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Thermochemical Behaviour and Stability of Aluminium Smelter Crust

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A thesis submitted in complete fulfilment of the requirements for the degree of Doctor of Philosophy in Chemical and Materials Engineering, the University of Auckland, 2014
Abstract

In aluminium reduction cell, anode cover is added onto the anodes and the bulk bath to maintain the cell heat balance, as well as to reduce the anode air burn and fluoride loss. Alumina and crushed bath are the most common raw materials for the anode cover. Investigation and understanding of the thermochemical behaviour and stability of the crust is important for maintaining the cell heat balance.

In a reduction cell, the anode cover at room temperature is heated by high heat flux from the hot bulk bath. Liquid bath appears in the anode cover due to the penetration of liquid bath from the bulk bath and melting of the crushed bath in the anode cover. The liquid bath penetrating upwards is cooled down by the cold upper part of the anode cover. As a result, the solid phases of cryolite and alumina crystallize out of the liquid bath, which reduces the cryolite ratio (CR) of the remaining liquid bath. The liquid bath and the precipitated crystals contribute to the formation of sintered crust at the bottom part of the anode cover. However, too much liquid phase in the crust can lead to the melting and weakening of the sintered crust.

Based on the heat and mass transfer theory and phase equilibrium diagrams, a theoretical thermochemical model was developed to quantitatively simulate the thermochemical evolution process during sintered crust formation. An effective specific heat capacity was deduced to couple the temperature and chemical composition variables together. The thermochemical model was solved by a designed computational code applying finite element method (FEM). The simulation results were compared with experimental data.

Seven crust pieces were taken from industrial reduction cells. According to their appearance, shape and crystal texture, three types of crystalline crust were distinguished from the sintered crust, and accounted for by crystallization from the bulk bath under different cooling rates.

Crust samples were taken from different vertical positions in these crust pieces. XRD analysis, Rietveld refinements, and LECO oxygen analysis were carried out to analyze the chemical compositions of the crust samples. A non-commercial and calibrated DTA
system was used to measure the liquidus and melting temperatures of the crust samples.

The measured results show that cryolite content and CR are 60~70 wt% and 2.58~2.64 in the lower crust respectively, and decrease significantly to 20~30 wt% and 1.75~2.10 in the upper crust. The liquidus temperature of the crust sample is depressed by the decreasing of CR and by other fluoride additives, and is consistent with the measured chemical composition by XRD.

The melting behaviour of the crust was studied by the shape analysis of the melting peak of the DTA heating curve. Crust samples with high cryolite content and CR have sharp peak shape indicating narrow melting temperature range. In chiolite enriched crust, high liquid bath content that incongruently melts from chiolite can melt solid cryolite over a wide temperature range with low energy intensity.
Dedication

I dedicate this work to my family.

Especially, I would like to express my sincerely love and thanks to my wife Lanning Li. I do not believe that my thesis could be completed without kindly encouragement, understanding and strong support from her.
Acknowledgements

I would like to express my sincere thanks to my respectable supervisors Professor Mark P. Taylor and Professor John J.J. Chen for their encouragement, guidance and supervision over a number of years. I am very grateful to have helpful advice from them. This thesis would not have been possible without their professional support.

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Abbreviations

AE      Anode effect
CCB     Coarse crushed bath, defined as full size range between 45 µm and 5.6 mm.
CR      Cryolite ratio, i.e. NaF mol%/AlF₃ mol%
DTA     Differential thermal analysis
FCB     Fine crushed bath, defined as no plus 150 µm fraction.
FEM     Finite element method
ICB     Intermediate crushed bath
LCB     Large crushed bath, defined as greater than 1mm.
LECO    LECO oxygen analysis
MCB     Medium crushed bath, defined as between 150 µm and 1mm.
PDEs    Partial differential equations
SEM     Scanning electron microscope
SD      Standard deviation
TC      Transient heat conduction
TCA     Transient heat conduction & advection
TCP     Transient heat conduction & phase transformation
TCAP    Transient heat conduction & advection & phase transformation
XRD     X-ray Diffraction
List of Abbreviations and Symbols

ZSL      Zehner-Schlunder-Laubitz

Latin symbols

A       Cross section area (m$^2$)

$a$    Thermal diffusion coefficient (m$^2$/s)

$c_{i}$ Mass concentration of $i$th species in the liquid bath (kg/m$^3$)

$c_{i}^\prime$ Mass concentration of $i$th species at the liquid/solid interface (kg/m$^3$)

$c_{i}^*$ Saturation mass concentration of $i$th species (kg/m$^3$)

$C$    Specific heat capacity (J/kgK)

$C_{L}$ Specific heat capacity of liquid bath (J/kgK)

$C_{S,i}$ Specific heat capacity of $i$th solid phase (J/kgK)

$C_{E}$ Effective specific heat capacity (J/kgK)

$C_{zs}$ Shape factor for Zehner and Schlunder model

$d$    Mean particle size (m)

$d_p$  Average particle diameter (m)

$D_{i}$ Diffusion coefficient of $i$th species (m$^2$/s)

$e$    Emissivity

$F$    Solution matrix for calculating $m_i$

$f$    Mathematic Function

$g$    Gravity acceleration (m/s$^2$)

$h$    Convective heat transfer coefficient (W/m$^2$K)
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<td>$h_p$</td>
<td>Height of liquid bath peritectic point position (m)</td>
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<td>$h_f$</td>
<td>Convective heat transfer coefficient between bulk bath and crust (W/m$^2$K)</td>
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<td>Definition</td>
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<td>$K_{Di}$</td>
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<td>$K_{Ri}$</td>
<td>Coupling coefficient between $\phi'_i$, $\phi^*_i$ and $m_i$</td>
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<td>Surface area of particle (m²/m³)</td>
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<td>$t$</td>
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<td>$\Delta t$</td>
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<td>$T_S$</td>
<td>Temperature of solid phase (°C)</td>
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<tr>
<td>$T_C$</td>
<td>Temperature of loose cover (°C)</td>
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List of Abbreviations and Symbols

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<tr>
<td>$T_M$</td>
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<td>$\Delta x$</td>
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**Greek symbols**

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<td>$\phi_i$</td>
<td>Weight fraction of $i$th species in the liquid bath</td>
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<td>$\phi_{3,8}$</td>
<td>Total weight fraction of species 3,4,5,6,7 and 8 in the liquid bath</td>
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<tr>
<td>$\phi_i^*$</td>
<td>Saturation concentration of $i$th species in the liquid bath</td>
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List of Abbreviations and Symbols

\( \phi \) Concentration of \( i \)th species at the solid-liquid interface

\( \phi_{Si} \) Weight fraction of \( i \)th solid phase in the solid mixture

\( \rho_a \) Bulk density of alumina (kg/m\(^3\))

\( \rho_c \) Bulk density of crushed bath (kg/m\(^3\))

\( \rho_L \) Density of liquid bath (kg/m\(^3\))

\( \rho_F \) Density of fluoride additives (kg/m\(^3\))

\( \rho_w \) Bulk density of crushed bath/alumina mixture (kg/m\(^3\))

\( \rho_\gamma \) Density of transition alumina (kg/m\(^3\))

\( \rho_{Si} \) Density of solid phase of \( i \)th species (kg/m\(^3\))

\( \varepsilon_a \) Volume fraction of residual air

\( \varepsilon_{a\_close} \) Close porosity of alumina

\( \varepsilon_{a\_open} \) Internal open porosity of alumina

\( \varepsilon_{a\_open} \) Inter-particle open porosity of alumina

\( \varepsilon_{c\_cover} \) Overall porosity of crushed bath

\( \varepsilon_{c\_open} \) Open porosity of crushed bath

\( \varepsilon_{cover} \) Overall porosity of anode cover

\( \varepsilon_{crust} \) Total porosity of recycled crust before crushing

\( \varepsilon_e \) Phase transformation volume fractions at the point \( h_e \)
List of Abbreviations and Symbols

\( \varepsilon_{m_{\text{open}}} \) Internal open porosity of crushed bath/alumina mixture cover

\( \varepsilon_{\text{open}} \) Open porosity of anode cover

\( \varepsilon_p \) Phase transformation volume fractions at the point \( h_p \)

\( \varepsilon_L \) Volume fraction of liquid bath

\( \varepsilon_{\text{lo}} \) Easy-filling porosity

\( \varepsilon_\gamma \) Volume fraction of transition alumina

\( \varepsilon_{\gamma A} \) Porosity of the transition alumina particle

\( \varepsilon_{\gamma 0} \) Initial volume fraction of transition alumina

\( \varepsilon_{S,i} \) Volume fraction of solid phase of \( i \)th species

\( \varepsilon_S \) Total volume fraction of solid phases

\( \varepsilon_{\text{sumf}} \) Total original volume fraction of all fluoride additives

\( \mu \) Viscosity of the liquid bath (Pa·s)

\( \delta \) Film thickness (m)

\( \psi \) Relaxation factor

\( \tau \) Tortuosity

\( \sigma \) Stefan-Boltzmann constant, \( 5.67 \times 10^{-8} \text{ (kg/s}^3\text{k}^4) \)

\( \gamma \) Surface tension (N/m)

\( \gamma_L \) Surface tension of liquid bath (N/m)
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<td>$\gamma_S$</td>
<td>Surface tension of solid phase (N/m)</td>
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<td>Surface tension between solid/liquid phases (N/m)</td>
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<tr>
<td>$\theta$</td>
<td>Contact angle</td>
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<tr>
<td>$\eta, \xi, \varphi$</td>
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**Subscript**

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<td>Peritectic point</td>
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<td>$S$ or $s$</td>
<td>Solid phase</td>
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# Declaration to Accompany a Doctoral Thesis on Final Submission

## Section 1. Candidate’s details

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<th>Qinsong Zhang</th>
<th>ID number:</th>
<th>4871786</th>
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<td>Degree:</td>
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<td>Thesis title:</td>
<td>Thermochemical Behaviour and stability of Aluminium Smelter Crust</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Address in full:</td>
<td>184, Hepingbei Street, Shenyang, Liaoning, 110001, China</td>
<td></td>
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## Section 2. Candidate’s declaration

I do solemnly and sincerely declare that:

1. I am currently registered as a candidate for the above degree at The University of Auckland.
2. I have attached to this declaration two bound copies of my thesis.
3. The digital copy of my thesis deposited with the University Library is identical to the attached hard bound copies.
4. The information provided in Sections 1 and 2 of this form is complete and accurate, no relevant information has been withheld that I am aware of, and I have complied with all of the University’s requirements in the statutes and regulations associated with my degree.

I make this solemn declaration conscientiously believing the same to be true, and by virtue of the Oaths and Declarations Act 1957.

Signed: Qinsong Zhang

DEclared at: Auckland

On: 15th day of October, 2014

Before me: Stanley Joseph Saw

Signed: S. J. Saw

(Justice of the Peace or Solicitor of High Court)

S. J. Saw, JP
#8101
AUCKLAND

(Justice of the Peace for New Zealand)
The undersigned hereby certify that:

1. the above statement correctly reflects the nature and extent of the PhD candidate’s contribution to this work, and the nature of the contribution of each of the co-authors; and
2. in cases where the PhD candidate was the lead author of the work that the candidate wrote the text.

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<td>John J.J. Chen</td>
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<tr>
<td>David Cotton</td>
<td>Assistance with DTA test implementation</td>
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<td>Tania Grountso</td>
<td>Assistance with XRD analysis</td>
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<td>Xiaodong Yang</td>
<td>Assistance with sampling method</td>
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Last updated: 25 March 2013
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Please indicate the chapter/section/pages of this thesis that are extracted from a co-authored work and give the title and publication details or details of submission of the co-authored work.

PhD Thesis Chapter 6

Nature of contribution by PhD candidate: Main Author. Sampling, experiment design, data collection and interpretation

Extent of contribution by PhD candidate (%): 95%

CO-AUTHORS

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Certification by Co-Authors

The undersigned hereby certify that:

- the above statement correctly reflects the nature and extent of the PhD candidate’s contribution to this work, and the nature of the contribution of each of the co-authors; and
- in cases where the PhD candidate was the lead author of the work that the candidate wrote the text.

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1 Introduction

The Hall-Heroult cell, which is the most important apparatus for primary aluminium production, is operating at higher amperages and become more energy intensive than before. During cell operation, nearly 50% of the input energy is dissipated as heat loss from the cell surface to the surroundings, which provides a huge potential for energy saving. The top heat loss accounts for almost 50% of the total surface heat loss. Because the anode cover must transmit a large proportion of the cell heat loss, it has a great impact on the cell heat balance. Without the anode cover, uncontrolled heat loss by radiation and convection from the exposed molten bath surface will be excessive, resulting in bad cell performance and excessive energy usage.

The crust, which is the bottom consolidated part of the anode cover, undergoes high temperature treatment due to the large heat flow from the hot bath. The lack of thermochemical stability of the crust at the service temperatures generated by the heat flow is still a crucial problem for modern high amperage reduction cells. The thermochemical stability is closely related to the changes in thermal, chemical and mechanical behaviour of the crust as it ages after anode setting. Understanding of the crust thermochemical behaviour is still very limited due to its complexity.

This study is significant in terms of reducing energy consumption in primary aluminium production. The smelters aim to reduce total cell voltage drop. As the energy input is decreased, the cell need to be more insulated to keep reasonable bath temperature. Other than the top part, the cell has no sufficient insulation potential. For instance, the side of the cell need to dissipate certain heat flux to maintain its proper ledge profile which protects the fragile sidewall, and the bottom of the cell has been already well insulated. If the thermochemical stability of the crust is improved, namely the crust becomes more stable with much less collapse, the top heat loss is reduced and cell voltage drop can be lower to save energy consumption. The ways to improve thermochemical stability of the crust are increasing granulometry/density and reducing liquid fraction in the crust which are all closely related with the thermochemical behaviour in the crust.
1.1 Research purpose

The main purpose of this research is to shed light on the detailed mechanism of crust formation and the internal thermochemical behaviour of the crust, including liquid bath penetration, melting and chemical composition changes of the crust. The research questions are related to the mechanism of the thermochemical behaviour during crust formation.

The theoretical bases for the study are heat and mass transfer theory, phase equilibria and the associated Navier-Stokes, continuity and heat flow equations with liquid advection and phase transformation condition. The experimental tools used are FEA numerical analysis, XRD analysis and LECO oxygen analysis, the latter two of which were used to determine the chemical composition of real industrial crusts, and a purpose-built DTA method to measure the melting and liquidus temperatures.

1.2 Coverage of the thesis

The second chapter provides a general background of the aluminium reduction cell, and illustrates the heat balance with the focus on the top heat loss in the reduction cell.

A literature review on anode cover and crust is given in chapter 3. The common raw anode cover material is listed. The physical properties such as porosity, bulk density, and thermal conductivity are described in detail. Some published research on crust formation is reviewed.

A mechanism of thermochemical behaviour during the crust formation is proposed based on some ideal conditions in chapter 4. In order to test the mechanism, a theoretical thermochemical model is developed in chapter 4. This model is numerically solved by a computational method in chapter 5.

In chapter 6, lab experiments are presented to measure the chemical composition and the melting/liquidus temperatures of the industrial crust samples by XRD and DTA analysis respectively. The thermal stability of industrial crust samples is studied by shape analysis of the DTA heating curve. The influence of chemical composition on the melting behaviour of the crust is demonstrated.
In chapter 7, the numerical correctness of the model is verified, and the model simulation results are compared with experimental data (validation process).
2 Background

2.1 Aluminium overview

Aluminium is the most abundant metallic element in the Earth’s crust, with excellent physical, chemical and mechanical properties. Aluminium is only one-third the weight of steel, has high thermal and electrical conductivity, and has high corrosion resistance. Nowadays, aluminium is one of the most versatile non-ferrous metals, being widely used in the transport and architectural construction industries, as well as having many domestic uses like cooking utensils and packaging.

2.2 Aluminium reduction cell

Because of its high chemical reactivity, almost all aluminium in nature exists in an oxidized state rather than an elemental form. Alumina (Al₂O₃) is the primary raw material for primary aluminium. Since 1886, the Hall-Heroult process has been the only process to produce primary aluminium in industry, using an electrolysis method to reduce alumina to aluminium in an apparatus called a reduction cell or pot.

So far, the centrally point-feed prebaked anode reduction cell (referred to as reduction cell or pot in the following text) has been the main type of reduction cell used. Figure 2-1 shows the typical structure of a reduction cell. It has a steel shell lined with refractory insulation and carbon cathode. Multiple prebaked anodes are placed along the length of the pot. The bottom part of the anode is immersed in the electrolyte (bulk bath). Above the anode and the bulk bath is the anode cover, which consists of a loose anode cover and a consolidated crust.
NOTE: Due to copyright reasons, this figure has been removed. Please refer to the original source:

Figure 1.1 in Dorreen, M., *Cell performance and anodic processes in aluminium smelting studied by product gas analysis*. 2000, University of Auckland: New Zealand.

Alternatively, refer to a hard copy of this thesis, as deposited in The University of Auckland Library.

Figure 2-1: Sketch of a typical prebaked anode reduction cell [1]

The electrolyte primarily consists of molten cryolite (Na$_3$AlF$_6$), which is the only known solvent for alumina. Alumina is fed in batches into the electrolyte periodically. The cryolite-based electrolyte (bulk bath) hence plays a crucial role in dissolving alumina and conducting electricity. In the molten electrolyte, the electricity transfers the electrons to ions, and the aluminium is reduced from the alumina. The aluminium deposits at the cathode surface because it has a higher density than the electrolyte. The oxygen from alumina combines with carbon at the anode surface to form carbon dioxide and some carbon monoxide. The overall reaction for this process is represented as equations (2.1).

\[ 2Al_2O_3 + 3C = 4Al + 3CO_2 \]  

(2.1)

The properties of the electrolyte are adjusted by some fluoride additives. For example, the melting point of pure cryolite is about 1010 °C, and can be depressed by the fluoride additives to about 930–960 °C. The most used fluoride additive is AlF$_3$, with other fluorides (e.g. CaF$_2$, LiF, KF and MgF$_2$) appearing in the electrolyte as impurities when impure alumina is used (particularly in China).

Reduction cell performance has improved rapidly around the world in recent decades, mainly reflecting a higher productivity and current efficiency with reduced energy consumption. Nowadays potlines with best performances are operating at high amperages (up to 500 kA), high current efficiencies (up to 96%), low energy consumption (less than 14 kWh/kg Al) and long cell life (more than 2500 days) [2]. The progress has resulted mainly from improvements in electro-magnetic stability, alumina feeding system, cell heat balance design, bath composition optimization, and process control for all of
2.3 Reduction cell heat balance

2.3.1 Heat balance overview

Aluminium smelting is energy intensive. Electrical power (up to 500 kA) is continuously input to the reduction cell. Cold materials (new anode, anode cover and alumina) are heated, while the hot anode butts and metal are taken out periodically. The surface of the reduction cell is hotter than its surroundings, and loses its heat to the latter mostly through convection and radiation.

Heat balance plays a very important role in cell performance. In order to keep the electrolyte molten and dissolve cold alumina, the temperature and superheat of the electrolyte is normally kept in the range of 930 ~ 970 °C and 5 ~ 15 °C, respectively. On the other hand, the electrolyte should be cooled to form a frozen ledge near the side walls. The frozen ledge protects the side wall from the corrosive electrolyte. The electrolyte is able to dissolve and physically erode most known materials (except the ledge) including refractory materials and carbon. A desired ledge also confines the metal pad within the anode shadow, reducing horizontal current components in the metal pad, and helping to stabilise the metal-bath interface, which may contribute to the high current efficiency [3, 4].

Figure 2-2 shows the balance between heat sources and heat sinks in a typical reduction cell [5]. Heat sources of anode voltage ($V_{anod}$), bubble voltage ($V_{bub}$), voltage across the ACD ($V_{ACD}$), cathode voltage ($V_{cath}$) and external voltage ($V_{ext}$) are generated from Joule heat due to the electrical resistance. Heat sources of equilibrium potential ($E_e$), anode surface overvoltage ($\eta_{sa}$), anode concentration overvoltage ($\eta_{ca}$), cathode concentration overvoltage ($\eta_{cc}$) are generated from electrochemical heat. Theoretical energy ($\Delta H_{Rea}$) is the heat sink used for produce aluminium in the cell, and the rest of heat is the heat sink as heat losses to the surroundings.

The total electrical potential of the reduction cell is normally in the range of 4.0 ~ 4.5 V. At 100% current efficiency, the theoretical lowest electrical potential for the prebaked anode cell is about 2.13 V, while at a lower 92% current efficiency, it yields 2.17 V [5].
Almost half of the total energy is lost to the surroundings (see Figure 2-2) [5, 6].

NOTE: Due to copyright reasons, this figure has been removed. Please refer to the original source:

Figure 2 in Bruggeman, J.N., *Pot heat balance fundamentals. 6th Australasian Aluminium Smelting Technology Conference and Workshop, 1998: p. 167-190.*

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Figure 2-2. The heat sources and heat sinks in a typical reduction cell [5]

2.3.2 Top heat loss

The heat loss of a reduction cell can be broken down into heat loss from specific areas of the cell (e.g. the top, side and bottom of the cell). Generally, the top heat loss accounts for about 50% of the total heat loss [5, 7-10]. A typical heat loss distribution is shown in Figure 2-3. Measured heat loss distributions of four 160 kA reduction cells by Shen [10] are shown in Table 2-1. For these four cells, top heat loss was the largest part of the total heat loss.
Chapter 2. Background

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Figure 2-3. A typical heat loss distribution in the reduction cell [9]

Table 2-1. Measured heat loss of 160 kA reduction cells using heat flux meter(SKD-HFM), data is from Shen [10]

<table>
<thead>
<tr>
<th></th>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
<th>Cell 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top,%</td>
<td>52.18</td>
<td>50.74</td>
<td>50.53</td>
<td>60.61</td>
</tr>
<tr>
<td>Side,%</td>
<td>31.93</td>
<td>32.88</td>
<td>31.66</td>
<td>27.46</td>
</tr>
<tr>
<td>Collector bars,%</td>
<td>4.23</td>
<td>2.50</td>
<td>3.57</td>
<td>2.50</td>
</tr>
<tr>
<td>Bottom,%</td>
<td>11.68</td>
<td>13.20</td>
<td>14.24</td>
<td>9.42</td>
</tr>
</tbody>
</table>

Furthermore, the top heat loss includes the heat loss from the anode stubs, the anode cover, the deck, and the open holes. The mechanism of top heat loss has been studied by Abbas [11] and Zhao et al. [12]. The anode cover plays an important role in the total top thermal resistance [9, 11, 12].

Abbas [11] simulated top heat loss by computational modelling. The model predicted that the thermal conductivity of the anode cover has a considerable effect on the top heat loss. Rye [13] measured the heat flux through different anode cover material in laboratory experiments, as shown in Table 2-2. It was found the more crushed bath in the anode cover the higher thermal conductivity the cover has and higher heat flux through the anode cover.
Table 2-2. The effect of anode cover material on heat flux [13].

