref 125 Ref 126</td>
</tr>
<tr>
<td>100 100 100</td>
<td>0 0</td>
<td>634 634</td>
</tr>
<tr>
<td>98 98</td>
<td>2 2</td>
<td>634 634</td>
</tr>
<tr>
<td>80 75 92 95</td>
<td>20 25 8 5</td>
<td>637 636 634</td>
</tr>
<tr>
<td>70 65 87 82</td>
<td>30 35 13 18</td>
<td>638 632 634</td>
</tr>
<tr>
<td>60 60 78 76</td>
<td>40 40 22 24</td>
<td>638 634 634</td>
</tr>
<tr>
<td>40 67 72</td>
<td>60 33 28</td>
<td>635 634 634</td>
</tr>
<tr>
<td>50 45 53 68</td>
<td>50 55 47 32</td>
<td>637 632 634</td>
</tr>
<tr>
<td>35 50 61</td>
<td>65 50 39</td>
<td>637 634 634</td>
</tr>
<tr>
<td>32 55</td>
<td>68 45</td>
<td>634 634</td>
</tr>
<tr>
<td>30 49</td>
<td>89 51</td>
<td>634 634</td>
</tr>
<tr>
<td>10 43</td>
<td>90 57</td>
<td>634 634</td>
</tr>
<tr>
<td>3 10</td>
<td>97 90</td>
<td>634 634</td>
</tr>
<tr>
<td>0 0</td>
<td>100 100</td>
<td>634 634</td>
</tr>
</tbody>
</table>

Table A3: Liquidus points for molten NaCl-Na₂CO₃ [124-126].
### Molten salt reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium expression</th>
<th>Standard potentials (V vs Cl₂/CT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂ (g) + 2e = 2Cl⁻</td>
<td>( E_{\text{Cl}^2+/\text{Cl}^-} = E^0_{\text{Cl}^2+/\text{Cl}^-} - \frac{2.3RT}{2F} \log P_{\text{Cl}_2} )</td>
<td>( E^0_{\text{Cl}^2+/\text{Cl}^-} = 0 )</td>
</tr>
<tr>
<td>( \text{Na}^+ + e = \text{Na} (l) )</td>
<td>( E_{\text{Na}^+/\text{Na}} = E^0_{\text{Na}^+/\text{Na}} - \frac{2.3RT}{F} \log a_{\text{Na}} )</td>
<td>( E^0_{\text{Na}^+/\text{Na}} = -3.21 )</td>
</tr>
<tr>
<td>( \text{O}_2 (g) + 4e = 2\text{O}^{2-} )</td>
<td>( E_{\text{O}<em>2} = E^0</em>{\text{O}<em>2/\text{O}^{2-}} - \frac{2.3RT}{4F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{O}_2/\text{O}^{2-}} = -1.89 )</td>
</tr>
</tbody>
</table>

**A5:** Molten salt reactions for the Na-O-Cl system, at 830°C, 1 atm.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium expression</th>
<th>Standard potentials (V vs Cl₂/CT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂ (g) + 2e = 2Cl⁻</td>
<td>( E_{\text{Cl}^-} = E^0_{\text{Cl}^-/\text{Cl}^2-} - \frac{2.3RT}{2F} \log P_{\text{Cl}_2} )</td>
<td>( E^0_{\text{Cl}^-/\text{Cl}^2-} = 0 )</td>
</tr>
<tr>
<td>( \text{Na}^+ + e = \text{Na} (l) )</td>
<td>( E_{\text{Na}} = E^0_{\text{Na}^+/\text{Na}} - \frac{2.3RT}{F} \log a_{\text{Na}} )</td>
<td>( E^0_{\text{Na}^+/\text{Na}} = -3.21 )</td>
</tr>
<tr>
<td>( \text{O}_2 (g) + 4e = 2\text{O}^{2-} )</td>
<td>( E_{\text{O}<em>2} = E^0</em>{\text{O}<em>2/\text{O}^{2-}} - \frac{2.3RT}{4F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{O}_2/\text{O}^{2-}} = -1.89 )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 3e = \text{Al} (s) )</td>
<td>( E_{\text{Al}^{3+}/\text{Al}} = E^0_{\text{Al}^{3+}/\text{Al}} - \frac{2.3RT}{3F} \log a_{\text{AlCl}_3} )</td>
<td>( E^0_{\text{Al}^{3+}/\text{Al}} = -1.75 )</td>
</tr>
<tr>
<td>( \text{Al}_2\text{O}_3 (s) + 6e = 2\text{Al} (s) + 3\text{O}^{2-} )</td>
<td>( E_{\text{Al}_2\text{O}<em>3/\text{Al}} = E^0</em>{\text{Al}_2\text{O}<em>3/\text{Al}} - \frac{2.3RT}{6F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{Al}_2\text{O}_3/\text{Al}} = -4.12 )</td>
</tr>
</tbody>
</table>