<table>
<thead>
<tr>
<th>Weight percentage (wt%)</th>
<th>Primary alumina</th>
<th>wt % Crushed bath* with balance primary alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of the crust (cm)</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Bath temperature (°C)</td>
<td>956</td>
<td>956</td>
</tr>
<tr>
<td>Heat flux (kW/m²)</td>
<td>1.79</td>
<td>3.33</td>
</tr>
<tr>
<td>Thermal conductivity of loose cover (W/mK)</td>
<td>0.15</td>
<td>0.3</td>
</tr>
<tr>
<td>Thermal conductivity of crust (W/mK)</td>
<td>0.55</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Note: * 40 wt% particles of less than 500 µm with a maximum particle size of 8mm.

Liu et al. [14] measured heat flux through the anode cover in industrial reduction cells A and B using a Showa-Denka heat flux device. The measured top surface temperature and heat flux through the anode cover are given in Table 2-3. The measurement was carried out about 70 hours after the anode cover was added. The locations of the sensor relative to the anode were the same on both cells. The heat flux in the industrial cells has similar trend with the Lab measurements in Table 2-2.

Table 2-3. Measured top surface temperature and heat flux through the anode cover in industrial cell [14]

<table>
<thead>
<tr>
<th>Cell A (Alumina based cover)</th>
<th>Cell B (Crushed bath cover)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top surface temperature °C</td>
<td>Heat flux kW/m²</td>
</tr>
<tr>
<td>94</td>
<td>0.80</td>
</tr>
<tr>
<td>122</td>
<td>1.35</td>
</tr>
<tr>
<td>108</td>
<td>1.15</td>
</tr>
<tr>
<td>123</td>
<td>1.85</td>
</tr>
<tr>
<td>Average 112</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Because the fine anode cover such as alumina based cover has a low thermal conductivity and transmits low heat flow, the heat will accumulate in the crust causing the electrolyte component to melt. It has been observed by Taylor et al. [15] that sometimes the fine anode cover collapses resulting in hole formation and much more heat loss. In the case of the crushed bath cover with a higher thermal conductivity, bath material is the dominant phase and more thermally sensitive to its composition than alumina is. Under the condition of high heat flux through the anode cover, the
thermochemical stability of the cover material is crucial for maintaining the cell heat balance.
3 A literature review on anode cover and crust

Anode cover is used to cover the surface of the anode and the bath. It prevents air and volatilised fluoride fumes from diffusing through it. Consequently, the air burn of anode and fluoride fumes losses can both be substantially reduced. As noted previously, the anode cover provides the main thermal barrier to heat loss, and can be the main determinant in the magnitude and stability of the top heat loss.

In practice for large modern smelter technologies, one or two anodes per pot are changed every day. During anode setting operation, the old anode cover, or ‘crust’ as it is known, is removed, and a new anode is placed to the specified position. Then, a new anode cover is added to the top surface of the new anode and the liquid bath adjacent to the new anode.

3.1 Raw anode cover material

The raw anode cover is a loosely packed granular material. The following materials are commonly used as anode cover sources [16]:

- Crushed tapped bath, which is tapped from operational pots, solidified and crushed;
- Primary alumina;
- Secondary alumina, which has been used for scrubbing the pot gas;
- Recycled anode cover material. This is usually the most common cover material and is collected from anode butts (used anode) and anode cover removed from the pot;
- Cavity cleaning material. This is scooped from the bath cavity after removal of the anode butt and is combined with the recycled anode cover during both crushing and sizing.
- Other recycled bath from crucible cleanings, pot reconstruction cleanings,
spillages of bath and alumina under the pots.

According to the raw material used, the anode cover is classed as the following,

- Alumina based cover which mainly contains alumina.
- Crushed bath based cover which mainly consists of cryolite, alumina and chiolite. It is usually recycled anode cover material blended with cavity cleanings and crushed bath.
- Alumina and crushed bath mixture cover. A certain controlled proportion of alumina is mixed with crushed bath.

Crushed bath based cover and crushed bath/alumina mixture cover are both referred to as crushed bath cover in this study. After being added to the pot, the lower part of the anode cover consolidates through sintering, and is referred to as the crust.

3.2 Synthetic crust formation experiments

A number of bench scale laboratory experiments were carried out by Eggen and Rye [13, 17, 18] to make synthetic crust. The experimental arrangement is shown in Figure 3-1. In each experiment, cold cover material was added to the surface of a molten cryolite bath in a crucible. This experiment is referred to as the synthetic crust formation experiment in this thesis.

![Figure 3-1. Experimental arrangement. 1-loose alumina cover, 2-crust, 3-crucible with molten bath inside, 4-sleeve, 5-adjusting screws, 6-steel tube, 7-insulation, 8-heating coil [17]. Figure adapted from Figure 2, page 496, Eggen et. al. [17] in TMS Light](image-url)
The bath temperature during the experiments was kept stable by a controllable heating coil. The crucible was adjusted manually to make sure that the bottom surface of the crust made contact with the molten bulk bath. The insulation material in the apparatus kept the isotherm in the cover approximately horizontal. Several thermocouples were initially placed at specific vertical positions in the cover to measure and record the temperature in situ.

Figure 3-2 shows the measured temperature evolution curves (i.e. cover/crust temperature measured in situ and plotted as temperature-time curves) in an experiment using smelter grade sandy alumina cover. In this experiment, the molten bath had a CR of 2.15, contained 5 wt% CaF₂, and was saturated with alumina.

![Figure 3-2](image-url)

Figure 3-2. Measured cover temperature evolution curves in the experiment using smelter grade sandy alumina cover [17]. Each curve is labelled with the position relative to the bottom of the crust (i.e. the position of thermocouples placed in advance). The symbols (*) indicate the time of arrival of the liquid bath front at each position. Figure adapted from Figure 6, page 498, Eggen et. al. [17] in TMS Light Metals 1992 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)
The cover material used in the experiment contained moisture. Because the absorbed water evaporated at the hot zone, penetrated through the cover, and condensed at the cold zone [17], the cover above 28mm is heated fast to 100 °C, and kept stable at this temperature for a period of time before heated up further, as shown in Figure 3-2.

Compared with temperature measurement in a practical cell, the lab experiment carried out above can avoid many disturbances and focus on the thermochemical mechanism, and thus can provide reliable temperature evolution data.

### 3.3 Physical properties of anode cover and crust

The physical properties of anode cover and crust have been measured by several researchers [10, 19-21]. The anode cover samples for measurement were commonly taken from the raw loose anode cover material before being added to the pot, and crust samples were from the spent crust after it had been removed from industrial pots.

#### 3.3.1 Granularity and porosity of anode cover

The porosity of smelter grade alumina was measured by Coque et al. [19]. In most cases, the alumina has 0.3~0.4 macroporosity (>6.8 µm), 0.2~0.25 microporosity (0.0037~6.8 µm), 0.5~0.6 open porosity, and 0.69~0.715 overall porosity [19]. This indicates that there is about 0.1~0.2 closed porosity (<0.0037 µm) in the alumina particles.

Shen [10] measured the size distribution of industrial primary alumina and four crushed bath materials (the granularity is given in Table 3-1). These four crushed bath materials were sieved from the same batch of raw cover materials which were sampled from an industrial smelter. The alumina was mixed with the coarse crushed bath (CCB) at the percentages of 20%, 40%, 60% and 80% wt. The porosity of the crushed bath and the crushed bath/alumina mixtures were measured by Shen [10], as shown in Table 3-1.

Figure 3-3 shows the theoretical porosity when two sizes of spherical particles are mixed. For a blended granular mixture, the porosity is related to the granularity and the size ratio (=small size/large size). The theoretical porosity has a minimum value at about 75% large component percentage (see Figure 3-3). In Table 3-1, each anode cover is divided into large and small fractions according to its granularity. For instance, the CCB consists of
the large fraction (+150 µm) and the small fraction (-150 µm). For FCB, the large and small fractions are +45 and -45 µm respectively.

Table 3-1. Granularity and porosity of the crushed bath and the crushed bath/alumina mixture (LCB- Large crushed bath, MCB- Medium crushed bath, FCB- Fine crushed bath, CCB- Coarse crushed bath) (from Shen [10])

<table>
<thead>
<tr>
<th>Granularity</th>
<th>-45µm</th>
<th>45-150µm</th>
<th>150µm-1mm</th>
<th>1-2mm</th>
<th>+2mm</th>
<th>Rough size ratio</th>
<th>Tapped porosity</th>
<th>Untapped porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCB (wt%)</td>
<td>1.6</td>
<td>47.7</td>
<td>50.7</td>
<td>0.38</td>
<td>0.478</td>
<td>0.515</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCB (wt%)</td>
<td>26.4</td>
<td>73.6</td>
<td>0.0</td>
<td>0.25</td>
<td>0.377</td>
<td>0.482</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FCB (wt%)</td>
<td>26.0</td>
<td>74.0</td>
<td>0.0</td>
<td>0.38</td>
<td>0.447</td>
<td>0.589</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCB (wt%)</td>
<td>24.6</td>
<td>75.4</td>
<td>0.0</td>
<td>0.05</td>
<td>0.348</td>
<td>0.473</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina+80%CCB (wt%)</td>
<td>39.7</td>
<td>60.3</td>
<td>0.0</td>
<td>0.05</td>
<td>0.378</td>
<td>0.489</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina+60%CCB (wt%)</td>
<td>54.8</td>
<td>45.2</td>
<td>0.0</td>
<td>0.05</td>
<td>0.495</td>
<td>0.546</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina+40%CCB (wt%)</td>
<td>69.8</td>
<td>30.2</td>
<td>0.0</td>
<td>0.05</td>
<td>0.626</td>
<td>0.647</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina+20%CCB (wt%)</td>
<td>84.9</td>
<td>15.1</td>
<td>0.0</td>
<td>0.05</td>
<td>0.660</td>
<td>0.666</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alumina</td>
<td>100</td>
<td>0.0</td>
<td>0.0</td>
<td>0.05</td>
<td>0.685</td>
<td>0.717</td>
<td></td>
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</tr>
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Figure 3-3: Porosity against volume fraction of large component [22].

Low size ratio is good for high bulk density (see Figure 3-3). The porosity of the mixture
can be reduced by filling the void space among the large particles with the small particles. Among these four crushed bath materials (i.e. FCB, MCB, LCB and CCB), porosity decreases slightly with the decrease of the size ratio. The CCB has the lowest porosity due to its lowest size ratio as long as the two particle sizes are blended in the right ratio with 75 wt% large particle size (see Table 3-1). A similar trend was reported by Wijayaratne et al. [20]. When the extra fine particles (< 45 µm) were removed from a crushed bath cover sample, the porosity decreased from 0.48 to 0.42.

3.3.2 Bulk density of anode cover

Shen [10] measured the bulk density of the crushed bath, and the crushed bath/alumina mixtures as listed in Table 3-1. The results are shown in Figure 3-4 and Table 3-2. The bulk density increases generally with the increased weight fraction of the crushed bath (see Figure 3-4).
Figure 3-4: Bulk densities of crushed bath/alumina mixtures [10] (Experimental: under experimental condition for thermal conductivity measurement)

Table 3-2. Measured bulk density of different crushed bath [10] (LCB, MCB, FCB and CCB refer to Table 3-1, Experimental: under experimental condition for thermal conductivity measurement)

<table>
<thead>
<tr>
<th></th>
<th>LCB</th>
<th>MCB</th>
<th>FCB</th>
<th>CCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untapped (g/cm$^3$)</td>
<td>1.445</td>
<td>1.542</td>
<td>1.225</td>
<td>1.571</td>
</tr>
<tr>
<td>Tapped (g/cm$^3$)</td>
<td>1.516</td>
<td>1.830</td>
<td>1.634</td>
<td>1.907</td>
</tr>
<tr>
<td>Experimental (g/cm$^3$)</td>
<td>1.554</td>
<td>1.856</td>
<td>1.647</td>
<td>1.942</td>
</tr>
</tbody>
</table>

3.3.3 Bulk density of crust

In the synthetic crust formation experiment reviewed in section 3.2, Rye [18] measured the bulk density vertical distributions in the alumina based crust in two experiments in which the superheat of the bulk bath were 55 °C and 10 °C respectively. The measured bulk density distribution is shown in Figure 3-5. In the lower part of the crust, the bulk density first increases with the height until it reaches the maximum and then decreases further in the upper zone of the crust.
Chapter 3. A literature review on anode cover and crust

3.3.4 Thermal conductivity of anode cover

The thermal conductivity of smelter grade alumina was measured by Llavona [23], Hatem et al. [24], Rye et al. [13], Shen [10], and Wijayaratne et al. [20]. Table 3-3 shows the experimental conditions and measured thermal conductivity. Shen [10] and Wijayaratne et al. [20] used the same experimental rig in the University of Auckland, and measured a higher thermal conductivity than others.

Table 3-3. Thermal conductivity of smelter grade alumina [10, 13, 20, 23, 24]

<table>
<thead>
<tr>
<th>Author</th>
<th>Powder properties</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alumina Type</td>
<td>Median Particle size (µm)</td>
</tr>
<tr>
<td>Shen</td>
<td>--</td>
<td>87</td>
</tr>
<tr>
<td>Wijayaratne</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Rye</td>
<td>Sandy</td>
<td>--</td>
</tr>
<tr>
<td>Hatem</td>
<td>--</td>
<td>76</td>
</tr>
<tr>
<td>Llavona</td>
<td>Sandy</td>
<td>--</td>
</tr>
<tr>
<td>Llavona</td>
<td>Sandy</td>
<td>--</td>
</tr>
</tbody>
</table>

--: Not given

In the steady state method, a plate specimen (or powder specimen filling in plate box)
with a certain thickness \( (L) \) is heated from a heat source at one side to temperature steady state. The temperature difference of two sides \( (\Delta T = T_1 - T_2) \) and the heat flux per unit area \( (q, \text{ W.m}^{-2}) \) through the plate are recorded. The average thermal conductivity \( (k) \) at temperature range \( T_1 \) to \( T_2 \) is calculated according to Fourier’s equation,

\[
k = \frac{q \cdot L}{\Delta T}
\]

Similarly, in the radial steady state method, a hollow cylinder specimen (or powder specimen filling in a hollow cylinder container) with outer radius \( (R) \) and inner radius \( (r) \) is heated from a heat source in the centre to temperature steady state. The temperature difference of outer and inner sides \( (\Delta T = T_o - T_i) \) and the heat flux per unit length \( (q, \text{ W.m}^{-1}) \) through the cylinder are recorded. The average thermal conductivity \( (k) \) at temperature range \( T_o \) to \( T_i \) is calculated as

\[
k = \frac{q}{2\pi\Delta T} \ln\left(\frac{R}{r}\right)
\]

The hot wire method measures the transient temperature rise in a specimen with a certain thickness which is heated from a linear heat source (hot wire) embedded in the test specimen. The thermal conductivity of the specimen can be calculated from the dynamic temperature change [25].

The advantage of the hot wire method is that the true thermal conductivity is determined directly in relation to a given temperature of the specimen. The steady state method (including radial steady state method) only measures the average thermal conductivity in a temperature range [26]. Complicated apparatus and strict measurement condition are required to reduce the temperature range [27].

The hot wire method is the optimum for low thermal conductivity (<2 W/m·K) materials, and has been given standard status in many countries [27-31]. By contrast, the steady state method has some limitations, such as complicated apparatus, strict measurement condition and the long time required for temperature equilibrium [27].

Figure 3-6 and Figure 3-7 show the measured thermal conductivity of crushed bath,
alumina and a blend of them from Shen [10] (the size distribution is given in Table 3-1).

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Figure 3-6. Thermal conductivity of the Crushed bath from Shen [10] (LCB, MCB, FCB and CCB refer to Table 3-1)

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Figure 3-7. Thermal conductivity of the CCB/Alumina mixtures from Shen [10] (CCB refer to Table 3-1)

3.3.5 Thermal conductivity of crust

Rye [13] measured the thermal conductivity of crust in-situ in the synthetic crust
formation experiment reviewed in section 3.2. The thermal conductivity of the crust increases with crushed bath content [13], as shown in Figure 3-8.

![Figure 3-8: Measured thermal conductivity of crust, data is from Rye [13].](image)

### 3.4 Thermal sintering of anode cover

#### 3.4.1 Alumina based cover

Smelter grade alumina usually contains meta-stable transition phases [32]. Transition phase alumina normally transforms to thermally stable alpha phase alumina (corundum) at the temperature of above 1100 °C. This transformation can take place at a lower temperature in the presence of AlF₃ and of Na₃AlF₆ [33]. For example, an alumina sample used for dry scrubbing of fluoride emissions has a measured transition alpha phase transformation temperature of 785 °C. The increased addition of AlF₃ from 1% to 10% had only a slight effect on the transformation temperature [33].

Some laboratory experiments have been carried out to investigate the relationship between transition → alpha alumina phase transformation and the mechanical strength of the crust [32-36]. As more and more alpha alumina grains are transformed and grow, they crosslink with adjacent grains and gradually form an interlocking network of alpha alumina, which can be described as a sintering process. This alpha alumina interlocking network contributes to the high cold mechanical strength of alumina based crusts [33-35].
However, there is no evidence at all that this strengthening mechanism plays a role in the hot strength of crushed bath based crusts.

Townsend [36] suggested that the interlocking network of alumina platelets in alumina based crusts occurs because of the alumina dissolution and precipitation mechanism via the cryolite bath.

3.4.2 Crushed bath cover

The mechanism of the crust formation from modern crushed bath cover is different from the alumina based crust. Crushed bath sinters much faster because of its high thermal conductivity, and at a lower temperature due to the thermally triggered sintering of grains containing low melting temperature bath component [14, 37]. The liquid phase plays an important role in the crushed bath crust formation (see section 3.6.2).

3.5 Condensation and decomposition of bath fume

The fume vaporized from the bulk bath contains NaAlF$_4$, which is meta-stable. When the fume permeates into the anode cover, it condenses and decomposes to chiolite (Na$_5$Al$_3$F$_{14}$) and aluminium fluoride (AlF$_3$) at about 680 °C [38].

3.6 Liquid bath in crust

3.6.1 Liquid bath penetration

The liquid bath penetration in the anode cover has been measured in some bench scale laboratorial experiments [17, 39, 40], for instance, the experiments reviewed in section 3.2. In these experiments, cover material was added into a tube above the surface of a molten bulk bath. A typical liquid detection method used a series of thermocouple probes placed in the loose anode cover in advance. Each thermocouple probe formed an electrical circuit and detected electricity when it made a contact with the liquid bath.

Because the raw cover material in some experiments is pure alumina, the only source of the liquid bath detected in the crust is the bulk bath. The liquid bath in the anode cover is driven from the bulk bath by capillary pressure against the force of gravity. This mechanism is verified by using water as the liquid phase [17]. The penetration rate of water in the anode cover can be predicted well by the Carman-Kozeny equation [41].
Gerlach et al. [39] measured the penetration rate of liquid bath in a preheated alumina based cover. The measured penetration rate is between 6 and 66 mm/min. Rolseth et al. [40] performed similar experiments and got the measured data between 20 and 50 mm/min. These results are of the order of the penetration rate of water (34 mm/min). A cold anode cover was used in the experiments by Eggen et al. [17]. The detected liquid bath penetration rate is only 0.3~0.7 mm/min, which is much lower than that in the preheated alumina cover.

Liquid bath may freeze as a solid phase in the cold anode cover. Eggen et al. [17] found that the liquid bath front moved upwards with its minimum freezing temperature range of about 660~730 °C.

### 3.6.2 Role of liquid bath in crust consolidation

In addition to the penetrated liquid bath, incongruent melting of chiolite is another major source of liquid bath in the anode cover. The existence of liquid bath in hot industrial crust samples (without liquid bath penetration) was observed by Liu et al. [14]. As noted earlier, the crushed bath cover usually contains cryolite, alumina and low melting phase chiolite. In the case of the alumina-based cover, chiolite is also present due to the condensation of the bath fume.

Liu et al [14] hypothesised that the liquid bath “glues” solid granules and grains together, thus contributing to the crust consolidation. Johnston and Richards [34] reveals that crust containing more absorbed liquid bath is stronger and more difficult to crush. Johnston considered that cryolite acted as a “binder phase” in hard crusts although later work by Groutso et al [32] determined that chiolite and not cryolite was the binding phase in these hard bath crusts.

### 3.6.3 Role of liquid bath in crust deterioration

The deterioration of the crust has been investigated by some researchers [14, 34, 36, 42]. The dissolution of alumina from the crust into the bulk bath is an important cause of the deterioration of the alumina based crust. Johnson [42] and Townsend et al. [36] measured the dissolution time of alumina based crust. Generally, the soft crust dissolves faster than hard crust in a stirred bath. However, the dissolution rates of soft and hard crusts in an
unstirred bath had no significant difference.

When an air gap exists between the crust and the bulk bath, there is still the possibility of dissolution of the crust. Rye [18] hypothesised that the bath fume was deposited as liquid bath layer at the bottom surface of the crust. The liquid bath could then dissolve/melt the alumina and the solid bath in the crust, allowing it to fall back into the bulk bath as droplets.

Another important cause of crust deterioration is the melting of crust bath components and the loss of liquid bath from the crust. In the experiments performed in an industrial reduction cell by Liu et al. [14], loss of large amount of crust bottom was observed immediately after an anode effect. This is very likely to have occurred due to the melting and weakening of bath component in the crust before or during the anode effect. Anode effect termination always leads to significant downward and then upward movement of the anodes, which would result in the fracture and falling of a weakened crust.

3.7 Chemical composition distribution in crust

Uneven chemical composition in the crust was found in a few studies [14, 32]. Liu et al. [14] analysed the chemical composition of crust samples from industrial reduction cells. It was found that the bottom layer of the crust (facing the bulk bath) had a higher CR than the upper section of the crust, and the chiolite content in the crust increased from the bottom to the top (see Table 3-4). Groutso et al. [32] showed a similar trend with the chiolite content increased from 23 wt% at the bottom to 48 wt% at the top in an industrial crust sample [32] (see Table 3-5).
Table 3-4. Thermochemical analysis of two crust samples from cell A and B [14] (cell A-alumina base cover; cell B-50:50 bath and alumina)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaF₂</th>
<th>MgF₂</th>
<th>Al₂O₃</th>
<th>NaF</th>
<th>BR</th>
<th>T°C</th>
<th>ΔH J/g</th>
<th>T°C</th>
<th>ΔH J/g</th>
<th>T°C</th>
<th>ΔH J/g</th>
<th>Wb% **</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>9.5</td>
<td>0.18</td>
<td>23.30</td>
<td>41.27</td>
<td>20.82</td>
<td>1.00</td>
<td>725</td>
<td>10</td>
<td>728</td>
<td>101</td>
<td>542</td>
<td>39</td>
</tr>
<tr>
<td>A2</td>
<td>2.52</td>
<td>0.18</td>
<td>21.80</td>
<td>53.26</td>
<td>18.60</td>
<td>0.85</td>
<td>720</td>
<td>155</td>
<td>920</td>
<td>3</td>
<td>31.3</td>
<td></td>
</tr>
<tr>
<td>A3</td>
<td>2.10</td>
<td>0.12</td>
<td>23.46</td>
<td>51.30</td>
<td>18.84</td>
<td>0.80</td>
<td>730</td>
<td>187</td>
<td>836</td>
<td>8</td>
<td>37.7</td>
<td></td>
</tr>
<tr>
<td>A4</td>
<td>1.62</td>
<td>0.25</td>
<td>31.28</td>
<td>40.32</td>
<td>23.22</td>
<td>0.74</td>
<td>720</td>
<td>200</td>
<td>850</td>
<td>3</td>
<td>40.3</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>2.04</td>
<td>0.71</td>
<td>34.18</td>
<td>30.89</td>
<td>29.22</td>
<td>0.85</td>
<td>528</td>
<td>241</td>
<td>873</td>
<td>23</td>
<td>48.6</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>1.34</td>
<td>0.21</td>
<td>35.04</td>
<td>31.43</td>
<td>29.46</td>
<td>0.84</td>
<td>743</td>
<td>316</td>
<td>850</td>
<td>8</td>
<td>63.7</td>
<td></td>
</tr>
</tbody>
</table>

* Sample A1 is the bottom 2-3 cm of the crust taken from cell A. Sample B4 is the top 2-3 cm (8 cm upper from sample B1) of the crust taken from cell B etc.

** Percentage of chiolite in a crust is estimated by dividing the measured ΔH by 496 J/g which is the ΔH value given in JANAF Table for pure chiolite transformation.

Table 3-5. Chemical composition analyses of a crust sample [32]

<table>
<thead>
<tr>
<th>Sample/Phases</th>
<th>Corundum</th>
<th>Transition</th>
<th>Cryolite</th>
<th>Chiolite</th>
<th>NaF₃, CaF₂</th>
<th>AlF₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>52</td>
<td>0</td>
<td>0</td>
<td>48</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Middle 10cm</td>
<td>42</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>48</td>
<td>0</td>
</tr>
<tr>
<td>Middle 5cm</td>
<td>33</td>
<td>0</td>
<td>37</td>
<td>24</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Bottom</td>
<td>14</td>
<td>12</td>
<td>47</td>
<td>23</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

There are two probable reasons for this uneven chemical composition distribution [14, 18]:

(i) During crust formation the cryolite component preferentially crystallizes from the penetrating liquid bath at the lower part of the crust. Thus, the liquid bath moving upward becomes increasingly enriched in AlF₃ and other fluoride additives.

(ii) NaAlF₄ decomposes to solid chiolite and AlF₃ below 680 °C which results in the enrichment of chiolite at the top of the crust.

It is possible that both of these mechanisms are occurring.
The experimental analyses above indicate that chemical composition in the crust is dependent on the thermochemical behaviour during the crust formation which has not been theoretically and quantitatively studied.

### 3.8 Research questions

As reviewed early, the physical properties (porosity, bulk density and thermal conductivity) of anode cover and crust were measured by a few researchers. Temperature evolution curves during a synthetic crust formation experiment were measured Eggen and Rye [13, 17, 18]. The chemical composition distribution in some crusts were analysed by Liu et al. [14] and Groutso et al. [32]. These physical and thermochemical properties are important for understanding the thermochemical behaviour.

A number of researchers [33-35] have proposed the mechanism for alumina based crust formation as the growth of an alpha alumina interlocking network. However, this mechanism does not take into account thermochemical behaviour which is important for the thermochemical stability of both alumina based crust and crushed bath crust. Though the phase equilibrium during liquid bath penetration in the crust was illustrated by Eggen and Rye et al. [17, 18], the mechanism for the thermochemical behaviours of sintering, liquid bath penetration and phase transformation has not been studied theoretically and quantitatively, and will be developed in this study.

The foregoing literature review has highlighted several knowledge gaps which are crucial to understanding the thermochemical behaviour of present anode cover/crust material and also to developing superior materials for anode cover in the future.

This thesis aims to answer the following research questions:

1. What is the mechanism of the thermochemical behaviour in the crust?
2. What impacts do the chemical compositions have on the thermal stability of the crust?
4 Theoretical development

4.1 Proposed thermochemical mechanism in this work

The mechanism is proposed in the following series of schematics and descriptions relating to the crust formation and aging process in reduction cells. Some idealisations of conditions are assumed and noted in the following descriptions.

4.1.1 The porosity of raw anode cover

When initially added to the surface of the anode and the bulk bath, raw anode cover is under loose granular condition, as shown in Figure 4-1. As reviewed in Chapter 3.3.1, the porosity of anode cover is affected by its granulometry. In addition, other factors such as pore structure, agglomeration and particle bridging may account for the porosity of the anode cover [43-45].

Figure 4-1. The formation and ageing process of the crust (1) the porosity of raw anode cover

Porous media may consist of both internal porosity and inter-particle porosity [45], as shown in Figure 4-2.
Figure 4-2. Sketches of different pore structures: (a) dense without pore; (b) closed internal pore; (c) open internal pore and (d) inter-particle pore. [45]

High untapped porosity might be attributed to the agglomeration of fine particles with high cohesive strength [43-45] and somewhat particle bridging [45], as shown in Figure 4-3. However, under the condition of sufficient vibration, the influence of agglomeration and particle bridging on tapped porosity are negligible [43-45].

Figure 4-3. Schematic diagrams of (a) particle bridging and (b) agglomeration [45]

As an important constituent of the anode cover, smelter grade alumina has a high porosity and a typical, complex pore structure. Figure 4-4 shows the SEM photographs of porous alumina particles. Smelter grade alumina generally has overall porosity as high as 0.65 ~ 0.75. Coque’s measurement [19] shows that smelter grade alumina has an open porosity of 0.6, and an average pore diameter of 0.033 µm. Alumina calcined at 1200 °C (i.e. alpha alumina) has a slightly higher open porosity of 0.7 and a larger average pore size of 0.37 µm [19].
Figure 4-4. Primary alumina (a) Sandy alumina with high transient phase content; (b) Highly calcined, floury alumina with high alpha phase content. [35]. Figure adapted from Figure 2, page 330, Less et al. [35] in TMS Light Metals 1976 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

The tapped density of smelter grade alumina is just slightly higher than the loose bulk density [10], which means that the particle bridging and agglomeration are negligible. Therefore, the internal open porosity is very likely the major reason for the high alumina porosity. In fact, an alumina particle may be considered as a hard agglomeration of finer crystals, which also explains the high porosity. In this case the internal pore is actually the intra-agglomerate pore (see Figure 4-3 (b)).

In the case of crushed bath cover, the porosity is much less than that of the alumina. The internal porosity of the crushed bath cover is likely to be insignificant. The reason will be explained in section 4.1.5.

4.1.2 Bulk bath freezing and recovering

The raw anode cover is at room temperature when it is initially added to the reduction cell. After added to the hot bulk electrolyte surface, the anode cover increases quickly to 100 °C when humidity in the cover materials begins to be released. The temperature of the bulk bath adjacent to the new anode drops significantly due to the cold new anode and anode cover, and the surface of the bulk bath around and under the anode cover material freezes locally [46].

The rapidly frozen bath begins to remelts within about 10 hours [46, 47]. In addition, the
insulation of the anode cover material and the convective heat transfer in the bulk bath help the bulk bath recover and reach a uniform temperature.

**Figure 4-5. The formation and ageing process of the crust (2) Bath freezing**

### 4.1.3 Liquid bath penetration

It is assumed that the crust is always in contact with the bulk bath during the crust formation. Driven by capillary pressure, the liquid bath penetrates deeper into the anode cover from the bulk bath if there is contact between the bulk bath and the anode cover, which is very likely at addition of the cover to the pot. The capillary pressure depends on the wettability of particles by the liquid bath. It appears justified that crushed bath particles are perfectly wetted by their own melt, the liquid bath. The alumina particles are also estimated to be readily wetted by the liquid bath (see Appendix A.3). This is also attested by the liquid bath penetration tests by researchers [17, 39]. Thus, it is assumed that the liquid bath can wet the anode cover particles well.
4.1.4 Crust consolidation

The anode cover directly above the hot bulk bath is heated at the bottom surface, whereas the cooler surroundings at the top surface extract heat. This creates a vertical temperature gradient which persists even after a steady temperature profile is established [17]. Because the heat flow through the anode cover/crust is mainly vertically from the bottom to the top, the isotherm in it is almost horizontal. It is reasonable to assume the anode cover/crust as one dimensional field.

As the temperature increases, a consolidated, liquid bath penetrated crust forms at the bottom of the anode cover and is able to support the loose cover above. For alumina based cover, the hardness of the crust mainly depends on the networking of alpha alumina platelet occurring above 800 °C [33-35].

Crushed bath particles have usually passed through a crusher and have certain strengths [32]. They are initially glued together by the liquid bath melting at about 685~725 °C and strengthened by the freezing of penetrated liquid bath [14].

However, in some cases the cover may collapse. Later in the ageing of the crust, the experiments done by Liu [14] show that the presence of a large proportion of liquid phase within the crust is the primary cause of the collapse of the crushed bath crust.
Chapter 4. Theoretical development

4. Crust consolidation

**Figure 4-7.** The formation and ageing process of the crust (4) Crust consolidation

### 4.1.5 Liquid bath filling pores

The volume fraction occupied by the penetrated liquid bath in the crust, called the liquid volume fraction, relates to the porosity and pore structure of the anode cover.

Johnston [34] measured the volume shrinking and bulk density of the synthetic crust. The results showed that there was just a very slight volume shrinkage (less than 5%) during the synthetic crust formation but with a significant increase of bulk density from 0.98 g/cm³ to 1.6~2.7 g/cm³. Under the condition of the liquid bath penetration, the densification of the crust is mainly because of the substantial volume fraction of the penetrated liquid bath rather than the volume shrinking.

**Figure 4-8.** The formation and ageing process of the crust (5) Liquid bath filling pores

In the study of synthetic crust formation by Townsend et al. [36], it was observed that the
liquid bath filled the inter-particle pores readily, as shown in Figure 4-9. The porosity readily filled by the liquid bath (0.3~0.4) was much less than the total open porosity of the alumina (about 0.6). There was clearly air trapped in the internal open pores with very fine pathways and these pathways were blocked by the frozen bath (as illustrated in Figure 4-10 (a)).

Figure 4-9. Inter-particle pores filled by the liquid bath [36]. Figure adapted from Figure 2, page 658, Townsend et. al. [36] in TMS Light Metals 1984 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

Since a single alumina particle is considered as a quasi-agglomeration of very fine crystals and most pores in it are just nano-size, the liquid bath tends to permeate into it with very slow rate.

Sandy alumina is associated with rounded and coarse transition phase alumina crystals (see Figure 4-4 (a)). After the transition $\rightarrow$ alpha phase transformation in the crust above
800 °C, sandy alumina gradually changes to a network of alpha alumina platelets (thickness 0.5~1.5 μm). The alpha alumina platelets result in a more open interlinking structure which contributes to an easier pathway for the liquid bath to penetrate through (see Figure 4-10 (b)) [48]. A study on the fabrication of C/SiC composites by Oh et al. [49] showed that a similar interlinking whisker structure maintained an open diffusion path for filling and increased the bulk density.

Since crushed bath material usually is recycled from the old crust, most internal pores in it might have already been filled. In fact, according to Shen’s measurement [10], it has much lower porosity than smelter grade alumina. Most remaining pores inside the crushed bath particles are likely to be isolated and closed.

The inter-particle porosity filled readily by the liquid bath is defined as ‘easy-filling porosity’ in this study. The value of this porosity is estimated in Appendix A.1.

4.1.6 Phase equilibrium in liquid bath

Because of the vertical temperature gradient in the anode cover/crust, the liquid bath cools as it penetrates upwards, and starts to crystallize at the liquidus temperature. The mechanism of the crystallization behaviour of the liquid bath is proposed below.

AlF3, CaF2, MgF2, LiF, KF and Al2O3 are the most common additives in industrial cryolite electrolytes in China where the crust samples were taken. In this study, these are the possible additives, and any other trace impurities can be ignored.

A phase diagram is essential for studying the phase equilibrium. Eggen et al. [17] and Rye [18] studied the crystallization behaviour of liquid bath with additives AlF3, CaF2 and Al2O3 using the appropriate phase diagram. However, the phase diagram for a cryolite-based system with all these additives (i.e. AlF3, CaF2, MgF2, LiF, KF and Al2O3) is extremely complicated and has not been fully studied. Nevertheless, some binary or ternary cryolite based systems including one or two such additives have been well studied by a number of researchers [50-57], and are relevant for understanding the crystallization behaviour of the liquid bath.

When liquid bath consisting of only cryolite and alumina is cooled slowly, the
composition change follows the binary phase diagram (see Figure 4-11 (a)). The cryolite liquidus curve represents the liquidus temperature for primary crystallization of cryolite. For the liquid bath at point ‘a’ initially, cryolite starts to crystallize when it is cooled to point ‘b’. The composition of the remaining liquid bath moves along the line ‘bE’ as it is cooled further. The liquid bath composition ceases to change when it reaches the binary eutectic point ‘E’ where cryolite and alumina crystallize simultaneously until all liquid disappears.

Fluoride additives change the crystallization behaviour of the liquid bath. For instance, in the system Na₃AlF₆-AlF₃-Al₂O₃, the AlF₃ concentration increases with the simultaneous crystallizations of cryolite and alumina. The eutectic point in Figure 4-11 (b) thus forms a eutectic curve. This cooling process is illustrated by the ternary phase diagram of Na₃AlF₆-AlF₃-Al₂O₃ as shown in Figure 4-12. As the temperature falls, the composition moves from point ‘a’ to the line ‘AB’, and changes further along the eutectic curve ‘ABPE’. The remaining liquid bath moving upward through the crust therefore becomes increasingly rich in AlF₃.

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Figure 4-11. (a) Binary phase diagram of system Na₃AlF₆-Al₂O₃; (b) Quasibinary phase diagram of system Na₃AlF₆-AlF₃-Al₂O₃ [50]
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Alternatively, refer to a hard copy of this thesis, as deposited in The University of Auckland Library.

Figure 4-12. Na$_3$AlF$_6$-AlF$_3$-Al$_2$O$_3$ phase diagram [51, 52]

When the liquid bath is cooled to the ternary peritectic point (‘P’ in Figure 4-12) at 723 °C, the following peritectic reaction takes place theoretically [52].

$$Na_3AlF_6(s) + L_p = Na_3AlF_{14}(s) + Al_2O_3(s) \quad (4.1)$$

where $L_p$ is the liquid bath at the ternary peritectic point.

However, actual progression of a peritectic reaction requires strict conditions, including a slow cooling rate, high diffusion in the solid phase and equilibrium crystallization [58, 59]. The peritectic reaction is therefore very likely to be suppressed greatly in the crust. Below 723 °C, chiolite and alumina will crystallize from the liquid bath. At the ternary eutectic point (‘E’ in Figure 4-12) 684 °C, the following eutectic crystallization takes place [52],

$$L_e = Na_3AlF_{14}(s) + AlF_3(s) + Al_2O_3(s) \quad (4.2)$$

where $L_e$ is the liquid bath at the ternary eutectic point.

Figure 4-13 shows the ternary phase diagram for the system Li$_3$AlF$_6$-Na$_3$AlF$_6$-Al$_2$O$_3$. Because cryolite is the major component in the liquid bath, the cryolite enriched portion is highlighted in Figure 4-13. Similarly to the last diagram, the liquid composition moves along the eutectic curve ‘AP’, with both solid alumina and cryolite crystallizing.
simultaneously, until it reaches the ternary peritectic point ‘P’ (683 °C).

NOTE: Due to copyright reasons, this figure has been removed. Please refer to the original source:

Figure 2 in Cassidy, R.T. and J.J. BROWN, *Phase equilibria in the system LiF - AlF₃ - Na₃AlF₆ - Al₂O₃*. *Journal of the American Ceramic Society*, 1979. 62(11 - 12): p. 547-551.

Alternatively, refer to a hard copy of this thesis, as deposited in The University of Auckland Library.

Figure 4-13. Phase diagram for ternary system Li₃AlF₆-Na₃AlF₆-Al₂O₃ [57]

Peritectic and eutectic reactions in some ternary systems (only cryolite enriched portion) are summarized in Table 4-1. All the peritectic and eutectic temperatures are between 645 °C and 735 °C.
Table 4-1. Peritectic and eutectic reactions in some ternary systems

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Type</th>
<th>T/°C</th>
<th>Primary solid phase fields</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>25CaF₂-45Na₃AlF₆-30AlF₆</td>
<td>per</td>
<td>688</td>
<td>Na₅AlF₁₆⁺Na₂Al₃F₁₄⁺NaCaAlF₆</td>
<td>[53]</td>
</tr>
<tr>
<td>18CaF₂-52Na₃AlF₆-30AlF₆</td>
<td>per</td>
<td>683</td>
<td>NaCaAl₂F₉⁺Na₃Al₃F₁₄⁺NaCaAlF₆</td>
<td>[53]</td>
</tr>
<tr>
<td>15CaF₂-55Na₃AlF₆-30AlF₆</td>
<td>eut</td>
<td>680</td>
<td>AlF₃⁺Na₂Al₃F₁₄⁺NaCaAlF₆</td>
<td>[53]</td>
</tr>
<tr>
<td>1.5MgF₂-55.5NaF-43.0AlF₆</td>
<td>per</td>
<td>700</td>
<td>Na₂Al₃F₁₄⁺Na₃MgAlF₇</td>
<td>[54]</td>
</tr>
<tr>
<td>1.5MgF₂-51.2NaF-47.3AlF₆</td>
<td>eut</td>
<td>688</td>
<td>Na₅AlF₁₆⁺NaAlF₄⁺Na₂MgAlF₇</td>
<td>[54]</td>
</tr>
<tr>
<td>2.0MgF₂-49.5NaF-48.5AlF₆</td>
<td>eut</td>
<td>685</td>
<td>NaAlF₄⁺NaMgAlF₇⁺Na₂MgAlF₇</td>
<td>[54]</td>
</tr>
<tr>
<td>1.5MgF₂-47.0NaF-51.5AlF₆</td>
<td>eut</td>
<td>687</td>
<td>NaAlF₄⁺NaMgAlF₇⁺AlF₃</td>
<td>[54]</td>
</tr>
<tr>
<td>30LiF-37NaAlF₆-33AlF₃</td>
<td>per</td>
<td>685</td>
<td>AlF₃⁺Na₂Al₃F₁₄⁺Na₃Li₃Al₂F₁₂</td>
<td>[55]</td>
</tr>
<tr>
<td>37LiF-17Na₃AlF₆-46AlF₃</td>
<td>eut</td>
<td>645</td>
<td>AlF₃⁺Na₂Al₃F₁₄⁺Na₃Li₃Al₂F₁₂</td>
<td>[55]</td>
</tr>
<tr>
<td>62.7KF-36.3NaF-1.0AlF₃</td>
<td>eut</td>
<td>711</td>
<td>NaF⁺KF⁺K₂AlF₆</td>
<td>[56]</td>
</tr>
<tr>
<td>27.4KF-51.9NaF-20.7AlF₃</td>
<td>eut</td>
<td>734.5</td>
<td>KF⁺K₂AlF₆⁺Na₃AlF₆</td>
<td>[56]</td>
</tr>
<tr>
<td>45.7NaAlF₆-48.1NaF₀₋₆.2Al₂O₃</td>
<td>per</td>
<td>723</td>
<td>Na₃AlF₁₄⁺Al₂O₃</td>
<td>[52]</td>
</tr>
<tr>
<td>37.4NaAlF₆-58.5AlF₆₋₄.1Al₂O₃</td>
<td>eut</td>
<td>684</td>
<td>Na₃AlF₁₄⁺AlF₃⁺Al₂O₃</td>
<td>[52]</td>
</tr>
<tr>
<td>51Li₃AlF₆₋₄.25Na₃AlF₆₋₆.5Al₂O₃</td>
<td>per</td>
<td>683</td>
<td>Li₃AlF₆⁺Na₃AlF₆⁺Al₂O₃</td>
<td>[57]</td>
</tr>
<tr>
<td>66Li₃AlF₆₋₄.29Na₃AlF₆₋₅Al₂O₃</td>
<td>eut</td>
<td>670</td>
<td>Li₃AlF₆⁺Na₃Li₃Al₂F₁₂⁺Al₂O₃</td>
<td>[57]</td>
</tr>
</tbody>
</table>

It is too complex to determine precisely each peritectic and eutectic reaction, along with the composition and the temperature in a cryolite-based system with all the additives mentioned above. To simplify the study, 725 °C and 685 °C are assumed as the peritectic and eutectic temperatures respectively. Above 725 °C only cryolite and/or alumina are assumed to crystallize from the liquid bath. Between 725 °C and 685 °C, chiolite, alumina and other fluoride additives compounds (e.g. NaCaAlF₆, Na₂MgAlF₇, etc) crystallize, and below 685 °C all components of the system are solid, even though it is possible for small amounts of lithium and potassium based eutectics to be liquid slightly below this. Thus, since sodium cryolite, alumina and chiolite still make up the majority of the crust material, 685 °C is assumed as the minimum freezing temperature of the liquid bath.

As noted above, it is assumed that fluoride additives stay in the liquid phase above 725 °C. Though the phase diagram for the cryolite system with all these additives is not available, if quasi-binary cryolite liquidus curve and alumina saturation solubility curve are able to be determined, the eutectic curve for the crystallizations of cryolite and alumina can be determined. An example of this is shown in Figure 4-11 (b). Empirical expressions have been proposed to fit the two curves, as discussed below.
(1) Cryolite liquidus curve

Pure cryolite has a melting point of 1011 °C [60]. The liquidus temperature for primary crystallization of cryolite from the liquid bath is depressed by the additives. The best empirical expression available to estimate liquidus temperature is the one proposed by Solheim et al. [61],

\[
T_{liq} = 1011 + 0.5[AlF_3] - 0.13[AlF_3]^2 - \frac{3.45[CaF_2]}{1 + 0.00173[CaF_2]}
+ 0.124[CaF_2][AlF_3] - 0.00542((CaF_2)[AlF_3])^{1.5}
- \frac{7.93[Al_2O_3]}{1 + 0.0936[Al_2O_3] - 0.0017[Al_2O_3]^2 - 0.0023[AlF_3][Al_2O_3]}
- \frac{8.90[LiF]}{1 + 0.0047[LiF] + 0.001[LiF]} - 3.95[MgF_2] - 3.95[KF]
\]

where \(T_{liq}\) is the liquidus temperature and the square brackets denote the weight percentage of the components in the bath. The composition limitations are \([AlF_3]\), \([CaF_2]\), \([LiF]<20\) wt pct, \([MgF_2]\), \([KF]<5\) wt pct, and \([Al_2O_3]\) up to saturation.

(2) Alumina saturation solubility curve

The saturation alumina solubility in the liquid bath is influenced by the additives. Skybakmoen et al. [50] proposed an empirical expression to predict the saturation solubility of alumina in molten bath,

\[
[Al_2O_3]_{sat} = A(T / 1000)^B,
A = 11.9 - 0.062[AlF_3] - 0.0031[AlF_3]^2 - 0.50[LiF] - 0.20[CaF_2] - 0.30[MgF_2] + \frac{42[LiF][AlF_3]}{2000 + [LiF][AlF_3]},
B = 4.8 - 0.048[AlF_3] + \frac{2.2[LiF]^{1.5}}{10 + [LiF] + 0.001[AlF_3]^{1.5}}
\]

where \(T\) is temperature.