**A6:** Molten salt reactions for the Al-Na-O-Cl system, metal ion activity 1, at 830°C, 1 atm.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium expression</th>
<th>Standard potentials (V vs Cl₂/CT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂ (g) + 2e = 2Cl⁻</td>
<td>( E_{\text{Cl}^-} = E^0_{\text{Cl}^-/\text{Cl}^2-} - \frac{2.3RT}{2F} \log P_{\text{Cl}_2} )</td>
<td>( E^0_{\text{Cl}^-/\text{Cl}^2-} = 0 )</td>
</tr>
<tr>
<td>( \text{Na}^+ + e = \text{Na} (l) )</td>
<td>( E_{\text{Na}} = E^0_{\text{Na}^+/\text{Na}} - \frac{2.3RT}{F} \log a_{\text{Na}} )</td>
<td>( E^0_{\text{Na}^+/\text{Na}} = -3.21 )</td>
</tr>
<tr>
<td>( \text{O}_2 (g) + 4e = 2\text{O}^{2-} )</td>
<td>( E_{\text{O}<em>2} = E^0</em>{\text{O}<em>2/\text{O}^{2-}} - \frac{2.3RT}{4F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{O}_2/\text{O}^{2-}} = -1.89 )</td>
</tr>
<tr>
<td>( \text{SiO}_2 (s) + 2e - \text{Si} (s) + \text{O}^{2-} )</td>
<td>( E_{\text{SiO}<em>2/\text{Si}} = E^0</em>{\text{SiO}<em>2/\text{Si}} - \frac{2.3RT}{2F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{SiO}_2/\text{Si}} = -3.73 )</td>
</tr>
<tr>
<td>( \text{Si}^{4+} + 4e = \text{Si} (s) )</td>
<td>( E_{\text{Si}^{4+}/\text{Si}} = E^0_{\text{Si}^{4+}/\text{Si}} - \frac{2.3RT}{4F} p_{\text{O}_2} )</td>
<td>( E^0_{\text{Si}^{4+}/\text{Si}} = -1.33 )</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SiO}_4 (s) + 4e = \text{Si} (s) + \text{Na}^+ + 4\text{O}^{2-} )</td>
<td>( E_{\text{Na}_2\text{SiO}<em>4/\text{Si}} = E^0</em>{\text{Na}_2\text{SiO}<em>4/\text{Si}} - \frac{2.3RT}{4F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{Na}_2\text{SiO}_4/\text{Si}} = -4.69 )</td>
</tr>
<tr>
<td>( \text{Na}_2\text{Si}_3\text{O}_5 (s) + 8e = 2\text{Si} (s) + 2\text{Na}^+ + 5\text{O}^{2-} )</td>
<td>( E_{\text{Na}_2\text{Si}_3\text{O}<em>5/\text{Si}} = E^0</em>{\text{Na}_2\text{Si}_3\text{O}<em>5/\text{Si}} - \frac{2.3RT}{8F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{Na}_2\text{Si}_3\text{O}_5/\text{Si}} = -4.05 )</td>
</tr>
<tr>
<td>( \text{Na}_2\text{Si}_3\text{O}_5 (s) + 8e = 2\text{Si} (s) + 6\text{Na}^+ + 7\text{O}^{2-} )</td>
<td>( E_{\text{Na}_2\text{Si}_3\text{O}<em>5/\text{Si}} = E^0</em>{\text{Na}_2\text{Si}_3\text{O}<em>5/\text{Si}} - \frac{2.3RT}{8F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{Na}_2\text{Si}_3\text{O}_5/\text{Si}} = -4.51 )</td>
</tr>
<tr>
<td>( \text{Na}_2\text{Si}_3\text{O}_5 (s) + 4e = \text{Si} (s) + 2\text{Na}^+ + 3\text{O}^{2-} )</td>
<td>( E_{\text{Na}_2\text{Si}_3\text{O}<em>5/\text{Si}} = E^0</em>{\text{Na}_2\text{Si}_3\text{O}<em>5/\text{Si}} - \frac{2.3RT}{8F} p</em>{\text{O}_2} )</td>
<td>( E^0_{\text{Na}_2\text{Si}_3\text{O}_5/\text{Si}} = -4.55 )</td>
</tr>
</tbody>
</table>