Unfortunately, KF is not included in the empirical expression above. Though the alumina solubility in Na_3AlF_6-K_3AlF_6-AlF_3 system has been frequently studied, there is
little agreement between investigators [62-64]. Fernandez et al. [65] gave a similar expression with equation (4.4) for molten cryolite with the only additive being KF,

\[ [Al_2O_3]_{sat} = 11.5 + 0.16[KF] - 1.24 \times 10^{-3}[KF]^2 \]  

(4.5)

In this study, the combination of equation (4.4) and (4.5) is used to predict the saturation solubility of alumina in cryolite based melts with additives AlF₃, CaF₂, MgF₂, LiF and KF, assuming that there is no interaction between these additives in determining the saturation solubility of alumina.

\[ [Al_2O_3]_{sat} = A(T / 1000)^B \]

\[ A = 11.9 - 0.062[AlF_3] - 0.003[AlF_3]^2 - 0.50[LiF] - 0.20[CaF_2] - 0.30[MgF_2] + \frac{42[LiF][AlF_3]}{2000 + [LiF][AlF_3]} \]

\[ + 0.16[KF] - 1.24 \times 10^{-3}[KF]^2, \]

\[ B = 4.8 - 0.048[AlF_3] + \frac{2.2[LiF]^{1.5}}{10 + [LiF] + 0.001[AlF_3]^3} \]

(4.6)

Table 4-2 shows the calculated and measured alumina solubility in some cases of cryolite based melts with CaF₂ and KF (W₁ and W₂ are calculated from expressions (4.4) and (4.6) respectively, Wₘ is the measured data from literature [66], D₁ and D₂ are deviation of W₁ and W₂ respectively). Though expression (4.6) is not very accurate, it seems to give better prediction than expression (4.4).

<table>
<thead>
<tr>
<th>Melt composition wt%</th>
<th>T °C</th>
<th>W₁ wt%</th>
<th>W₂ wt%</th>
<th>Wₘ wt%</th>
<th>D₁ wt%</th>
<th>D₂ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(74Na₃AlF₆+26AlF₃)+3CaF₂+3KF</td>
<td>880</td>
<td>5.13</td>
<td>5.40</td>
<td>5.31</td>
<td>0.18</td>
<td>-0.09</td>
</tr>
<tr>
<td>(78Na₃AlF₆+22AlF₃)+3CaF₂+3KF</td>
<td>980</td>
<td>8.36</td>
<td>8.75</td>
<td>9.40</td>
<td>1.04</td>
<td>0.65</td>
</tr>
<tr>
<td>(78Na₃AlF₆+22AlF₃)+3CaF₂+3KF</td>
<td>950</td>
<td>7.39</td>
<td>7.73</td>
<td>8.80</td>
<td>1.41</td>
<td>1.07</td>
</tr>
</tbody>
</table>

There are two kinds of nucleation related to alumina or cryolite crystallisation: homogeneous and heterogeneous nucleation. Genuine homogeneous nucleation may require high super-saturation or a microgravity environment [67]. Heterogeneous nucleation is induced by foreign nuclei or surfaces present in the solution [68]. This is readily satisfied in the porous anode cover. The nucleation in the anode cover is very
likely to be heterogeneous nucleation.

Figure 4-14. The formation and ageing process of the crust (6) Partial crystallization of alumina and cryolite

4.1.7 Liquid bath front in crust

Crystallization of cryolite and alumina solid phase reduces the liquid volume fraction. If the crystallization rate is very high, the crust becomes blocked and the liquid supply to the crust is then restrained. Therefore, the upper part of the anode cover undergoes only thermal sintering in this case.

Figure 4-15. The formation and ageing process of the crust (7) Fluid bath front

Under conditions of low crystallization rate, the crust remains unblocked. As long as there is sufficient liquid supply to the crust from the bulk bath, the liquid bath front will move up with the minimum freezing isotherm of the liquid bath, namely the eutectic temperature. Then the movement of the liquid bath front position is determined by the Stefan heat balance condition – describing generation and transmission of the latent heat.
released at the interface to allow the melting or freezing to continue.

### 4.1.8 Partial crust melting

As noted above, crystallization takes place during the crust formation. The solidified phase in the lower part of the crust may melt or dissolve later if the anode cover is well insulated. This is more likely to occur after the liquid bath stops penetrating. Based on the same assumptions, the melting behaviour may proceed by the reverse of the crystallization process discussed above - all solid fluoride additives and chiolite would then melt at 725 °C, and cryolite and alumina melt or dissolve in the liquid bath above 725 °C.

After melting has proceeded to some extent, the lower parts of the crust affected may fall into the bulk bath when the liquid volume fraction is high enough. An air gap will therefore form between the crust and the bulk bath surface, and this is observed in practice as shown in the typical crust profiles in the photographic below (crust age 10-15 days).

![Diagram of partial crust melting](image)

**Figure 4-16. The formation and ageing process of the crust (8) partial crust melting**

### 4.1.9 Three possibilities for crust evolution after partial crust melting

1. **Crust becomes stable**

   When the heat loss to the surroundings from the anode cover top equals the heat input at the crust bottom, the temperature at the crust bottom surface reaches an equilibrium position where further internal melting and increase of the liquid fraction inside the crust will not occur. The thickness of the crust will thereafter remain stable, as long as the
remaining solid crust has sufficient strength to resist falling into the bath.

(2) Weakening

If heat continues to accumulate at the bottom of the crust due to poor transmission through the top sections of crust and low thermal conductivity of the anode cover, the crust might continue melting, and its thickness will decrease gradually. The crust eventually becomes weakened through a high liquid fraction permeating a large proportion of its depth, leading to the collapse of the lower sections of crust triggered by movements of the anodes during cell operations or by high cell bath temperatures. The deposited liquid bath from the bath fume at the bottom surface of the crust may also contribute to the high liquid fraction. This situation leads to a thin crust/cover which conducts much more heat out of the top of the cell.

(3) Repair during or after crust weakening

When conditions in the cell stabilise, the heat flux into the crust may reduce. The remaining thin cover/crust then may not provide enough insulation, causing the bulk bath
to solidify as a crystalline layer under the crust (if there is contact between the bulk bath and the crust)- repairing the crust or creating a second lower crust, until physical repair of the crust occurs by the cell operators.

Figure 4-19. The formation and ageing process of the crust (9-3) Repair during or after crust weakening

4.2 Thermochemical model

To quantitatively simulate the thermochemical behaviour relating to the crust formation process as proposed in above sections 4.1.3 to 4.1.7, a thermochemical model is developed in this section.

4.2.1 Simplifications and assumptions

The model is based on some simplifications and assumptions, as summarized below.

1) Continuity

(1.1) The bottom surface of the anode cover makes full contact with the top surface of the bulk bath.

(1.2) The raw anode cover is mixed fully and evenly. It is assumed as a homogeneous porous media.

(1.3) Under the condition of liquid bath penetration, the volume shrinkage during crust sintering is ignored – based on the high porosity of the anode cover material this shrinkage is not important in the thermochemical process occurring there.

(1.4) The liquid bath is incompressible flow.
2) Dimensional simplification

The simulation domain of the model is the anode cover. The model is simplified as a one-dimension problem, based on the mainly horizontal isotherms predicted for the main parts of the cover in [69]. The interface between the bulk bath and the anode cover is set as the coordinate origin. Coordinate \( x \) is along the anode cover height dimension from the bottom surface to the top surface.

![Figure 4-20. Design of simulation domain](image)

3) Composition

(3.1) The raw anode cover initially contains cryolite, alumina, and chiolite. The bulk liquid bath contains dissociated ions from cryolite, chiolite, alumina, and possible fluoride additives such as AlF$_3$, LiF, KF, MgF$_2$, and CaF$_2$. All NaF and AlF$_3$ in the liquid bath are expressed as Na$_3$AlF$_6$ and AlF$_3$ to maintain continuity of species.

(3.2) Above 725 °C, fluoride additives such as AlF$_3$, LiF, KF, MgF$_2$, and CaF$_2$ stay in the liquid phase, although it is known that calcium fluoride is not rejected quantitatively from the freezing interface – this is accounted for in the phase change temperature itself.

(3.3) In the temperature range of 685–725 °C, though solid phases other than cryolite and alumina also crystallize, it is very difficult to determine the exact chemical composition. It is assumed that the crystallization at 685 °C (namely the liquid bath front) accounts for overall crystallization in the range of 685–725 °C, and is governed by Stefan boundary condition as discussed in section 4.2.5. The solid phases crystallized at 685 °C will melt when temperature reaches 725 °C. This assumption is justified by the DTA test in section 6.5.2 which shows that there is crystallization peak at 685 °C on cooling curve while melting peak at 725 °C on heating cover for chiolite enriched samples.
(3.4) Alumina, cryolite, AlF3, chiolite, LiF, KF, MgF2, and CaF2 are denoted as species 1, 2, 3, 4, 5, 6, 7, and 8 respectively. \( \phi_i \) denotes the weight fraction of each in the liquid bath respectively.

\[
\sum_{i=1}^{8} \phi_i = 1 \quad (4.7)
\]

\[
\rho_L \phi_i = c_i \quad (4.8)
\]

where \( c_i \) denotes the mass concentration (kg/m³), \( \rho_L \) is the density of the liquid bath.

\( m_i \) denotes the overall volumetric phase transformation rate of \( i \)th species, kg/(m³s), meaning the liquid phase generation amount over per volume (m³) of the anode cover per second (\( m_i > 0 \) means dissolution or melt of solid phase to liquid phase for the \( i \)th species, \( m_i < 0 \) means crystallization of liquid phase to solid phase for the \( i \)th species).

### 4.2.2 Governing equations

In the model, temperature, concentration, and phase transformation rate are averaged volumetric properties within the discrete finite volumes in the numerical scheme. The governing equations are based on macroscopic laws of conservation [70, 71].

1. **The conservation equation of momentum**

The liquid bath penetration in the crust is a laminar flow with very slow velocity (The kinetic energy, accelerated speed and inertia force are ignored. for more details, see Appendix A.5). The conservation equation of momentum [72, 73] (i.e. incompressible Navier-Stokes equation) is:

\[
0 = \frac{\partial p}{\partial x} + \rho_L g + \frac{\mu}{K_h} u + m u \quad (4.9)
\]

where \( \mu \) is viscosity of the liquid bath, \( \rho_L \) is the density of the liquid bath, \( m \) is overall phase transformation rate, kg/(m³s), means the liquid phase generation amount over per volume (m³) of the anode cover per second (\( m > 0 \) means dissolution of solid phase to liquid phase, \( m < 0 \) means crystallization of liquid phase to solid phase), \( u \) is superficial
fluid velocity (m/s),

\[ u = v \varepsilon_L \]  \hspace{1cm} (4.10)

where \( v \) is interstitial fluid velocity, m/s, \( \varepsilon_L \) is volume fraction of the liquid bath.

\( K_b \) is the hydraulic conductivity, and is estimated from the Carman-Kozeny equation [41] (see Appendix A.5)

\[ K_b = \frac{\rho_L g \varepsilon^3}{5S^2} \]  \hspace{1cm} (4.11)

where \( S \) is the surface area per unit volume.

In terms of pressure equilibrium, giving

\[ \int_0^{h_e} \left[ \frac{\mu}{K_b} u + mu \right] dx = \frac{2\gamma_L \cos \theta}{R} - \rho_L g h_e \]  \hspace{1cm} (4.12)

where \( h_e \) is the liquid bath front position, \( R \) is effective capillary radius, \( \gamma_L \) is the surface tension of the liquid bath, \( \theta \) is contact angle between the liquid bath and the solid phase (see Appendix A.2).

The relationship between the liquid front movement rate and \( u \) is,

\[ \frac{dh_e}{dt} = v = \left( \frac{u}{\varepsilon_L} \right) \bigg|_{x=h_e} \]  \hspace{1cm} (4.13)

(2) The conservation equation of mass

The mass conservation equations for each species in the liquid phase with temperature above 725 °C are:

\[ \varepsilon_L \rho_L \frac{\partial}{\partial t} \phi_L + \phi_L \rho_L \frac{\partial \varepsilon_L}{\partial t} + u \rho_L \frac{\partial \phi_L}{\partial x} + \phi_L \rho_L \frac{\partial u}{\partial x} + \frac{\partial J_L}{\partial x} = m_1 \]  \hspace{1cm} (4.14)

\[ \varepsilon_L \rho_L \frac{\partial}{\partial t} \phi_L + \phi_L \rho_L \frac{\partial \varepsilon_L}{\partial t} + u \rho_L \frac{\partial \phi_L}{\partial x} + \phi_L \rho_L \frac{\partial u}{\partial x} + \frac{\partial J_2}{\partial x} = m_2 \]  \hspace{1cm} (4.15)
Chapter 4. Theoretical development

\[ \varepsilon_L \rho_L \frac{\partial \varepsilon_L}{\partial t} + \phi \rho_L \frac{\partial \varepsilon_L}{\partial t} + u \rho_L \frac{\partial \varepsilon_L}{\partial x} + \phi \rho_L \frac{\partial u}{\partial x} + \frac{\partial J_i}{\partial x} = 0, i \geq 3 \]  

(4.16)

\[ J_i = -\rho_L D_i \varepsilon_L \frac{\partial \phi}{\partial x} \]  

(4.17)

\[ \sum J_i = 0 \]  

(4.18)

where \( D_i \) is diffusion coefficient, \( J_i \) is diffusion flux, \( \varepsilon_L \) is the volume fraction of liquid bath, \( m_i \) (i = 1, 2) is the phase transformation rate, \( u \) is the superficial fluid velocity of penetrated liquid bath in the crust. Equations (4.14) to (4.16) are valid based on the fact that the fluid is incompressible, thus \( \text{div}(\nu) = 0 \).

The mass conservation equations for the solid phase with temperature above \( 725 \, ^\circ C \) are

\[ \rho_{S,i} \frac{\partial \varepsilon_{S,i}}{\partial t} = -m_i \]  

(4.19)

\[ \rho_{S,2} \frac{\partial \varepsilon_{S,2}}{\partial t} = -m_2 \]  

(4.20)

where \( \varepsilon_{S,1}, \varepsilon_{S,2} \) are the volume fractions of the solid phase, \( \varepsilon_S \) is the total volume fraction of the solid phase, \( \varepsilon_S = \varepsilon_{S,1} + \varepsilon_{S,2} \), \( \rho_{S,1}, \rho_{S,2} \) are the true densities of the solid phase.

The volume fraction satisfies,

\[ \varepsilon_S + \varepsilon_L + \varepsilon_A = 1 \]  

(4.21)

where \( \varepsilon_A \) is residual air volume fraction (i.e. the volume fraction of air trapped in the internal pores).

Based on the assumption (3.3) in section 4.2.1, the phase transformation \( m_i \) in the temperature range of 685 and \( 725 \, ^\circ C \) is assumed as zero, and superficial fluid velocity \( u \) is assumed as constant.

\[ m_i = 0, i = 1, 2, \ldots, 8 \]  

(4.22)
\( \frac{\partial u}{\partial x} = 0 \) (4.23)

(3) The conservation equation of energy

Conservation equation of energy transfer with advection flow in porous media is given as:

\[
\frac{\partial}{\partial t} (\varepsilon_L \rho_L H_L) + \frac{\partial}{\partial x} (u \rho_L H_L) = \frac{\partial}{\partial x} (\varepsilon_L k_{\text{eff}} \frac{\partial T_L}{\partial x}) - h_v (T_L - T_M), x \leq h_e
\] (4.24)

\[
\frac{\partial}{\partial t} \left[ \sum (\varepsilon_{S,i} \rho_{S,i} H_{S,i}) \right] = \frac{\partial}{\partial x} (\varepsilon_S k_{\text{eff}} \frac{\partial T_S}{\partial x}) + h_v (T_L - T_M), x \leq h_e
\] (4.25)

\[
\frac{\partial}{\partial t} \left[ \sum (\varepsilon_{S,i} \rho_{S,i} H_{S,i}) \right] = \frac{\partial}{\partial x} (k_c \frac{\partial T_C}{\partial x}), x > h_e
\] (4.26)

where \( T_L \) is the temperature of the liquid bath in the crust, \( T_S \) is the temperature of the solid phase in the crust, \( T_M \) is the temperature at the interface between the liquid bath and the solid phase. \( T_C \) is the temperature of the loose cover, \( H_L \) and \( H_{S,i} \) are enthalpy of the liquid bath and the solid phase respectively, \( k_{\text{eff}} \) is effective thermal conductivity of the crust, \( k_c \) is effective thermal conductivity of the loose cover, \( h_v \) is volumetric heat transfer coefficient between the liquid bath and the solid phase.

If there is sufficient high contact surface area between the solid and liquid phase, it is very fast to reach local temperature equilibrium in the crust due to the high the heat transfer rate. It is assumed that,

\[
T_L \approx T_S \approx T_M, \frac{\partial T_L}{\partial x} \approx \frac{\partial T_M}{\partial x} \approx \frac{\partial T_M}{\partial t} \approx \frac{\partial T_S}{\partial t}
\] (4.27)

The conservation equation of energy becomes,

\[
\frac{\partial}{\partial t} (\varepsilon_L \rho_L H_L) + \frac{\partial}{\partial x} \left[ \sum (\varepsilon_{S,i} \rho_{S,i} H_{S,i}) \right] + \frac{\partial}{\partial x} (u \rho_L H_L) = \frac{\partial}{\partial x} (k_{\text{eff}} \frac{\partial T_L}{\partial x}), x \leq h_e
\] (4.28)

4.2.3 Effective thermal conductivity

For a porous media, an effective thermal conductivity is widely used as an approximate
representation of the thermal conductivity. Experimentation is the best way to determine the effective thermal conductivity.

In the case of the effective thermal conductivity of the anode cover, different sets of experimental data were obtained by a few researchers as reviewed in Chapter 3. However, these sets of data are not fully in agreement with each other, and have limited use in proposing a thermal conductivity prediction model. As reliable measured data is not available for some specific cover materials, the use of published empirical model is the alternative way to predict the effective thermal conductivity in this study.

The effective thermal conductivity of crust/cover is predicted by Zehner-Schlunder model [74-76] (without taking into account the thermal radiation and convection in air pores):

\[
\frac{k_{zs}}{k_L} = 1 - \sqrt{1 - \varepsilon_L} + \frac{2\sqrt{1 - \varepsilon_L}}{1 - \lambda B} \left( \frac{(1 - \varepsilon_L) B}{(1 - \lambda B)^2} \ln \frac{1}{\lambda B} - \frac{B - 1}{2} - \frac{B - 1}{1 - \lambda B} \right)
\]

where \( k_{zs} \) is the effective thermal conductivity without taking into account the effect of thermal radiation and convection in air pores, \( k_S \) is the thermal conductivity of solid phase, \( k_L \) is the thermal conductivity of liquid phase, \( \varepsilon_L \) is the volume fraction of liquid phase. \( C_{zs} \) and \( m_{zs} \) are shape factors that depend on the general shape of the particles in the material. Zehner and Schunder proposed \( C_{zs} = 1.40 \) and \( m_{zs} = 10/9 \) for irregularly shaped particles [74].

For packed powder with \( 0 < k_S/k_L < 1000 \), Zehner-Schunder model [74-76] is found to predict effective thermal conductivity in reasonably good agreement with experimental data when effects of thermal radiation and convection in air pores are not significant [75, 77, 78]. \( k_S \) and \( k_L \) are both temperature dependent. In the cases of the anode cover and crust, the \( k_S/k_L \) is less than 500, and further below 100 at above 300 °C.

The solid proportion of the crushed bath cover mainly consists of frozen cryolite and alumina. The mean thermal conductivity of the solid mixture is calculated by the
following equation,

\[ k_s = \sum \phi_i k_i \]  

(4.30)

where \( \phi_i \) is the concentration of the component in the solid mixture.

The radiation in the air pore enhances heat transfer in air porous media, and thus the effective thermal conductivity. For packed powder with gas and solid phases, the Laubitz model [77] gives reasonable estimation for the contribution of thermal radiation to the effective thermal conductivity [77].

In this study, the equivalent radiant conductivity is calculated by the Laubitz model [77],

\[ k_r = 4Ed\sigma(T + 273)^3 \]  

(4.31)

\[ E = \frac{e[1-(1-\varepsilon_A)^{2/3}+(1-\varepsilon_A)^{4/3}]}{1-\varepsilon_A} \]  

(4.32)

where \( k_r \) is the thermal conductivity due to thermal radiation, \( \varepsilon_A \) is the air porosity, \( d \) is the mean particle size, \( \sigma \) is the Stefan-Boltzmann constant, \( e \) is the emissivity of the solid particle.

The convective heat transfer in an air porous media is influenced by the pore size. For pores less than 10 mm diameter, the air convective heat transfer is not significant [76, 79]. In this study, the pore size of the loose anode cover is less than 10 mm. Thus the effect of convective heat transfer is neglected.

The combination of above two models called Zehner-Schlunder-Laubitz (ZSL) model is applied to predict the effective thermal conductivity in this study,

\[ k_{eff} = k_{zs} + k_r \]  

(4.33)

The crust contains three phases, i.e. liquid, air and solid phases. It is assumed that air is mostly in the internal pores of the particles in the crust. The Z-S-L model is firstly applied to the particle consisting of solid and air phases, and then to the crust made up of the liquid bath and the particle.
4.2.4 Transition alpha alumina phase transformation

The transition to alpha alumina phase transformation occurs at a wide temperature range above 800 °C [33], and has an exothermic reaction enthalpy (-22 kJ/mol) [80, 81]. Volumetric heat generation is added in the conservation equation of energy to simulate the heat released in this situation,

$$\frac{\partial}{\partial t}(\varepsilon_L \rho_L H_L) + \frac{\partial}{\partial t} \left[ \sum (\varepsilon_s \rho_s H_s) \right] + \frac{\partial}{\partial x} (u \rho_L H_L) = \frac{\partial}{\partial x} (k_{eff} \frac{\partial T}{\partial x}) + q_{\gamma\alpha}$$ \hspace{1cm} (4.34)

where $q_{\gamma\alpha}$ is volumetric heat generation rate.

It is assumed that gamma alumina is the major phase of the transition alumina. The order of this reaction (i.e. gamma to alpha alumina phase transformation) is one [33, 82]. The reaction rate constant $K_R$ is about 0.05 /min [33]. The changing of the concentration of transition alumina with time is given by,

$$\ln(\varepsilon_\gamma \rho_\gamma) = -K_R(t-t_\alpha) + \ln(\varepsilon_\gamma,0 \rho_\gamma) \rightarrow \varepsilon_\gamma = \frac{1}{\rho_\gamma} e^{-K_R(t-t_\alpha)+\ln(\varepsilon_\gamma,0 \rho_\gamma)}$$ \hspace{1cm} (4.35)

where $\varepsilon_\gamma$ is the volume fraction of transition alumina, $\rho_\gamma$ is the transition alumina density, $\varepsilon_\gamma,0$ is the initial volume fraction of transition alumina, $t_\alpha$ is the time when the temperature reaches 800 °C.

The volumetric heat generation rate $q_{\gamma\alpha}$ by this reaction is calculated by:

$$q_{\gamma\alpha} = \frac{d(\varepsilon_\gamma \rho_\gamma)}{dt} L_{\gamma\alpha} = -K_R \varepsilon_\gamma \rho_\gamma L_{\gamma\alpha}$$ \hspace{1cm} (4.36)

where $L_{\gamma\alpha}$ is transition alpha phase transformation latent heat (-22 kJ/mol). $q_{\gamma\alpha}$ equals to zero below 800 °C.

The residual air volume fraction relates to the transition → alpha alumina phase transformation rate, and is assumed to be:
\[
\frac{d\varepsilon_A}{dt} = K_{\gamma a} + \frac{d\varepsilon_\gamma}{dt} \frac{\varepsilon_\gamma}{1 - \varepsilon_\gamma} = K_{\gamma a} - \frac{\varepsilon_\gamma}{1 - \varepsilon_\gamma} K_{\alpha} \varepsilon_\gamma
\]  

(4.37)

where \( K_{\gamma a} \) is the normal air volume fraction shrinking rate without transition \( \rightarrow \) alpha alumina phase transformation, \( \varepsilon_\gamma \) is the volume fraction of the transition alumina, \( \varepsilon_\gamma \) is the porosity of the transition alumina particle.

### 4.2.5 Moving boundary of liquid bath front

When the liquid bath front reaches isotherm range 685~725 °C, chiolite melting and eutectic reactions take place. It is assumed that local temperature equilibrium is achieved in this temperature range. The exact reactions are not determined, and approximate averaged porosity and reaction enthalpy are used. The moving rate of the liquid front is related to the temperature gradient and reaction enthalpy.

The Stefan boundary condition has been widely used to predict the moving boundary condition, for instance with the solidification interface of water transport [83] and metal infiltration [84]. In a finite element at the liquid bath front, the heat flux enters the temperature range is \( q_{in} \), while the heat flux exits is \( q_{out} \). According to conservation of energy, the difference between \( q_{in} \) and \( q_{out} \) should be equal to the reaction enthalpy released, as shown in Figure 4-21.
The moving boundary condition at point $h_e$,

$$
\rho_s L_e \varepsilon_e \frac{dh_e}{dt} - k_{\text{eff}} \frac{\partial T_{L_e}}{\partial x}|_{x=h_e} = -k_c \frac{\partial T_c}{\partial x}|_{x=h_e},
$$

(4.38)

$$
T_c|_{x=h_e} = 685
$$

(4.39)

The moving boundary condition at point $h_p$,

$$
\rho_p L_p \varepsilon_p \frac{dh_p}{dt} - k_{\text{eff}} \frac{\partial T_{L_p}}{\partial x}|_{x=h_p} = -k_{\text{eff}} \frac{\partial T_{L_p}}{\partial x}|_{x=h_p},
$$

(4.40)

$$
T_{L_p}|_{x=h_p} = 725
$$

(4.41)

Where $L_e$ and $L_p$ are the enthalpy of eutectic reaction and chiolite melting respectively, $\varepsilon_e$ and $\varepsilon_p$ are the average phase transformation volume fractions of liquid which freezes (positive) or melts (negative) at the point $h_e$ and $h_p$ respectively.

It is assumed that, at time $t=t_p$, all fluoride additives melt above 725 °C (including original ones plus the ones freeze at time $t=t_e$, satisfying that $h_e$ at time $t=t_e$ equals to $h_p$ at time $t=t_p$), the value of $\varepsilon_p$ is
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\[
\varepsilon_p \bigg|_{t=t_e} = -(\varepsilon_{sumf} + \varepsilon_e) \bigg|_{t=t_e}, h_p \bigg|_{t=t_e} = h_e \bigg|_{t=t_e}, t > t_e
\] (4.42)

where \( \varepsilon_{sumf} \) is the total original volume fraction of all fluoride additives in the raw anode cover, which is known.

The liquid bath freezes at \( h_e \), and at the same time, the temperature at it increases with time. Unlike \( \varepsilon_p \), the value of \( \varepsilon_e \) is determined by Stefan condition in equation (4.38) because the temperature increasing is the converse process with the freezing process which makes \( \varepsilon_e \) can’t be determined in the same way with \( \varepsilon_p \).

In addition, \( u \) in the region \( x = (h_p, h_e) \) is assumed as an average constant value. At position of \( h_p \) there is a jump value of \( u \) because that fluoride additives (density \( \rho_F \)) melt as liquid bath (density \( \rho_L \)) with volume change,

\[
\rho_L u \bigg|_{x=h_p} + \frac{d\rho_p}{dt} \varepsilon_p \bigg|_{x=h_p} (\rho_F - \rho_L) = \rho_L u \bigg|_{x=h_p} \rightarrow u \bigg|_{x=h_p} = \frac{d\rho_p}{dt} \varepsilon_p \frac{\rho_F - \rho_L}{\rho_L} + u \bigg|_{x=h_p} (4.43)
\]

where \( \rho_F \) is the true density of fluoride additives (the internal air porosity in it is ignored).

4.2.6 Correlation between phase transformation rate and concentration

The correlation between phase transformation rate and concentration is deducted as (see Appendix A.6),

\[
\phi_i = \phi_i^* - K_i m_i, i=1,2
\] (4.44)

where \( \phi_1^* \) and \( \phi_2^* \) is saturation concentration of alumina and cryolite respectively.

According to liquidus temperature empirical expressions (4.3) and (4.4), the liquidus temperature is determined by,
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\[ T_M = 1011 + 0.5 \times 100\phi_3^* - 0.13(100\phi_3^*)^{2.2} - \frac{3.45 \times 100\phi_6^*}{1 + 0.00173 \times 100\phi_6^*} \]

\[ 7.93 \times 100\phi_1^* \]

\[ 1 + 0.0936 \times 100\phi_1^* - 0.0017(100\phi_1^*)^2 - 0.0023 \times 100\phi_3^* \times 100\phi_1^* + 0.124 \times 100\phi_5^* \times 100\phi_3^* - 0.00542(100\phi_8^* \times 100\phi_1^*)^{1.5} \]

\[ + 0.0047 \times 100\phi_5^* + 3.95(100\phi_6^* + 100\phi_7^*) \]

\[ \frac{8.9 \times 100\phi_5^*}{1 + 0.001 \times 100\phi_5^*} \]

\[ 100\phi_1^* = [11.9 - 0.062 \times 100\phi_3^* - 0.0031 \times (100\phi_3^*)^2 - 0.5 \times 100\phi_5^* - 0.2 \times 100\phi_5^* - 0.3 \times 100\phi_7^* + \frac{42 \times 100\phi_5^* \times 100\phi_7^*}{2000 + 100\phi_5^* + 100\phi_7^*} + 0.16 \times 100\phi_6^* - 1.24 \times 10(\phi_5^*)^2] \times (T_M / 1000) \]  

(4.45) 

(4.46) 

Based on the assumption that fluoride additives stay in the liquid bath, the ratio between the concentration of them is nearly constant and depends on the initial value of the bulk bath, i.e.

\[ k_{\text{ALF}_3} \phi_3^* \approx k_{\text{LiF}} \phi_5^* \approx k_{\text{KF}} \phi_6^* \approx k_{\text{MgF}_2} \phi_7^* \approx k_{\text{CaF}_2} \phi_8^* \]  

(4.47) 

\[ \sum \phi_i^* = 1 \]  

(4.48) 

The above equations indicate that the saturation concentration \( \phi_i^* \) and \( \frac{\partial \phi_i^*}{\partial T_M} \) is function of the temperature \( T_M \). For a certain temperature \( T_M \), the saturation concentration \( \phi_i^* \) and differential \( \frac{\partial \phi_i^*}{\partial T_M} \) is determined. Since \( T_L \) is approximate to \( T_M \), \( \phi_i^* \) is determined by \( T_L \) as,

\[ \phi_i^* = f_i(T_L) \ , \ i=1,2 \]  

(4.49)
where function $f_i()$ is determined according to equations (4.45), (4.46) and (4.47).

Equation (4.44) takes into account both melting and freezing process. When the liquid bath penetrates into a porous cover with high contact surface area, if there is sufficient solid cryolite in the cover, the liquid bath temperature will drop to the liquidus temperature very fast due to the melting of the solid cryolite. However, if there is no solid cryolite, the liquid bath temperature can stay higher than the liquidus temperature. For example, above 965 °C (the eutectic temperature for cryolite and alumina mixture), liquid bath can exist with solid alumina, but not with the mixture of solid cryolite and solid alumina.

In the case of alumina based cover, $\phi_2 = \phi_2' - K_2 m_2$ is not valid for cryolite in a region where both following conditions meet meanwhile: (1) there is no cryolite solid phase and (2) the liquid bath temperature is higher than the liquidus temperature. This region is called as ‘hot’ region in this study.

As the crust is heated from the bottom, if ‘hot’ region exists, it starts from the bottom surface of the crust. Thus, the liquid bath penetrates directly into the ‘hot’ region from the bulk bath. It is reasonable to assume that the ratio between cryolite and other fluoride additives of the liquid bath in ‘hot’ region is constant and depends on the initial value of the bulk bath,

$$k_{Cry} \phi_2^* \approx k_{ALF} \phi_3^* \approx k_{LiF} \phi_5^* \approx k_{KF} \phi_6^* \approx k_{MgF_2} \phi_7^* \approx k_{CaF_2} \phi_8^*$$

(4.50)

Therefore, $\phi_i^*$ can be calculated from equations (4.46) (4.48) and (4.50).

### 4.2.7 Boundary condition

At the crust’s bottom surface, a convection boundary condition is applied.

$$k_{ef} \frac{\partial T_0}{\partial X} = h_f (T_0 - T_B)$$

(4.51)

where $h_f$ is convective heat transfer coefficient between the bulk bath and the crust bottom surface, $T_B$ is the temperature of the bulk bath.
At the anode cover top surface, convection and radiation boundary conditions are applied.

\[
k_c \frac{\partial T_c}{\partial x} = (h_c + h_r)(T_c - T_a) \quad (4.52)
\]
\[
h_r = e\sigma \frac{[(T_c + 273)^4 - (T_a + 273)^4]}{T_c - T_a} \quad (4.53)
\]

where \(h_c\) is convective heat transfer coefficient between the air and the anode cover top surface, \(h_r\) is effective radiative heat transfer coefficient, \(T_B\) is the temperature of the ambient air, \(e\) is emissivity of the anode cover, \(\sigma\) is Stefan-Boltzmann constant, \(5.67 \times 10^{-8}\) kg/s\(^3\)k\(^{-4}\).

### 4.3 Variables and equations for model development

The independent variables for the model are \(x\) and \(t\). Dependent variables in the model include \(\varnothing_i (i=1-8), \varepsilon_L, \varepsilon_{S,1}, \varepsilon_{S,2}, u, m_1, m_2, \varepsilon_A, T_L (H_1, H_S), T_C (H_1), \varepsilon_r, \varepsilon_v, h_c, h_r\). Due to the assumptions made before, \(\varnothing_i (i=3-8)\) have constant proportion over time, and they can be combined as one variable \(\varnothing_{3-8}\). Therefore, dependent variables number for the model is reduced to 17, which requires 17 equations noted above to solve those variables, as listed below.

1. \[
\int_0^{b_i} \left[ \frac{\mu}{K_h} \right] u + mu \right] dx = \frac{2\gamma_L \cos \theta}{R} - \rho_L gh_c, K_h = \frac{\rho_L g\varepsilon^3}{5S^2} \quad \text{(refer to eq. (4.12))}
\]
2. \[
\varepsilon_L \rho_L \frac{\partial \phi}{\partial t} + \phi \rho_L \frac{\partial \varepsilon_L}{\partial t} + u \rho_L \frac{\partial \phi}{\partial x} + \phi \rho_L \frac{\partial u}{\partial x} + \frac{\partial J_1}{\partial x} = m_1 \quad \text{(refer to eq. (4.14))}
\]
3. \[
\varepsilon_L \rho_L \frac{\partial \phi}{\partial t} + \phi \rho_L \frac{\partial \varepsilon_L}{\partial t} + u \rho_L \frac{\partial \phi}{\partial x} + \phi \rho_L \frac{\partial u}{\partial x} + \frac{\partial J_2}{\partial x} = m_2 \quad \text{(refer to eq. (4.15))}
\]
4. \[
\varepsilon_L \rho_L \frac{\partial \phi_s}{\partial t} + \phi_s \rho_L \frac{\partial \varepsilon_L}{\partial t} + u \rho_L \frac{\partial \phi_s}{\partial x} + \phi_s \rho_L \frac{\partial u}{\partial x} + \frac{\partial J_{3,s}}{\partial x} = 0 \quad \text{(refer to eq. (4.16))}
\]
5. \[
\phi_1 = \phi_1^* - K_1 m_1, \quad \phi_1^* = f_1(T_L) \quad \text{(refer to eq. (4.44) and (4.49))}
\]
6. \[
\phi_2 = \phi_2^* - K_2 m_2, \quad \phi_2^* = f_2(T_L) \quad \text{(refer to eq. (4.44) and (4.49))}
\]
7. \[
\phi_1 + \phi_2 + \phi_{3,s} = 1 \quad \text{(refer to eq. (4.7))}
\]
(8) $\rho_{s,1} \frac{\partial \varepsilon_{s,1}}{\partial t} = -m_1$ (refer to eq. (4.19))

(9) $\rho_{s,2} \frac{\partial \varepsilon_{s,2}}{\partial t} = -m_2$ (refer to eq. (4.20))

(10) $\varepsilon_{s,1} + \varepsilon_{s,2} + \varepsilon_{e} + \varepsilon_{a} = 1$ (refer to eq. (4.21))

(11) $\frac{\partial}{\partial t} (\varepsilon_{s,1} \rho_{s} H_{L}) + \frac{\partial}{\partial t} \left[ \sum (\varepsilon_{s,j} \rho_{s,j} H_{S,j}) \right] + \frac{\partial}{\partial x} (u \rho_{s} H_{L}) = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_{L}}{\partial x} \right) + q_{ze}$

$\left. q_{ze} = -k_{R} \varepsilon_{e} \rho_{e} L_{ge} \right|$ (refer to eq. (4.34) and (4.36))

(12) $\frac{\partial}{\partial t} \left[ \sum (\varepsilon_{s,j} \rho_{s,j} H_{S,j}) \right] = \frac{\partial}{\partial x} \left( k_{c} \frac{\partial T_{c}}{\partial x} \right), x > h_{e}$ (refer to eq. (4.26))

(13) $\rho_{s} L_{e} \varepsilon_{e} \left. \frac{dh_{e}}{dt} - k_{eff} \frac{\partial T_{e}}{\partial x} \right|_{x=h_{e}^{-}} = -k_{c} \left. \frac{\partial T_{c}}{\partial x} \right|_{x=h_{e}^{-}}$, $\left. \frac{dh_{e}}{dt} = \left( \frac{u}{\varepsilon_{e,0} - \varepsilon_{e}} \right) \right|_{x=h_{e}^{-}}$ (refer to eq. (4.38) and (4.13))

(14) $\rho_{L} L_{e} \varepsilon_{p} \left. \frac{dh_{p}}{dt} - k_{eff} \frac{\partial T_{e}}{\partial x} \right|_{x=h_{p}^{-}} = -k_{eff} \left. \frac{\partial T_{e}}{\partial x} \right|_{x=h_{p}^{-}}$ (refer to eq. (4.40))

(15) $\varepsilon_{p \mid_{x=h_{p}^{-}}} = -(\varepsilon_{s,1} \mid_{x=h_{p}^{-}})$, $h_{p \mid_{x=h_{p}^{-}}} = h_{e \mid_{x=h_{p}^{-}}}$ (refer to eq. (4.42))

(16) $\ln(\varepsilon_{e,0} \rho_{e}) = -K_{R} (t - t_{a}) + \ln(\varepsilon_{e,0} \rho_{e})$ (refer to eq. (4.35))

(17) $\frac{d \varepsilon_{a}}{dt} = K_{A} \frac{\varepsilon_{a}}{1 - \varepsilon_{a}} - K_{R} \varepsilon_{a}$ (refer to eq. (4.37))

All 17 dependent variables are included in these 17 equations, and each equation contains at least one dependent variable. In addition, these 17 equations are linear independent, namely each of them can’t be deduced from any others of them.

### 4.4 Coupling relationship of temperature and concentration

The equations listed in section 4.3 include the temperature $T_{L}$, the concentration $\Theta_{i}$ and the phase transformation rate $m_{i}$. In order to solve the equations, it is necessary to find out the mutual coupling interaction relationships between these variables.

In addition, these equations are complicated, especially the conservation equations of energy. They can be more concrete and easy to be solved by transferring them to more simple equations.
Equation (4.14)+(4.15)+(4.16) gives:
\[
\rho_L \left( \frac{\partial \varepsilon_i}{\partial t} + \frac{\partial u}{\partial x} \right) = m_1 + m_2
\]  
(4.54)

Equation (4.19), (4.20), (4.21) gives:
\[
\frac{\partial \varepsilon_i}{\partial t} = \frac{m_1}{\rho_{S1}} + \frac{m_2}{\rho_{S2}} - \frac{d \varepsilon_A}{dt}
\]  
(4.55)

where \( \frac{d \varepsilon_A}{dt} \) is the volume fraction shrinking rate of residual air in the porous transition alumina particles due to the liquid bath permeating in it.

Equation (4.54), (4.55) give:
\[
\frac{\partial u}{\partial x} = m_1 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S1}} \right) + m_2 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{d \varepsilon_A}{dt}
\]  
(4.56)

According to the rule of differentiation, energy equation (4.24) is written as:
\[
\varepsilon_i \rho_L \frac{\partial H_L}{\partial T_L} + u \rho_L \frac{\partial H_L}{\partial T_L} + H_L \rho_L \left( \frac{\partial \varepsilon_i}{\partial t} + \frac{\partial u}{\partial x} \right) + \sum (\varepsilon_{Sj} \rho_{Sj} \frac{\partial H_{Sj}}{\partial T_S}) \frac{\partial T_S}{\partial t} + \sum (\rho_{Sj} H_{Sj} \frac{\partial \varepsilon_{Sj}}{\partial t}) = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_L}{\partial x} \right) + q_{nr}, x \leq h_e
\]  
(4.57)

Substituting equations (4.19), (4.20) and (4.54) in equation (4.57) gives
\[
\varepsilon_i \rho_L \frac{\partial H_L}{\partial T_L} + u \rho_L \frac{\partial H_L}{\partial T_L} + \left[ \sum (\varepsilon_{Sj} \rho_{Sj} \frac{\partial H_{Sj}}{\partial T_S}) \right] \frac{\partial T_S}{\partial t} + \sum (\rho_{Sj} H_{Sj} \frac{\partial \varepsilon_{Sj}}{\partial t}) = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_L}{\partial x} \right), x \leq h_e
\]  
(4.58)

According to specific heat capacity \( C \) and latent heat \( L_i \) definition
\[
\frac{\partial H}{\partial T} = C_L, \frac{\partial H_{Sj}}{\partial T_S} = C_{Sj}
\]  
(4.59)

\[
H_L m - \sum (H_{Sj} m_j) = \sum (\Delta H_i m_i) = \sum (L m_i)
\]  
(4.60)
Therefore,

\[
\varepsilon_L \rho_L C_L \frac{\partial T_L}{\partial t} + u \varepsilon_L C_L \frac{\partial T_L}{\partial x} + \sum (\varepsilon_{s,i} \rho_{s,i} C_{s,i}) \frac{\partial T_{s,i}}{\partial t} + \sum (L_i m_i)
\]

\[
\frac{\partial}{\partial x} \left( k_{ef} \frac{\partial T_{L}}{\partial x} \right) + q_{sw}, x \leq h_e
\]

\[
\left[ \sum (\varepsilon_{s,i} \rho_{s,i} C_{s,i}) \right] \frac{\partial T_C}{\partial t} = \frac{\partial}{\partial x} \left( k_c \frac{\partial T_C}{\partial x} \right), x > h_e
\]

Substituting \( \phi_i = \phi_i^* - K_i m_i \) (\( \phi_i^* \) denotes saturation concentration, see Appendix A.6) in the continuity equation (4.14), (4.15), and (4.16), the concentration and phase transformation rate are the solution of following equations (equation (4.54) is applied), (In case of the porous crust with fine pore size, the effect of mass diffusion (\( D \)) in the liquid bath on the model result is likely to be insignificant. Thus the mass diffusion might be neglected in the application of the model in this case.)

\[
(1 - \phi_i^* + m_i K_i) m_i - (\phi_i^* - m_i K_i) m_2 + K_i \varepsilon_L \rho_L \left( \frac{\partial m_1}{\partial t} + u \frac{\partial m_1}{\partial x} \right)
\]

\[
= \rho_L (\varepsilon_L \frac{\partial \phi_i^*}{\partial t} + u \frac{\partial \phi_i^*}{\partial x})
\]

\[
(1 - \phi_2^* + m_2 K_2) m_2 - (\phi_2^* - m_2 K_2) m_1 + K_2 \varepsilon_L \rho_L \left( \frac{\partial m_2}{\partial t} + u \frac{\partial m_2}{\partial x} \right)
\]

\[
= \rho_L (\varepsilon_L \frac{\partial \phi_2^*}{\partial t} + u \frac{\partial \phi_2^*}{\partial x})
\]

According to inequation (9.42), in the case of high surface area \( S, K_i < 10^{-6} \). The items with \( K_i \) is negligible in Equations (4.63) and (4.64) comparing with remaining items like \( \phi_i^* \) (the range of \( \phi_i^* \) is about 0.1~0.8) (see Appendix A.9), thus

\[
(1 - \phi_1^*) m_1 - \phi_1^* m_2 = \rho_L (\varepsilon_L \frac{\partial \phi_1^*}{\partial t} + u \frac{\partial \phi_1^*}{\partial x})
\]

\[
-\phi_2^* m_1 + (1 - \phi_2^*) m_2 = \rho_L (\varepsilon_L \frac{\partial \phi_2^*}{\partial t} + u \frac{\partial \phi_2^*}{\partial x})
\]

In addition,
Substituting equations (4.67) and (4.68) in equations (4.65) and (4.66) can be simplified as

\[
(1 - \phi_1^*) m_1 - \phi_1^* m_2 = \rho_L (\varepsilon_L \frac{\partial \phi_1^*}{\partial T_M} \frac{\partial T_M}{\partial t} + u \frac{\partial \phi_1^*}{\partial T_M} \frac{\partial T_M}{\partial x})
\]

\[
-\phi_2^* m_1 + (1 - \phi_2^*) m_2 = \rho_L (\varepsilon_L \frac{\partial \phi_2^*}{\partial T_M} \frac{\partial T_M}{\partial t} + u \frac{\partial \phi_2^*}{\partial T_M} \frac{\partial T_M}{\partial x})
\]

The solution for above equations is,

\[
\begin{bmatrix}
  m_1 \\
  m_2
\end{bmatrix}
= \begin{bmatrix}
  1 - \phi_1^* & -\phi_1^* \\
  -\phi_2^* & 1 - \phi_2^*
\end{bmatrix}^{-1}
\begin{bmatrix}
  \frac{\partial \phi_1^*}{\partial T_M} & \frac{\partial \phi_1^*}{\partial T_M} \\
  \frac{\partial \phi_2^*}{\partial T_M} & \frac{\partial \phi_2^*}{\partial T_M}
\end{bmatrix}
\begin{bmatrix}
  \rho_L \varepsilon_L \frac{\partial T_M}{\partial t} \\
  \rho_L u \frac{\partial T_M}{\partial x}
\end{bmatrix}
= \begin{bmatrix}
  \frac{\partial \phi_1^*}{\partial T_M} \\
  \frac{\partial \phi_2^*}{\partial T_M}
\end{bmatrix}
\]

In the case of pure alumina cover, in ‘hot’ region (i.e. where the liquid bath temperature is higher than the liquidus temperature and \(\varepsilon_{S,2} = 0\)), it comes that \(m_2 = 0\), and \(\phi_1 = \phi_2^* - K_2 m_2\) is not valid as noted in section 4.2.6. Thus by using the similar way,
Chapter 4. Theoretical development

\[ m_i = \frac{1}{(1 - \phi_i^*)} \rho_L (\varepsilon_i \frac{\partial \phi_i^*}{\partial T_M} \frac{\partial T}{\partial t} + u \frac{\partial \phi_i^*}{\partial T_M} \frac{\partial T}{\partial x}) \quad (4.74) \]

By assuming \( \phi_2^* = 0 \) in above case, equations (4.71) and (4.74) are consistent.