**A7:** Molten salt reactions for Na-Si-O-Cl system, metal ion activity 1, at 830°C, 1 atm.
<table>
<thead>
<tr>
<th>Molten salt reactions</th>
<th>Equilibrium expression</th>
<th>Standard potentials (V vs Cl\textsubscript{2}/Cl\textsuperscript{−})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl\textsubscript{2} + 2e = 2Cl\textsuperscript{−}</td>
<td>E\textsubscript{Cl\textsuperscript{2}/Cl\textsuperscript{−}} = \frac{2.3RT}{2F} \log P\textsubscript{Cl\textsubsuperscript{2}}</td>
<td>E\textsuperscript{0}\textsubscript{Cl\textsuperscript{2}/Cl\textsuperscript{−}} = 0</td>
</tr>
<tr>
<td>Na\textsuperscript{+} + e = Na (l)</td>
<td>E\textsubscript{Na\textsuperscript{+}/Na} = \frac{2.3RT}{2F} \log a\textsubscript{Na}</td>
<td>E\textsuperscript{0}\textsubscript{Na\textsuperscript{+}/Na} = −3.21</td>
</tr>
<tr>
<td>O\textsubscript{2} (g) + 4e = 2O\textsuperscript{2−}</td>
<td>E\textsubscript{O\textsubscript{2}/O\textsuperscript{2−}} = \frac{2.3RT}{4F} \log P\textsubscript{O\textsubscript{2}}</td>
<td>E\textsuperscript{0}\textsubscript{O\textsubscript{2}/O\textsuperscript{2−}} = −0.83</td>
</tr>
<tr>
<td>CaSiO\textsubscript{3} (s) + 4e = Si (s) + Ca\textsuperscript{2+} + 3O\textsuperscript{2−}</td>
<td>E\textsubscript{CaSiO\textsubscript{3}/Si} = \frac{2.3RT}{4F} \log a\textsubscript{Si}</td>
<td>E\textsuperscript{0}\textsubscript{CaSiO\textsubscript{3}/Si} = −2.99</td>
</tr>
<tr>
<td>Ca\textsubscript{3}Si\textsubscript{4}O\textsubscript{7} (s) + 8e = 2Si (s) + 3Ca\textsuperscript{2+} + 7O\textsuperscript{2−}</td>
<td>E\textsubscript{Ca\textsubscript{3}Si\textsubscript{4}O\textsubscript{7}/Si} = \frac{2.3RT}{8F} \log a\textsubscript{Si}</td>
<td>E\textsuperscript{0}\textsubscript{Ca\textsubscript{3}Si\textsubscript{4}O\textsubscript{7}/Si} = −3.15</td>
</tr>
<tr>
<td>Ca\textsubscript{2}SiO\textsubscript{4} (s) + 4e = Si (s) + 2Ca\textsuperscript{2+} + 4O\textsuperscript{2−}</td>
<td>E\textsubscript{Ca\textsubscript{2}SiO\textsubscript{4}/Si} = \frac{2.3RT}{4F} \log a\textsubscript{Si}</td>
<td>E\textsuperscript{0}\textsubscript{Ca\textsubscript{2}SiO\textsubscript{4}/Si} = −3.24</td>
</tr>
<tr>
<td>SiO\textsubscript{2} (s) + 4e = Si (s) + 2O\textsuperscript{2−}</td>
<td>E\textsubscript{SiO\textsubscript{2}/Si} = \frac{2.3RT}{4F} \log a\textsubscript{Si}</td>
<td>E\textsuperscript{0}\textsubscript{SiO\textsubscript{2}/Si} = −2.63</td>
</tr>
<tr>
<td>Si\textsuperscript{4+} + 4e = Si (s)</td>
<td>E\textsubscript{Si\textsuperscript{4+}/Si} = \frac{2.3RT}{4F} \log a\textsubscript{Si}</td>
<td>E\textsuperscript{0}\textsubscript{Si\textsuperscript{4+}/Si} = −1.28</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+} + 2e = Ca (l)</td>
<td>E\textsubscript{Ca\textsuperscript{2+}/Ca} = \frac{2.3RT}{2F} \log a\textsubscript{Ca}</td>
<td>E\textsuperscript{0}\textsubscript{Ca\textsuperscript{2+}/Ca} = −3.28</td>
</tr>
</tbody>
</table>

\textit{A8: Molten salt reactions for the Ca-Na-Si-O-Cl system, metal ion activity 1, at 830°C, 1 atm.}