By assuming \( T_L \approx T_M, \frac{\partial T_L}{\partial x} \approx \frac{\partial T_M}{\partial x}, \frac{\partial T_L}{\partial t} \approx \frac{\partial T_M}{\partial t}, \)

\[ L_em_1 + L_rm_2 = F_L \rho_L (\varepsilon_i \frac{\partial T_L}{\partial t} + u \frac{\partial T_L}{\partial x}) \quad (4.75) \]

For saturated Na\(_3\)AlF\(_6\)-Al\(_2\)O\(_3\) binary system (\(1 - \phi_1^* - \phi_2^* = 0\)) the phase transformation temperature fixes at the eutectic temperature about 965 °C, which is not applied in the present work. If there is other additives, \(1 - \phi_1^* - \phi_2^* > 0\).

Since \(1 - \phi_1^* - \phi_2^* > 0\) and \([F]_{11} = [F]_{12}, [F]_{21} = [F]_{22}\), define

\[ C_E = C_L + F_L \]
\[ F_L = [F]_{11} L_1 + [F]_{21} L_2 = [F]_{12} L_1 + [F]_{22} L_2 \quad (4.76) \]

\(C_E\) is effective specific heat capacity.

Substituting \(C_E\), the energy equations are integrated as,

\[ C_E \rho_L \varepsilon_L \frac{\partial T_L}{\partial t} + C_E \rho_L u \frac{\partial T_L}{\partial x} + \sum (\varepsilon_{j,i} \rho_{S,i} C_{S,i}) \frac{\partial T_L}{\partial t} = \frac{\partial}{\partial x} (k_{eff} \frac{\partial T_L}{\partial x}) + q_{net}, x \leq h_e \quad (4.77) \]

Because the coefficient \(C_E\) is determined by the temperature and the eutectic curve, the temperature and the concentration are strongly coupled through equation (4.77).

Effective specific heat capacity has been applied in a similar problem of freezing and thawing of subsurface water which has been widely studied. McKenzie [85] studied groundwater flow with energy transport and water-ice phase transformation. In his study, a similar effective specific heat capacity is used that incorporates both the specific heat capacity of ice and the latent heat.
4.5 Equations for the thermochemical model

New equations, as listed as following, are simplified and deduced from the original equations in section 4.3. The following 17 equations represent the thermochemical model in this study.

1. \[ \int_0^h \left( \frac{\mu}{K_h} u + mu \right) dx = \frac{2\gamma_L \cos \theta}{R} - \rho_L g h_s, K_h = \frac{\rho_L g e_L^3}{5S^2} \] (refer to eq. (4.12))

2. See (3)

3. \[ \begin{bmatrix} m_1 \\ m_2 \end{bmatrix} = \left[ F \right] \begin{bmatrix} \rho_L e_L \frac{\partial T_L}{\partial t} \\ \rho_L u \frac{\partial T_L}{\partial x} \end{bmatrix}, \quad [F] = \begin{bmatrix} 1 - \phi_2^* & \phi_1^* \\ \phi_2^* & 1 - \phi_1^* \end{bmatrix} \begin{bmatrix} \frac{\partial \phi_1^*}{\partial T_L} \\ \frac{\partial \phi_2^*}{\partial T_L} \end{bmatrix}, \quad \phi_i^* = f_i(T_L), i = 1, 2 \] (refer to eq. (4.71))

4. \[ \frac{\partial u}{\partial x} = m_1 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{SL}} \right) + m_2 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{dE_A}{dt} \] (refer to eq. (4.56))

5. \[ \phi_1 = \phi_1^* - K_m m_1, \quad \phi_1^* = f_1(T_L) \] (refer to eq. (4.44) and (4.49))

6. \[ \phi_2 = \phi_2^* - K_m m_2, \quad \phi_2^* = f_2(T_L) \] (refer to eq. (4.44) and (4.49))

7. \[ \phi_1 + \phi_2 + \phi_{x,y} = 1 \] (refer to eq. (4.7))

8. \[ \rho_{S1} \frac{\partial E_{S1}}{\partial t} = -m_1 \] (refer to eq. (4.19))

9. \[ \rho_{S2} \frac{\partial E_{S2}}{\partial t} = -m_2 \] (refer to eq. (4.20))

10. \[ \varepsilon_{S1} + \varepsilon_{S2} + \varepsilon_L + \varepsilon_A = 1 \] (refer to eq. (4.55))

11. \[ C_F \rho_L e_L \frac{\partial T_L}{\partial t} + C_F \rho_L u \frac{\partial T_L}{\partial x} + \sum \left( \varepsilon_{S,i} \rho_{S,i} C_{S,i} \right) \frac{\partial T_L}{\partial t} = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_L}{\partial x} \right) + q_{xy} \]

\[ q_{xy} = -k_e \varepsilon_L \rho_L L_{xy} \] (refer to eq. (4.77))

12. \[ \frac{\partial T_c}{\partial t} = \frac{\partial}{\partial x} \left( k_c \frac{\partial T_c}{\partial x} \right), x > h_c \] (refer to eq. (4.62))
Like those in section 4.3, above 17 equations are linear independent as well. The 17 dependent variables in section 4.3 (i.e. $\Omega_1$, $\Omega_2$, $\Omega_3$, $\gamma$, $\epsilon_L$, $\epsilon_S$, $\epsilon_{S,1}$, $\epsilon_{S,2}$, $u$, $m_1$, $m_2$, $\epsilon_A$, $T_L$, $T_C$, $\epsilon_r$, $\epsilon_e$, $\epsilon_p$, $h_e$, $h_p$) are solved from above 17 equations if proper boundary conditions are applied.

4.6 The innovation step in the model

The high heat flow from the hot bulk bath is the driving force for the thermochemical evolution of the anode cover during both crust formation and melting. How this heat flow behaves in the crust is very important.

In a normal case without phase transformation, Fourier’s Heat Equation (see equation (4.78)) is used to solve the relationship between heat conduction and the internal energy in a dense object (to simplify the discussion here, just heat flow is considered, and the liquid penetration and the mass diffusion are ignored).

$$C\rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}(k \frac{\partial T}{\partial x})$$

(4.78)

As a result, the transient temperature evolution is determined. The solution highly depends on the parameters of the specific heat capacity ($C$) and the thermal conductivity ($k$). Higher thermal conductivity results in that more heat is transferred away as well as less heat is accumulated to increase the internal energy. Lower specific heat capacity means the temperature changes faster.
When phase transformation occurs in heat transfer, an effective specific heat capacity can be used to incorporate together both the sensible heat and the latent heat. One example is given in the study on groundwater flow with energy transport and water-ice phase transformation [85].

However, the phase transformation in this study is characterized by two species partial phase transformations simultaneously over a wide temperature range. To our knowledge, few researchers have focused on this kind of phase transformation. An effective specific heat capacity \( C_E \) taking into account phase transformation during the crust formation is derived in section 4.4. Unlike the effective thermal conductivity \( k_{\text{eff}} \), the effective specific heat capacity \( C_E \) for crust formation or melting has not been measured or predicted by other researchers. Thus the computation from first principles of this property is important for this study since it determines the split between heat transmitted through the anode cover and that accumulated as internal energy. In the modelling predictions appearing later in Chapter 7, the effective heat capacity computation carries great significance in the final temperature and concentration profiles for the crust, and therefore its physical and chemical evolution.

Hence, a Fourier’s Heat Equation with the effective thermal conductivity \( k_{\text{eff}} \) and the effective specific heat capacity \( C_E \) which takes into account the coupling of cryolite and chiolite concentrations to compute the large latent heat component of this effective heat capacity as a function of the phase equilibria of bath in the crust is derived in section 4.4. This equation makes the complex thermochemical evolution tractable. Realistic effective heat capacity properties and conclusions derived from their use in the normal Fourier’s Heat Transfer Equation are only obtained through this coupling of the phase equilibria with the predicted bath composition and temperature evolution.

4.7 The role of the model

4.7.1 To solve major variables

The model focuses on the thermochemical evolution during the crust formation. The chemical composition \( (\theta_i) \), the temperature \( (T) \) and the liquid bath volume fraction \( (\varepsilon_L) \) are the major time dependent variables predicted by the model, all as a function of height.
in the crust, \(x\). These major variables interact with each other. Some indirect variables are used to build the coupling relationships between them (see section 4.4). These indirect variables include surface area, internal heat transfer coefficient, interface reaction constant etc. The values of these are estimated approximately but have insignificant impact on the model result. As the boundary conditions and bulk properties of the anode cover/crust are given, these major variables (i.e. \(\theta_i\), \(T\), \(\epsilon_L\)) will be predicted by solving the model.

4.7.2 To test the mechanism

Section 4.1 proposed the mechanism for crust formation, which the model is based on. The solved answers of these major variables directly reflect the thermochemical evolution during the crust formation.

The correctness of the model mathematics will be verified by comparing it with the analytical solutions of standard cases in Appendix A.10. The model hypothesis will be validated by comparison of the model results and the experimental data of both synthetic crust and real industrial result in Chapter 7.1 and 7.2, to attempt to confirm the mechanism proposed in Chapter 4.

The melting and disappearance of the crust depends on not only the thermochemical behaviour, but also mechanical disturbances such as movements of the anodes, and dynamic dropping down of the liquid bath from the crust bottom surface. It is difficult to predict the exact position of crust melting front. Since high liquid bath fraction contributes to the weakening of the crust as reviewed in Chapter 3, the model can predict \(\epsilon_L\) which is practically relevant in terms of avoiding high liquefied or fatally weakened crust.
5 Computational methodology

A computational code based on the software MATLAB® is designed to codify and run the model. The key concepts in the code design are introduced here.

5.1 Coordinate transformation

As noted in Chapter 4, there are different governing equations for different regions, between which the boundaries are moving with time. This moving boundary problem, known as the Stefan problem [86], is solved using a coordinate transformation technique based on a boundary fixing method coupled with implicit time schemes [83, 87], as presented below.

For a new coordinate system $\eta = f(x,t)$, the physical space $(x, t)$ is transformed to the mapping space $(\eta, t)$, and the differential operators are mathematically transformed to the following equations [83],

$$
\frac{\partial}{\partial x} = \frac{\partial \eta}{\partial x} \frac{\partial}{\partial \eta}, \quad \frac{\partial}{\partial t} = \frac{\partial \eta}{\partial t} \frac{\partial}{\partial \eta} + \frac{\partial}{\partial t}
$$

Table 5-1 listed the detailed coordinate transformation of conservation equations of energy for the different regions. For the new coordinate systems, the mapping spatial spaces are fixed at $[0,1]$ to reduce the complication of numerical solution.
Table 5-1. The detailed coordinate transformation of governing equations

<table>
<thead>
<tr>
<th>For the lower part of the crust</th>
<th>For the upper part of the crust</th>
<th>For loose cover</th>
</tr>
</thead>
<tbody>
<tr>
<td>$725^\circ C \leq T, 0 \leq x \leq h_p(t)$</td>
<td>$685^\circ C \leq T \leq 725^\circ C, h_p(t) \leq x \leq h_c(t)$</td>
<td>$T \leq 685^\circ C, h_c(t) \leq x \leq h_0$</td>
</tr>
</tbody>
</table>

The original coordinate system:

$$\begin{align*}
[C_e \rho_L \varepsilon_L + \sum (\varepsilon_{S,L} \rho_{S,L} C_{S,L})] \frac{\partial T_L}{\partial t} + C_e \rho_L u \frac{\partial T_L}{\partial x} &= \frac{\partial}{\partial x} (k_{\text{eff}} \frac{\partial T_L}{\partial x}) + q_{\text{ny}} \\
[C_L \rho_L \varepsilon_L + \sum (\varepsilon_{S,L} \rho_{S,L} C_{S,L})] \frac{\partial T_L}{\partial t} + C_L \rho_L u \frac{\partial T_L}{\partial x} &= \frac{\partial}{\partial x} (k_{\text{eff}} \frac{\partial T_L}{\partial x}) \\
[\sum (\varepsilon_{S,L} \rho_{S,L} C_{S,L})] \frac{\partial T_c}{\partial t} &= \frac{\partial}{\partial x} (k_c \frac{\partial T_c}{\partial x})
\end{align*}$$

New coordinate system: $\eta = \frac{x}{h_p(t)}, 0 \leq \eta \leq 1$

$$\begin{align*}
\frac{\partial}{\partial x} &= \frac{\partial}{\partial \eta} \frac{\partial \eta}{\partial x} = \frac{1}{h_p} \frac{\partial}{\partial \eta} \\
\frac{\partial}{\partial t} &= \frac{\partial}{\partial \eta} \frac{\partial \eta}{\partial t} = \frac{1}{h_p} \frac{\partial}{\partial \eta} \\
\frac{\partial}{\partial t} &= \frac{\partial}{\partial \eta} \frac{dh_p}{dt} \frac{\partial}{\partial \eta} \\
\frac{\partial}{\partial t} &= \frac{\partial}{\partial \eta} \frac{1}{h_c - h_p} \left[ \varepsilon \frac{dh_p}{dt} + (1 - \varepsilon) \frac{dh_p}{dt} \right] \frac{\partial}{\partial \eta} \\
\frac{\partial}{\partial t} &= \frac{\partial}{\partial \eta} \left[ \frac{1}{h_c - h_p} \left( \varepsilon \frac{dh_p}{dt} + (1 - \varepsilon) \frac{dh_p}{dt} \right) \right] \frac{\partial}{\partial \eta} \\
\frac{\partial}{\partial t} &= \frac{\partial}{\partial \eta} \left[ \frac{1}{h_c - h_p} \left( \varepsilon \frac{dh_p}{dt} + (1 - \varepsilon) \frac{dh_p}{dt} \right) \right] \frac{\partial}{\partial \eta} \\
\frac{\partial}{\partial t} &= \frac{\partial}{\partial \eta} \left[ \frac{1}{h_c - h_p} \left( \varepsilon \frac{dh_p}{dt} + (1 - \varepsilon) \frac{dh_p}{dt} \right) \right] \frac{\partial}{\partial \eta}
\end{align*}$$
After coordinate transformation

\[
\left[ C_L \rho L e_L + \sum (\varepsilon_{S,i} \rho_{S,i} C_{S,i}) \right] \frac{\partial T_L}{\partial t} = \frac{1}{h_p} \frac{\partial}{\partial \eta} \left( k_{\text{eff}} \frac{\partial T_L}{\partial \eta} \right) + q_{\text{in}} - C_L \rho L u \frac{1}{h_p} \frac{\partial T_L}{\partial \eta} +
\]

\[
\left[ C_L \rho L e_L + \sum (\varepsilon_{S,i} \rho_{S,i} C_{S,i}) \right] \frac{\eta}{h_p} \frac{\partial T_L}{\partial t} = \frac{1}{(h_e - h_p)^2} \frac{\partial}{\partial \zeta} \left( k_{\text{eff}} \frac{\partial T_L}{\partial \zeta} \right) - C_L \rho L u \frac{1}{h_e - h_p} \frac{\partial T_L}{\partial \zeta} +
\]

\[
\left[ C_L \rho L e_L + \sum (\varepsilon_{S,i} \rho_{S,i} C_{S,i}) \right] \frac{1}{h_e - h_p} \left[ \frac{\partial h_p}{\partial \tau} + (1 - \zeta) \frac{\partial h_p}{\partial \zeta} \right] \frac{\partial T_L}{\partial \zeta} = \frac{1}{(h_0 - h_e)^2} \frac{\partial}{\partial \phi} \left( k_c \frac{\partial T_C}{\partial \phi} \right)
\]
The coordinate transformation between $T_L(\eta,t)$ and $T_L(x,t)$ is

$$T_L(x,t) = T_L(h_p \eta, t), 0 \leq x \leq h_p, 0 \leq \eta \leq 1$$  \hspace{1cm} (5.2)

$$\frac{\partial T_L(x,t)}{\partial t} \bigg|_{x=a} = \left( \frac{\partial T_L(\eta,t)}{\partial t} - \frac{\eta}{h_p} \frac{dh_p}{dt} \frac{\partial T_L(\eta,t)}{\partial \eta} \right) \bigg|_{\eta=0}^{\eta=1}, 0 \leq a \leq h_p$$  \hspace{1cm} (5.3)

$$\frac{\partial T_L(x,t)}{\partial x} \bigg|_{x=a} = \frac{1}{h_p} \frac{\partial T_L(\eta,t)}{\partial \eta} \bigg|_{\eta=0}^{\eta=1}, 0 \leq a \leq h_p$$  \hspace{1cm} (5.4)

Since $T_L(x,t)$ and $T_L(\eta,t)$ are corresponding to each other, $T_L$ is used to present either $T_L(\eta,t)$ or $T_L(x,t)$ depending on the particular situation in the below text (The same for other dependent variables).

The motions of boundary interfaces are also transformed to the following equations:

$$\rho_S L_p \varepsilon_p \frac{dh_p}{dt} = \frac{k_{eff}}{h_p} \frac{\partial T_L}{\partial \eta} \bigg|_{x=h_p} - \frac{k_{eff}}{h_e - h_p} \frac{\partial T_L}{\partial \xi} \bigg|_{x=h_p}$$  \hspace{1cm} (5.5)

$$\rho_L L_e \varepsilon_e \frac{dh_e}{dt} = \frac{k_{eff}}{h_e - h_p} \frac{\partial T_L}{\partial \xi} \bigg|_{x=h_e} - \frac{k_e}{h_e - h} \frac{\partial T}{\partial \phi} \bigg|_{x=h_e}$$  \hspace{1cm} (5.6)

where $\varepsilon_p$ is the volume fraction of solid chiolite and fluoride additives melting at 725 °C, and $\varepsilon_e$ is the volume fraction of liquid bath freezing at 685 °C. At the same time, $\varepsilon_e$ is related to the fluid velocity $u$ (equation (5.7)).

$$\frac{dh_e}{dt} \bigg|_{x=h_e} = \frac{u}{\varepsilon_e} \left( \frac{u}{\varepsilon_{t0} - \varepsilon_e} \right) \bigg|_{x=h_e}$$  \hspace{1cm} (5.7)

Note that the effect of crystallization on the laminar flow is neglected under the condition of slow crystallization rate [41].

**5.2 Finite element method (FEM)**

Some equations of the thermochemical model listed in the section 4.5 are partial differential equations (PDEs) that are difficult to solve analytically. Alternatively
therefore numerical methods are applied here to solve these PDEs approximately.

The equation like the following one is convection diffusion PDE,

\[ \rho C \frac{\partial T}{\partial t} + \rho u \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) + q \]  \hspace{1cm} (5.8)

The conservation equations of energy listed in the section 4.5 are all second order PDEs, and have been coordinate transformed in Table 5-1.

The finite element method (FEM) [88-90] is an extensively used numerical technique for finding approximate solutions for second order PDEs. It is based on the way of dividing the solution domain into a number of discrete subregions, or “elements”. Each element includes a certain number of nodes. Within the element, an interpolation function is applied to relate the solution at the nodes to the solution at any point in the element [89].

Since the equations listed in Table 5-1 are similar, a general equation (5.9) is applied here to simplify the discussion. The symbols \( c, k, b_1, b_2 \) and \( q \) in equation (5.9) represent the corresponding items in these governing equations.

\[ c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + (b_1 + b_2 x) \frac{\partial T}{\partial x} + q \]  \hspace{1cm} (5.9)

Using the finite element technique, the region is divided into \( n \) smaller elements with the length \( l \) as shown in Figure 5-1. Galerkin approach [88-90] is used to convert the partial differential continuous equation to \( n+1 \) discrete equations (5.28).

![Figure 5-1](image)

Figure 5-1. One dimensional heat transfer in a region divided into \( n \) elements

Assume an approximated temperature field variable \( T^e \), satisfying
\( T^* = \sum_{i=1}^{n+1} (N_i(x)T_i) = N\{T\} \)  
\[ (5.10) \]

\[ N = [N_1 \quad N_2 \quad \cdots \quad N_{n+1}], T = [T_1 \quad \cdots \quad T_i \quad T_{n+1}] \]

where \( N \) is the interpolation function. \( T_i \) is the temperature at the \( i \)th node.

In \( i \)th element, the interpolation function is chosen as (\( N \) only has two nonzero values in each element),

\[ N = [0\ldots0 \quad N_i(x) \quad N_{i+1}(x) \quad 0\ldots0] = \begin{bmatrix} 0\ldots0 & \frac{x-x_i}{l} & \frac{x-x_{i+1}}{l} & 0\ldots0 \end{bmatrix} \quad (5.11) \]

By substituting \( T^* \), the residuals in the region \( \Omega \) and at the boundary \( \Gamma_2 \) (heat flux \( p \) is given) and \( \Gamma_3 \) (convective heat transfer coefficient \( h \) is given) are,

\[ R_{\Omega} = k \frac{\partial^2 T^*}{\partial x^2} + (b_1 + b_2 x) \frac{\partial T^*}{\partial x} + q - c \frac{\partial T^*}{\partial t} \quad (5.12) \]

On the one of the 2 boundaries,

\[ q_f = p \quad (5.13) \]

On the other boundary,

\[ q_f = h(T_0 - T^*) \quad (5.14) \]

Using Galerkin approach [88-90], weighted integration of the above residual sum equals zero,

\[ R = \int_{0}^{h} R_{\Omega} w dx = \int_{0}^{h} \left[ k \frac{\partial^2 T^*}{\partial x^2} + (b_1 + b_2 x) \frac{\partial T^*}{\partial x} + q - c \frac{\partial T^*}{\partial t} \right] w dx = 0 \quad (5.15) \]

\[ R = \int_{0}^{h} R_{\Omega} w dx \]

\[ = \int_{0}^{h} \left[ k \frac{\partial T^*}{\partial x} \frac{\partial w}{\partial x} + (b_1 + b_2 x) \frac{\partial T^*}{\partial x} w + qw - c \frac{\partial T^*}{\partial t} w \right] dx + q_f \bigg|_0^h = 0 \quad (5.16) \]
Using FE \([88-90]\),

\[
R = \bigcup_{x_i}^{x_{i+1}} \left( k \left\{ \frac{\partial N}{\partial x} \right\} \frac{\partial T^+}{\partial x} - (b_1 + b_2x) \left\{ N \right\} \frac{\partial T^+}{\partial x} - q \left\{ N \right\} + c \left\{ N \right\} \frac{\partial T^+}{\partial t} \right) dx + q_f \left|_{x_i}^{x_{i+1}} \right. = 0 \quad (5.17)
\]

Thus, in each element,

\[
R^{(e)} = \int_{x_i}^{x_{i+1}} \left[ k \left\{ \frac{\partial N}{\partial x} \right\} \frac{\partial T^+}{\partial x} - (b_1 + b_2x) \left\{ N \right\} \frac{\partial T^+}{\partial x} - q \left\{ N \right\} + c \left\{ N \right\} \frac{\partial T^+}{\partial t} \right] dx
\]

\[-k \left\{ N \right\} \frac{\partial T^+}{\partial x} \bigg|_{x_i}^{x_{i+1}} + q_f \bigg|_{x_i}^{x_{i+1}} \quad (5.18)
\]

Substituting (5.11) into (5.18), gives

\[
R^{(e)} = \left( k \int_{x_i}^{x_{i+1}} \left\{ \frac{\partial N}{\partial x} \right\} \frac{\partial N}{\partial x} dx + \int_{r_{\Gamma_3}} h \left\{ N \right\}Nd\Gamma_3 \right)T
\]

\[-(b_1 + b_2x) \left( \int_{x_i}^{x_{i+1}} \left\{ N \right\} dx \right)T + \left( c \int_{x_i}^{x_{i+1}} \left\{ N \right\} dx \right) \left( \frac{dT}{dt} \right) \quad (5.19)
\]

Or

\[
R^{(e)} = Q^{(e)} + P^{(e)} + \left( K^{(e)} + H^{(e)} - B_{1j}^{(e)} - B_{2j}^{(e)} \right)T + C_j \frac{dT}{dt} \quad (5.20)
\]

Each item in equation (5.20) is defined by the following equations from 5.20 to 5.26

\[
K^{(e)} = \int_{x_i}^{x_{i+1}} \left\{ \frac{\partial N}{\partial x} \right\} \frac{\partial N}{\partial x} dx = \frac{k}{l} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \quad (5.21)
\]

\[
H^{(e)} = \int_{r_{\Gamma_3}} h \left\{ N \right\} Nd\Gamma_3 \quad (5.22)
\]
\[
B_{1,j}^{(e)} = b_1 \int_{x_i}^{x_{i+1}} \{N\} \frac{\partial N}{\partial x} \, dx = \frac{b_1}{2} \begin{bmatrix}
-1 & 1 \\
-1 & 1
\end{bmatrix}
\]  
(5.23)

\[
B_{2,j}^{(e)} = b_2 \int_{x_i}^{x_{i+1}} x \{N\} \frac{\partial N}{\partial x} \, dx = \frac{b_2}{6} \begin{bmatrix}
-2x_i - x_{i+1} & 2x_i + x_{i+1} \\
-x_i - 2x_{i+1} & x_i + 2x_{i+1}
\end{bmatrix}
\]  
(5.24)

\[
Q_j^{(e)} = -q \int_{x_i}^{x_{i+1}} \{N\} \, dx = -\frac{q \cdot l}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix}
\]  
(5.25)

\[
P^{(e)} = -p \int_{x_i}^{x_{i+1}} \{N\} \, dx - hT_0 \int_{x_i}^{x_{i+1}} \{N\} \, dx
\]  
(5.26)

\[
C_i^{(e)} = c \int_{x_i}^{x_{i+1}} \{N\} \, N \, dx = \frac{c \cdot l}{6} \begin{bmatrix}
2 & 1 \\
1 & 2
\end{bmatrix}
\]  
(5.27)

Note that \(K_i^{(e)}, H^{(e)}, B_{1,j}^{(e)}, B_{2,j}^{(e)}\) and \(C_i^{(e)}\) are \((n+1)\times(n+1)\) matrices in which there are only four non-zero elements at position \((i,i), (i,i+1), (i+1,i),\) and \((i+1,i+1)\). \(Q_j^{(e)}\) and \(P^{(e)}\) are \((n+1)\times1\) matrices in which there are only two non-zero elements at position \(i\) and \(i+1\),

Assembling all elements together, the discrete equations for the whole region is given as,

\[
R = Q + KT + C \left( \frac{dT}{dt} \right) = 0
\]

\[
Q = \sum_{i=1}^{n} Q_i^{(e)}, K = \sum_{i=1}^{n} \left( K_i^{(e)} + B_{1,j}^{(e)} + B_{2,j}^{(e)} \right) + H^{(e)}, C = \sum_{i=1}^{n} C_i^{(e)}
\]  
(5.28)

The time is divided into as many smaller time steps as well. Nested algorithm for FEM with Backward Euler finite difference method (FDM) [91] in outer loop is applied.
\[ \frac{T^{m+1} - T^m}{\Delta t} = (\frac{dT}{dt})^{m+1} \]  
(5.29)

\[ \frac{C}{\Delta t} + K)T^{m+1} = -Q + \frac{C}{\Delta t}T^m \]  
(5.30)

where the superscript \( m \) denotes the time step.

The above discrete equations are solved by commercial software MATLAB\textsuperscript{®} which has powerful matrix operation capability [92]. A function ‘fun_FEM’ with array parameters \( c \), \( k \), \( b1 \), \( b2 \), \( q \) in equation (5.9), as well as \( l \) and \( n \) is developed based on MATLAB\textsuperscript{®} code according to above equations (5.21) ~ (5.30). When any PDE in pattern of equation (5.9) need to solved, these parameters (as well as the results in last step or iteration) are passed to this function, and results can be returned by it. Thus discrete equations for PDEs in pattern of equation (5.9) are not listed in following text particularly.

Backward Euler FDM is implicit stable method [93]. In Appendix A.10, numerical correctness of this function is carried out to three cases, which demonstrates that it can give precise and stable result when small mesh size and time step are applied. In the case of advection-diffusion equation in Appendix A.10, the advection item is not the domination item which is consistent with the practical situation, as well as the simulation result of superficial velocity (see Figure 7-7).

### 5.3 Iteration method

Those 17 equations listed in section 4.5 need to be solved in certain sequence. Though an equation may contain a couple of variables, it can only be applied once in each iteration to solve one of the variables. The other variables may have or have not been solved from prior equations. Implicit iterative solution method [94] is applied to deal with these unknown variables with a number of iterations in each time step.

For example, a model contains dependent variables \( T, \phi, u \) which are calculated from,

\[
T = f_T(x, t, \phi, u) \\
\phi = f_\phi(x, t, T, u) \\
u = f_u(x, t, T, \phi) 
\]  
(5.31)
The iterative solution is shown in Figure 5-2 (the symbol ‘=’ is the assignment operator in MATLAB code, rather than the equality symbol in mathematics). In each iterative solution, all dependent variables and parameters are assigned with the value of them in the last iteration or just assumed as initial value in the first time step. Iterations are repeated until all dependent variables and parameters change in small tolerances $\delta$. Relaxation factor $\psi = 0.8$ is applied to control the convergence rate according to experience.

Figure 5-2. Flowchart of iterative solution

5.4 Solution procedure of the model simulation

This section details the solution procedure of those 17 equations listed in section 4.5 which represent the thermochemical model. The values of physical properties and constants involved refer to Appendix A.14. In the solution procedure, some further simplifications or assumptions are made to ignore some minor factors.
The whole period of simulation is from the beginning of the contact between the cold anode cover and the bulk bath \((t=0)\) to the time when all dependent variables become almost steady state. The whole period can be divided into three sub-periods depends on the temperature variable, as discussed below. In each sub-period, there are a number of time steps.

The space is also divided into a number of elements and nodes. The values of variables at these discrete nodes are calculated by numerical method, and that at other position in the simulation region can be calculated by linear interpolation method.

### 5.4.1 Initial value

At time \(t=0\), the initial values of dependent variables are assigned,

\[
\begin{align*}
\varepsilon_{S,1} \big|_{t=0} &= \varepsilon_{S,2} \big|_{t=0} = \varepsilon_{A} \big|_{t=0} = \varepsilon_{s} \big|_{t=0}; \\
\eta \big|_{t=0} &= 0; m_{1} \big|_{t=0} = 0; m_{2} \big|_{t=0} = 0; \\
T_{L} \big|_{t=0} &= 100; T_{C} \big|_{t=0} = 100; \\
h \big|_{t=0} &= 0; h_{p} \big|_{t=0} = 0; \varepsilon_{e} \big|_{t=0} = 0; \varepsilon_{p} \big|_{t=0} = 0; \\
\end{align*}
\]

\(5.32\)

The initial values of volume fraction of solid \((\varepsilon_{S,1}^{0} \text{ and } \varepsilon_{S,2}^{0})\) and air internal porosity \((\varepsilon_{A}^{0})\) are known according to the initial porosity and composition of the raw cover material.

\[
\varepsilon_{S,1}^{0} + \varepsilon_{S,2}^{0} + \varepsilon_{A}^{0} + \varepsilon_{\text{sumf}}^{0} + \varepsilon_{L,0} = 1
\]

\(5.33\)

where \(\varepsilon_{\text{sumf}}\) is volume fraction of fluoride additives in the raw anode cover, \(\varepsilon_{L,0}\) is the easy-filling porosity (refer to Appendix A.1).

The chemical composition of the bulk bath is also known. It is assumed that the liquid bath is saturated with alumina before penetrating into the anode cover, and has liquidus temperature \(T_{\text{liq}}\).

### 5.4.2 Solution procedure of first sub-period

Sub-period 1: when \(T_{C} \big|_{t=0} < 685\) (from time \(t=0\) to \(t=t_{1}\)); dependent variable: \(T_{C}\)
As the initial cover temperature is $100 \, ^\circ C$, there is no liquid penetration until $T_C\big|_{x=0} > 685 \, ^\circ C$. The thickness of the anode cover is constantly $h_0$. The time interval is $\Delta t = 1 \, s$.

Cover temperature $T_C$ is solved from following temperature governing equation by using Galerkin approach (more details refer to section 5.2) (no coordinate transformation is needed in this case). The region $x = [0, h_0]$ is meshed into 100 elements.

Let $C_{Si}$, $C_{Si}$, $C_{Si}$, $k_C$, $k_C$, $\xi$, $\xi$, $\xi$, $\epsilon$ be the parameters in above equation. They are passed to the MATLAB code function ‘fun_FEM’ to calculate $T_C$ (more details see section 5.2, detailed discrete equations are not listed here).

**5.4.3 Solution procedure of second sub-period**

Sub-period 2: when $685 < T_L\big|_{x=0} < 725$ (from time $t=t_1$ to $t=t_2$); dependent variables: $u$, $T_C$, $T_L$, $\epsilon$, $h_e$ and $\epsilon_L$.

The time interval in this sub-period is $\Delta t = 0.1 \, s$. When $T_C\big|_{x=0}$ is greater than $685 \, ^\circ C$, $h_e$ is the position where $T_C\big|_{x=h_e} = 685$ and $t=t_1$. $h_e$ can be between $h_0/100$ and $h_0/80$ by controlling time step ($h_0/100$ is set to avoid that $h_e$ is too small to solve the model, $10^{-3} \, m < h_e\big|_{x=h_e} < 1.25 \times 10^{-3} \, m$). It is assumed that liquid bath penetration has reached $h_e$ at time $t=t_1$. This assumption is made to simplify the simulation. Since $h_e$ is much smaller than $h_0$, this assumption has negligible impact on the final results. The temperature $T_L$ in the region of $[0, h_e]$ is assigned with $T_L\big|_{x=0,j=t_1} = T_C\big|_{x=0,j=t_1}$, $T_L\big|_{x=h_e,j=t_1} = T_C\big|_{x=h_e,j=t_1} = 685 \, ^\circ C$.

Apply following coordinate system (refer to section 5.1),
\[ \zeta = \frac{x}{h_e}, 0 \leq \zeta \leq 1 \]
\[ \phi = \frac{x - h_e}{h_0 - h_e}, 0 \leq \phi \leq 1 \]

The region \( \zeta = [0,1] \) is meshed into \( n \) elements \((n=20)\) and \( n+1 \) discrete nodes with \( \zeta = 0, 1, \ldots, \left( \frac{n-1}{n} \right), 1 \). For coordinate system \( \zeta \), \( n \) does not change with time, thus the region, the elements and nodes are all fixed. The similar mesh strategy \((n=100)\) is applied to coordinate system \( \phi \) as well. The corresponding \( n+1 \) discrete nodes for coordinate system \( x \) in region \( x = [0, h_e] \) are \( x = 0, \frac{h_e}{n}, \frac{2h_e}{n}, \ldots, \left( \frac{n-1}{n} \right) h_e, h_e \).

The initial value of \( T_C \) and \( T_L \) of each node in Sub-period 2 is set from the value of last time step in Sub-period 1 by linear interpolation method.

1) Calculate \( u \)

In the region \( x = [0, h_e] \), it is assumed that \( m=0, \) and \( u \) is constant over the region rather than a function of \( x \).

According to,

\[ \int_0^{h_e} \left[ \frac{\mu}{K_h} u + mu \right] dx = \frac{2\gamma_L \cos \theta}{R} - \rho_L g h_e, K_h = \frac{\rho_L g e^3}{5S^2} \]

\( u \) is calculated from

\[ u = \frac{2\gamma_L \cos \theta}{R} - \rho_L g h_e = \frac{2\gamma_L \cos \theta}{R} - \rho_L g h_e, w(\zeta) = \frac{\mu}{K_h} \]  \( (5.34) \)

The integration of \( \int_0^1 w(\zeta) d\zeta \) is calculate according to the composite Simpson's rule,
\[
\int_0^1 w(\xi) d\xi \approx \frac{1}{3n} [w(0) + 2\sum_{j=1}^{n/2} w(\frac{2j}{n}) + 4\sum_{j=1}^{n/4} w(\frac{2j-1}{n}) + w(1)]
\]  \hspace{1cm} (5.35)

2) Calculate \(T_L\) and \(T_C\)

Following equations are solved to get \(T_L\) and \(T_C\).

\[
[C_L \rho_L c_L + \sum (\epsilon_S \rho_S c_S)] \frac{\partial T_L}{\partial t} + C_L \rho_L u \frac{\partial T_L}{\partial x} = \frac{\partial}{\partial x} (k_{\text{eff}} \frac{\partial T_L}{\partial x}), x \leq h_e
\]

\[
k_{\text{eff}} \frac{\partial T_L}{\partial x} \bigg|_{x=0} = h_f (T_L - T_B)
\]

\[
T_L \bigg|_{x=h_e} = 685
\]

\[
\left[ \sum (\epsilon_S \rho_S c_S) \right] \frac{\partial T_C}{\partial t} = \frac{\partial}{\partial x} (k_c \frac{\partial T_C}{\partial x}), x > h_e
\]

\[
T_C \bigg|_{x=h_e} = 685
\]

\[
k_c \frac{\partial T_C}{\partial x} \bigg|_{x=h_e} = (h_c + h_R)(T_C - T_A)
\]

Coordinate transformed equations for \(T_L\),

\[
[C_L \rho_L c_L + \sum (\epsilon_S \rho_S c_S)] \frac{\partial T_L}{\partial t} = \frac{1}{h_e^2} \frac{\partial}{\partial \xi} (k_{\text{eff}} \frac{\partial T_L}{\partial \xi}) - C_L \rho_L u \frac{1}{h_e} \frac{\partial T_L}{\partial t} + \frac{\partial}{\partial \xi} \left( \sum (\epsilon_S \rho_S c_S) \right) \frac{\xi}{h_e} \frac{dh_e}{dt} \frac{\partial T_L}{\partial \xi}
\]

With boundary condition:

\[
k_{\text{eff}} \frac{\partial T_L}{\partial \xi} \bigg|_{\xi=0} = h_f (T_L - T_B)
\]

\[
T_L \bigg|_{\xi=1} = 685
\]

Coordinate transformed equations for \(T_C\),
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\[
[\sum (\varepsilon_{s_j} \rho_{s_j} C_{s_j})] \frac{\partial T_c}{\partial t} = [\sum (\varepsilon_{s_j} \rho_{s_j} C_{s_j})] \left(1 - \frac{h_c}{h_{0} - h_e}\right) \frac{dh_c}{dt} \frac{\partial T_c}{\partial \varphi} + \frac{1}{(h_{0} - h_e)^2} \frac{\partial}{\partial \varphi} (k_c \frac{\partial T_c}{\partial \varphi})
\]  

(5.38)

With boundary condition:

\[
T_c \bigg|_{\varphi=0} = 685
\]

\[
\frac{k_c}{h_{0} - h_e} \frac{\partial T_c}{\partial \varphi} \bigg|_{\varphi=1} = (h_c + h_k)(T_c - T_A)
\]

(5.39)

Equations (5.36) and (5.38) have same pattern with equation (5.9). Galerkin approach is applied to solve them by passing parameters to the MATLAB code function ‘fun_FEM’ to calculate \(T_L\) and \(T_C\) respectively (more details see section 5.2, detailed discrete equations are not listed here). For instance, parameters \(c, k, b_1, b_2, q\) in equation (5.36) are shown in equation (5.40).

\[
c \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial \xi^2} + (b_1 + b_2 \varepsilon_e) \frac{\partial T}{\partial \xi} + q
\]

\[
c = [C_L \rho L \varepsilon_e + \sum (\varepsilon_{s_j} \rho_{s_j} C_{s_j})]
\]

\[
k = \frac{k_{eff}}{h_e}
\]

\[
b_1 = -C_L \rho L \varepsilon_L \frac{1}{h_e}
\]

\[
b_2 = [C_L \rho L \varepsilon_L + \sum (\varepsilon_{s_j} \rho_{s_j} C_{s_j})] \frac{1}{h_e} \frac{dh_c}{dt}
\]

\[
q = 0
\]

(5.40)

3) Calculate \(\varepsilon_e\), and \(h_e\)

Following equations are solved to get \(\varepsilon_e\), and \(h_e\).

\[
\rho_{s_L} \varepsilon_e \frac{dh_e}{dt} - k_{eff} \frac{\partial T_L}{\partial x} \bigg|_{x=h_e} = -k_c \frac{\partial T_c}{\partial x} \bigg|_{x=h_e},
\]

\[
\frac{dh_e}{dt} = \left( \frac{u}{\varepsilon_{L0} - \varepsilon_e} \right) \bigg|_{x=h_e}
\]

(5.41)
Coordinate transformed equations for $h_e$ and $\varepsilon_e$,

$$
\rho_s L_e \varepsilon_e \frac{dh_e}{dt} = \frac{k_{ef} \partial T_e}{h_e} \left|_{x = h_e^k} \right. - \frac{k_c \partial T_c}{h_0 - h_e} \left|_{x = h_e^k},
$$

$$
\frac{dh_e}{dt} = \left( \frac{u}{\varepsilon_{L0} - \varepsilon_e^k} \right) \left|_{x = h_e^k} \right.
$$

(5.42)

Finite difference method is applied to discretize equation (5.42) as following,

$$
\rho_L L_e \varepsilon_e^{k+1} \frac{h_e^{k+1} - h_e^k}{\Delta t} = \frac{k_{ef} 3T_{Ln+1}^{k+1} - 4T_{Ln}^{k+1} + T_{Ln-1}^{k+1}}{2\Delta \zeta} - \frac{k_c}{h_0 - h_e^{k+1}} \frac{-3T_{C1,3}^{k+1} + 4T_{C2}^{k+1} - T_{C3}^{k+1}}{2\Delta \varphi} \left(5.43\right)
$$

$$
\frac{h_e^{k+1} - h_e^k}{\Delta t} = \left( \frac{u}{\varepsilon_{L0} - \varepsilon_e^{k+1}} \right)
$$

(5.44)

where $h_e^k$ is the value of $h_e$ of last time step $k$.

Substituting equation (5.44) into (5.43),

$$
\rho_L L_e \left( \varepsilon_{L0} - \frac{u\Delta t}{h_e^{k+1} - h_e^k} \right) \frac{h_e^{k+1} - h_e^k}{\Delta t} = \frac{k_{ef} 3T_{Ln+1}^{k+1} - 4T_{Ln}^{k+1} + T_{Ln-1}^{k+1}}{2\Delta \zeta} - \frac{k_c}{h_0 - h_e^{k+1}} \frac{-3T_{C1,3}^{k+1} + 4T_{C2}^{k+1} - T_{C3}^{k+1}}{2\Delta \varphi}
$$

(5.45)

After arrangement,

$$
\varepsilon_{L0} \left( h_e^{k+1} \right)^3 + \left( (h_0 + h_e^k) \varepsilon_{L0} + \Delta tu \right) \left( h_e^{k+1} \right)^2 + (-h_0 h_e^k \varepsilon_{L0} + a_1 + a_2 - h_0 \Delta tu) h_e^{k+1} - a_1 h_0 = 0
$$

(5.46)

$$
a_1 = \frac{3T_{Ln+1}^{k+1} - 4T_{Ln}^{k+1} + T_{Ln-1}^{k+1}}{2\Delta \zeta} \frac{\Delta t k_{ef}}{\rho_L L_e}
$$

$$
a_2 = \frac{-3T_{C1,3}^{k+1} + 4T_{C2}^{k+1} - T_{C3}^{k+1}}{2\Delta \varphi} \frac{\Delta t k_c}{\rho_L L_e}
$$

Equations (5.46) is an nonlinear equation for unknown $h_e^{k+1}$ at current time step $k+1$, and $h_e^{k+1}$ is calculated from Equations (5.46) by using the Newton-Raphson method [95] with
an iteration phase. The initial value for $h_{e}^{k+1}$ is assumed as

$$h_{e}^{k+1} = \frac{u}{\varepsilon_{t,0} - \varepsilon_{e}^{k}} \Delta t + h_{e}^{k}$$  \hspace{1cm} (5.47)$$

Then $\varepsilon_{e}^{k+1}$ is calculated from,

$$\varepsilon_{e}^{k+1} = \varepsilon_{t,0} - \frac{u \Delta t}{h_{e}^{k+1} - h_{e}^{k}}$$  \hspace{1cm} (5.48)$$

4) Calculate $\varepsilon_L$

If $h_{e} = x_1$ at time $t = k \Delta t$, therefore $\varepsilon_L$ is calculated as $\varepsilon_{L}\big|_{x=x_2} = \varepsilon_{L,0} - \varepsilon_{L} \big|_{t=k \Delta t}$ when $t > k \Delta t$.

The value of $\varepsilon_{L}$ at any position in $x=[0, h_{e}]$ is calculated by linear interpolation method.

**5.4.4 Solution procedure of third sub-period**

Sub-period 3: when $T_L\big|_{x=0} > 725$ (from time $t=t_2$ to $t=t_3$); all dependent variables (i.e. $\Theta_L$, $\Theta_2$, $\Theta_3$, $\varepsilon_L$, $\varepsilon_{S,1}$, $\varepsilon_{S,2}$, $u$, $m_1$, $m_2$, $\varepsilon_{A}$, $T_L$, $T_C$, $\varepsilon_{o}$, $\varepsilon_e$, $\varepsilon_{e}$, $\varepsilon_{e}$, $h_{e}$, $h_{p}$)

The initial time interval in this sub-period is $\Delta t = 0.1$ s. When $T_L\big|_{x=0}$ first satisfies

$$\frac{(T_L\big|_{x=0} - 725)h_{e}}{T_L\big|_{x=0} - 685} > 0.5$$ at $t = t_2$, $h_{p} = \frac{(T_L\big|_{x=0} - 725)h_{e}}{T_L\big|_{x=0} - 685}$ is assumed (too small $h_{p}$ should be avoided, $h_{p}\big|_{x=t_2} > 2 \times 10^{-4}$ m).

Applying coordinate system (refer to section 5.1),

$$\eta = \frac{x}{h_{p}}, 0 \leq \eta \leq 1$$

$$\zeta = \frac{x - h_{e}}{h_{e} - h_{p}}, 0 \leq \zeta \leq 1$$  \hspace{1cm} (5.49)$$

$$\varphi = \frac{x - h_{e}}{h_{0} - h_{e}}, 0 \leq \varphi \leq 1$$

The region $\eta = [0,1]$ is meshed into $n$ elements ($n=100$) with $n+1$ discrete nodes with
\( \eta = \frac{1}{n}, \frac{2}{n}, \ldots, \frac{(n-1)}{n}, 1. \) \( n \) does not change with time. For coordinate system \( \eta \), the region, the elements and nodes are all fixed. The corresponding \( n+1 \) discrete nodes for coordinate system \( x \) in region \( x = [h_p, h_p] \) are \( x = 0, \frac{h_p}{n}, \frac{2h_p}{n}, \ldots, \frac{(n-1)h_p}{n}, h_p \).

The region \( \varsigma = [0,1] \) is meshed into 20 elements and \( \phi = [0,1] \) is meshed into 100 elements. The coordinate transformations in \( \varsigma \) and \( \phi \) are similar with \( \eta \) (more details, see section 5.1).

The initial value of \( T_C \) and \( T_L \) of each node in Sub-period 3 is set from the value of last time step in Sub-period 2 by linear interpolation method. The initial value of volume fraction of liquid bath \( \varepsilon_L \) in region \( x = [0, h_p] \) in Sub-period 3 is assumed as

\[
\varepsilon_L \bigg|_{n+1} = \varepsilon_L^0 = \varepsilon_{\text{surf}} + \varepsilon_{L,0} \quad (5.50)
\]

The initial value of \( u \) in Sub-period 3 is constant over the region rather than a function of \( x \), and equals to the value of the last iteration in step 2.

1) Calculate \( T_L, T_C, h_e, h_p, \varepsilon_p \) and \( \varepsilon_e \)

As noted in section 4.2.6, there may be ‘hot’ region (refer to section 4.2.6) in the region \( x = [0, h_p] \) where \( T_L > T_{\text{liq}} \) and \( \varepsilon_{s,2} = 0 \). Depending on the temperature and solid phase concentration, the movement of the ‘hot’ region is very complicated. It is very difficult to apply the coordinate transformation method here. The ‘hot’ region is include in the region \( x = [0, h_p] \) with the same coordinate system. When \( n \) is high enough, the error caused by this simplification can be limited.

In each iteration, the value of \( \phi_1^*, \phi_2^*, k_{\text{eff}} \) and \( C_E \) (refers to section 4.2.3, 4.2.6 and 4.4 respectively) at the \( n+1 \) discrete nodes are updated based on the last value of the variables such as \( T_L \).

\( \varepsilon_p \) is calculate from
\[
\varepsilon_{f}\left|_{t=t_p} = -\left(\varepsilon_{surf} + \varepsilon_{f,\eta}\right), \right. \\
\frac{dT_L}{dt} = \frac{\partial}{\partial x} \frac{\partial T_L}{\partial x} - k_\varepsilon \varepsilon f \rho_f L_{\eta}, t > t_e
\]

Following equations are solved to get \( T_L, T_C, h_p, h_e \) and \( \varepsilon_e \).

\[
\left[ C_L \varepsilon_L + \sum \left( \varepsilon_S L \beta S \right) \right] \frac{\partial T_L}{\partial t} + C_L \varepsilon L u \frac{\partial T_L}{\partial x} = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_L}{\partial x} \right), x \leq h_p
\]

\[
k_{eff} \frac{\partial T_L}{\partial x} \bigg|_{x=0} = h_f (T_L - T_h)
\]

\[
T_L \bigg|_{x=h_p} = 725
\]

\[
\left[ C_L \varepsilon_L + \sum \left( \varepsilon_S L \beta S \right) \right] \frac{\partial T_L}{\partial t} + C_L \varepsilon L u \frac{\partial T_L}{\partial x} = \frac{\partial}{\partial x} \left( k_{eff} \frac{\partial T_L}{\partial x} \right), h_p < x \leq h_e
\]

\[
T_L \bigg|_{x=h_p} = 725
\]

\[
T_L \bigg|_{x=h_e} = 685
\]

\[
\left[ \sum \left( \varepsilon_S L \beta S \right) \right] \frac{\partial T_C}{\partial t} = \frac{\partial}{\partial x} \left( k_C \frac{\partial T_C}{\partial x} \right), x > h_e
\]

\[
T_C \bigg|_{x=h_e} = 685
\]

\[
k_C \frac{\partial T_C}{\partial x} \bigg|_{x=h_e} = (h_C + h_h) (T_C - T_A)
\]

\[
\rho L f \varepsilon_p \frac{dh_p}{dt} - k_{eff} \frac{\partial T_L}{\partial x} \bigg|_{x=h_p} = -k_{eff} \frac{\partial T_L}{\partial x} \bigg|_{x=h_p'}
\]

\[
\rho S L f \varepsilon_e \frac{dh_e}{dt} - k_{eff} \frac{\partial T_L}{\partial x} \bigg|_{x=h_e} = -k_C \frac{\partial T_C}{\partial x} \bigg|_{x=h_e'}
\]

\[
\frac{dh_e}{dt} = \left( \frac{u}{\varepsilon_{f,0} - \varepsilon_e} \right) \bigg|_{x=h_e}
\]

Coordinate transformation (refer to section 5.1, more details see Table 5-1), finite difference method [91], Newton-Raphson method [95] and Galerkin approach (refer to section 5.2) are applied in the similar way with Sub-period 2 to solve above equations.

2) Calculate \( m_1, m_2, \Omega_1, \Omega_2, \) and \( \Omega_{3,8} \) in region \( x = [0, h_p] \)

\( m_1 \) and \( m_2 \) at the \( n+1 \) discrete nodes are calculated from
\[ \begin{bmatrix} m_1 \\ m_2 \end{bmatrix} = [F] \begin{bmatrix} \rho_L e_l \frac{\partial T_L}{\partial t} \\ \rho_L u \frac{\partial T_L}{\partial x} \end{bmatrix} = [F] \begin{bmatrix} \rho_L e_l \left( \frac{\partial T_L}{\partial t} - \frac{\eta}{h_p} \frac{\partial h_p}{\partial \eta} \frac{\partial T_L}{\partial \eta} \right) \\ \rho_L u \frac{\partial T_L}{\partial \eta} \end{bmatrix}, \]

\[ [F] = \begin{bmatrix} 1 - \phi_2^* & \phi_1^* \\ \phi_2^* & 1 - \phi_1^* \\ 1 - \phi_1^* - \phi_2^* \end{bmatrix} \begin{bmatrix} \frac{\partial \phi_1^*}{\partial T_L} \\ \frac{\partial \phi_2^*}{\partial T_L} \\ \frac{\partial \phi_1^*}{\partial T_L} \end{bmatrix}, \phi_i^* = f_i(T_L) \]

\( \phi_1, \phi_2, \) and \( \phi_{3,8} \) are calculated from

\[ \begin{align*}
\phi_1 &= \phi_1^* - K_i m_1, \phi_1^* = f_1(T_L) \\
\phi_2 &= \phi_2^* - K_2 m_2, \phi_2^* = f_2(T_L) \\
\phi_1 + \phi_2 + \phi_{3,8} &= 1
\end{align*} \]

As note in section 4.2.6, in ‘hot’ region, it comes that \( \phi_2^* = 0, m_2 = 0 \), \( \phi_1, \phi_2, \) and \( \phi_{3,8} \) are calculated from

\[ \begin{align*}
\phi_1 &= \phi_1^* - K_i m_1, \phi_1^* = f_1(T_L) \\
\frac{\phi_2}{\phi_{3,8}} &= k_{Cry} \\
\phi_1 + \phi_2 + \phi_{3,8} &= 1
\end{align*} \]

where \( k_{Cry} \) is constant and depends on the initial value of the bulk bath.

In the case of high surface area, \( K_i \) is assigned as approximately \( K_i \approx 5 \times 10^{-7} \) which is in the reasonable region (see Appendix A.6). It comes that \( \phi \approx \phi^* \) due to the fact that \( K_i m_i << \phi_i^* \). As long as \( K_i \) is in the reasonable region, it has negligible impact on the results.

3) Calculate \( \varepsilon_{S,1} \) and \( \varepsilon_{S,2} \) in region \( x=[0, h_p] \).

\( \varepsilon_{S,1} \) and \( \varepsilon_{S,2} (\varepsilon_{S,i}, i=1,2) \) are calculated from
Chapter 5. Computational methodology

\[ \rho_{s,i} \frac{\partial \varepsilon_{s,i}}{\partial t} = -m_i, i = 1,2 \]

By applying the coordinate system,

\[ \eta = \frac{x}{h_p}, 0 \leq \eta \leq 1 \] (5.51)

\[ \frac{\partial \varepsilon_{s,i}}{\partial t} - \frac{\eta}{h_p} \frac{dh_p}{dt} \frac{\partial \varepsilon_{s,i}}{\partial \eta} = - \frac{m_i}{\rho_{s,i}}, i = 1,2 \] (5.52)

\[ \varepsilon_{s,j} \bigg|_{\eta=1} = \varepsilon_{s,j}^0 \]

The boundary condition of \( \varepsilon_{s,j} \) at the position \( h_p \) is always the initial value \( \varepsilon_{s,j}^0 \) because it reaches new position where \( \varepsilon_{s,j} = \varepsilon_{s,j}^0 \) when \( h_p \) moves, or there is no phase transformation \( (m_i=0) \) when the flow stops.

According to upwind difference method \([91, 96]\) (\( \varepsilon_{s,1} \) is taken as example),

\[ \frac{\varepsilon_{s,1,j}^{k+1} - \varepsilon_{s,1,j}^{k}}{\Delta t} - \frac{(j-1)\Delta \eta}{h_p} \frac{dh_p}{dt} \left( \frac{\varepsilon_{s,1,j+1}^k - \varepsilon_{s,1,j}^k}{\Delta \eta} \right) = - \frac{m_{s,j}}{\rho_{s,1,j}}, j = 1,2,3,...n \] (5.53)

Set \( \lambda = \frac{j-1}{h_p} \frac{dh_p}{dt} \Delta t \),

\[ \varepsilon_{s,1,j}^{k+1} = (1 - \lambda) \varepsilon_{s,1,j}^k + \lambda \varepsilon_{s,1,j+1}^k - \frac{m_{s,j}}{\rho_{s,1,j}} \Delta t, j = 1,2,3,...,n \] (5.54)

The above difference pattern is stable if following condition is satisfied \([96-98]\),

\[ |1 - \lambda| \leq 1 \text{ and } |\lambda| \leq 1 \] (5.55)

Since \( \lambda = \frac{j-1}{h_p} \frac{dh_p}{dt} \Delta t \geq 0 \), thus the condition becomes,
\[
\lambda = \frac{j-1}{\Delta t} \frac{dh_p}{dt} \Delta t \leq 1 \tag{5.56}
\]

According to the practical situation [17], it is reasonable to assume that \( \frac{dh_p}{dt} < 2 \times 10^{-5} \). In addition, \( h_p > 2 \times 10^{-4}, j \leq 100 \), therefore,

\[
\Delta t \leq \frac{10}{99} \approx 0.101 \tag{5.57}
\]

As time step \( \Delta t \) is initially 0.1 s, difference equation (5.54) is stable. In fact, with time \( t \) increases, \( \frac{dh_p}{dt} \) decreases while \( h_p \) increases. As a consequence, difference equation (5.54) becomes more and more stable with time \( t \) increases. Time step \( \Delta t \) increases from \( \Delta t =0.1 \) s to \( \Delta t=1 \) s gradually according to equation (5.56) and then keep as \( \Delta t=1 \) s.

4) Calculate \( \varepsilon_r, \varepsilon_A, \) and \( \varepsilon_L \)

The value of \( \varepsilon_r \) and \( \varepsilon_A \) depends on the temperature and time, not the liquid bath penetration. Therefore, coordinate transformation is not needed for \( \varepsilon_r, \) and \( \varepsilon_A. \)

\( \varepsilon_r \) is calculated from

\[
\ln(\varepsilon_r \rho_\gamma) = -K_\gamma (t-t_a) + \ln(\varepsilon_{r,0} \rho_\gamma) \rightarrow \varepsilon_r = \frac{1}{\rho_\gamma} e^{-K_\gamma (t-t_a) + \ln(\varepsilon_{r,0} \rho_\gamma)}
\]

\( \varepsilon_A \) is calculated from

\[
\frac{d\varepsilon_A}{dt} = K_{\gamma A} - \frac{\varepsilon_{r A}}{1-\varepsilon_{r A}} K_\gamma \varepsilon_r
\]

\[
= K_{\gamma A} - \frac{\varepsilon_{r A}}{(1-\varepsilon_{r A})\rho_\gamma} K_\gamma e^{-K_\gamma (t-t_a) + \ln(\varepsilon_{r,0} \rho_\gamma)}
\]

\[
\rightarrow \varepsilon_A = K_{\gamma A} (t-t_a) + \frac{\varepsilon_{r A}}{(1-\varepsilon_{r A})\rho_\gamma} e^{-K_\gamma (t-t_a) + \ln(\varepsilon_{r,0} \rho_\gamma)} + \varepsilon_{A0} - \frac{\varepsilon_{r A}}{(1-\varepsilon_{r A})\rho_\gamma} e^{\ln(\varepsilon_{r,0} \rho_\gamma)}
\]

If \( h_e=x_1 \) when at time \( t=t_a \), therefore \( \varepsilon_L \) in the region \([h_p,h_e]\) is calculated as
\( \varepsilon_L \bigg|_{x=x_1} = \varepsilon_{L,0} - \varepsilon_{L,t_0} \) when \( t \geq t_0 \) until \( h_p \) reaches \( x_1 \).

In the region \((0,h_p)\), \( \varepsilon_L \) is calculated from

\[
\varepsilon_L = 1 - \varepsilon_A - \varepsilon_{S,1} - \varepsilon_{S,2}
\]

5) Calculate \( u \)

\( u \) in region \([0,h_p]\) is calculated from

\[
\frac{\partial u}{\partial x} - m \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S1}} \right) + m_s \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{d \varepsilon_A}{dt} = 0
\]

\[
\int_0^{h_p} \left( \frac{\mu}{K_h} u + mu \right) dx = \frac{2 \gamma_L \cos \theta}{R} - \rho_L g h_e, K_h = \frac{\rho_L \varepsilon_L^3}{5S^2}
\]

\[
\left. u \right|_{x=h_p} = \frac{dh_p}{dt} \varepsilon_A \frac{\rho_F - \rho_L}{\rho_L} + u \bigg|_{x=h_p}
\]

By applying the coordinate system,

\[
\eta = \frac{x}{h_p}, 0 \leq \eta \leq 1
\]

\[
\frac{1}{h_p} \frac{\partial u}{\partial \eta} = m \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S1}} \right) + m_s \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{d \varepsilon_A}{dt}
\]

\[
\int_0^{h_p} \left( \frac{\mu}{K_h} u + mu \right) dx = \frac{2 \gamma_L \cos \theta}{R} - \rho_L g h_e
\]

\[
\rightarrow \int_0^{h_p} \left( \frac{\mu}{K_h} u + mu \right) dx + u \bigg|_{x=h_p} \int_{h_p}^{h_p} \frac{\mu}{K_h} dx = \frac{2 \gamma_L \cos \theta}{R} - \rho_L g h_e
\]

\[
\rightarrow h_p \int_0^1 w \cdot u d \eta + u \bigg|_{x=h_p} \int_{h_p}^{h_p} \frac{\mu}{K_h} dx = \frac{2 \gamma_L \cos \theta}{R} - \rho_L g h_e
\]

\[
w = \frac{\mu}{K_h} + m
\]

\[
\rightarrow h_p \frac{1}{3n} [w(0)u(0) + 2 \sum_{i=1}^{n/2-1} [w(2i/n)u(2i/n)] + 4 \sum_{i=1}^{n/2} [w(2i-1/n)u(2i-1/n)] + w(1)u(1)]
\]

\[
+ [u(1) - \frac{dh_p}{dt} \varepsilon_A \frac{\rho_F - \rho_L}{\rho_L}] \int_{h_p}^{h_p} \frac{\mu}{K_h} dx = \frac{2 \gamma_L \cos \theta}{R} - \rho_L g h_e
\]
\[ \int_{h_p}^{h} \frac{\mu}{K_h} dx \text{ can be calculated by equation (5.35). According to upwind difference method [91], the } n+1 \text{ equations used for calculating } u \text{ are listed as,} \]

\[
\frac{u_2 - u_1}{\Delta \eta h_p} = \left[ m_1 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S1}} \right) + m_2 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{d\varepsilon_A}{dt} \right]_{x=0} \\
\frac{u_3 - u_2}{\Delta \eta h_p} = \left[ m_1 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S1}} \right) + m_2 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{d\varepsilon_A}{dt} \right]_{x=b_a} \\
\frac{u_4 - u_3}{\Delta \eta h_p} = \left[ m_1 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S1}} \right) + m_2 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{d\varepsilon_A}{dt} \right]_{x=b_a} \\
\vdots \\
\frac{u_{n+1} - u_n}{\Delta \eta h_p} = \left[ m_1 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S1}} \right) + m_2 \left( \frac{1}{\rho_L} - \frac{1}{\rho_{S2}} \right) + \frac{d\varepsilon_A}{dt} \right]_{x=(n-1)b_a} \\
\frac{h}{3n} \left[ w_{u_1} + 2 \sum_{j=1}^{n/2-1} w_{u_{2j+1}} + 4 \sum_{j=1}^{n/2} w_{u_{2j}} + w_{u_{n+1}} \right] \\
+ \left[ u_{n+1} - \frac{dh_p}{dt} \varepsilon_p \frac{\rho_F - \rho_L}{\rho_L} \right] \int_{h_p}^{h} \frac{\mu}{K_h} dx = \frac{2\gamma_L \cos \theta}{R} - \rho_L gh_e \\
\Delta \eta = \frac{1}{n} \quad (5.61) \]

These equations are implicit because \( m_1, m_2 \) and \( \frac{d\varepsilon_A}{dt} \) in the right item are calculated from current time step. In addition, the iteration method also contributes to the stability of these equations.

\( u \) in region \([h_p, h_e]\) is assumed constantly as,

\[
u \bigg|_{x=h_p} = u \bigg|_{x=h} - \frac{dh_p}{dt} \varepsilon_p \frac{\rho_F - \rho_L}{\rho_L} \quad (5.62)\]
6 Experimental

The theoretical development regarding the mechanism of the thermochemical evolution of the crust is presented in Chapter 4. To confirm some assumptions made in this development, and also to establish the chemical composition distribution in the crust, the experimental tests of XRD, LECO and DTA have been performed on industrial crust samples and are reported in this chapter.

6.1 Experimental materials

Seven pieces of crust (designated as Crust A, B, C, D, E, F, and G) were taken from industrial reduction cells three months after they had been started, giving an undamaged but new cell status. They were from different location in several different cells, as shown in Figure 6-1. Crust pieces, A, B, C, and D, are the whole crust from the bottom to the top while crust pieces E, F, and G are just the bottom part of the whole crust. These crust pieces represent the most common crust types in industrial cells, as described below.

![Figure 6-1](image)

Figure 6-1. The sketch of positions from which crust pieces were taken. Figure adapted from Figure 6, page 593 in TMS Light Metals 2014 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

These crust pieces were selected because of their typical visual features. Firstly, they are clean, i.e. there are few visible impurities such as carbon or iron. Secondly, some crust pieces have typical, clearly distinguishable features between the lower and the upper part. As shown in Figure 6-2 (a), while the lower part is crystalline, the portion above the
crystalline crust is not and will be referred to as sintered crust in this thesis.

The raw anode cover material for the reduction cells was crushed bath/alumina mixture. All the crust samples are from this raw cover material except that Crust C is an alumina based crust because of the alumina feeding in its close proximity. The original position of Crust C in the cell was close to the feeding hole, and was covered by alumina due to some abnormal but rather typical feeding operations which spread excess alumina onto the crust.

Based on their difference in appearance and shape, crystalline crusts can also be categorised into following three types (see Figure 6-2): Type I is the crystalline crust of a single layer with nearly uniform thickness (lower part of Crust A, B, C, and D); Type II crystalline crust has an irregular surface and stalactitic shape crystals (Crust F); Type III is the crystalline crust consisting of stratified layers (Crust E). The thickness of each layer is approximately 1~5 mm.
Figure 6-2. Photo of different types of crystalline crust (the arrow indicates from the bottom to the top). Figure adapted from Figure 1, page 676 in TMS Light Metals 2013 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

Each crust piece was then divided vertically into a number of sections starting from the crystalline crust at the bottom, as shown in Figure 6-3. One sample was taken from each section.

Figure 6-3. Example of sampling from a crust piece

These crust samples are used for the experimental analysis discussed below.

### 6.2 Optical microscope observations

A small slice was taken from each of the crystalline crust types, and the surface was polished. The morphology of the crystalline crust was observed using the ordinary optical microscope. The magnification was 50 times.
6.2.1 Three types of crystalline texture

Crystalline texture has been classified into the following three types in the literature [99-102]. Macrocrystalline texture: crystals are visible to the naked eye. Microcrystalline texture: crystals are small enough to be visible only under the microscope. Microaphanitic (or cryptocrystalline) texture: crystals are too small to be recognized even under the microscope.

The cooling rate during crystallization accounts for the contrasts in crystallite size between these three types [103]. When the cooling rate is slow (less than 30 °C/hr), slow nucleation rate lead to the formation of macrocrystalline crystals. When cooling rate is fast (between 30 and 100 °C/hr), microcrystalline crystals are formed due to high nucleation rate and slow growth rate. When cooling rate is too fast (>100 °C/hr), crystal nucleation and growth is stunted and microaphanitic crystal is formed.

6.2.2 Crystalline crust texture

Obvious macro crystal can be observed by the naked eye for the type I crystalline crust, as shown in Figure 6-4. Thus the type I crystalline crust is made of mainly macrocrystalline texture.

![Figure 6-4](image-url) Surface morphology of type I crystalline crust B1 (macrocrystalline texture) magnification: 50x. Figure adapted from Figure 6, page 679 in TMS Light Metals 2013 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

Crystals can be observed under optical microscope for the type II crystalline crust, which
indicates that it is made of microaphanitic texture (see Figure 6-65).

Figure 6-5. Surface morphology of the type II crystalline crust F1 (microcrystalline texture) magnification: 50x. Figure adapted from Figure 6, page 679 in TMS Light Metals 2013 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

The crystal structure in the type III crystalline crust is too fine to be observed even under optical microscope (see Figure 6-56). The type III crystalline crust has microcrystalline texture.

Figure 6-6. Surface morphology of the type III crystalline crust E1 (microaphanitic texture) magnification: 50x. Figure adapted from Figure 6, page 679 in TMS Light Metals 2013 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

The observations of the crystalline crust support the discussions of crystalline crust formation in section 6.6 of this chapter below.
6.3 Chemical composition analysis methodology

6.3.1 XRD analysis

Each sample was crushed by a hammer mill into a fine powder and dried (~8 hours, 150 °C). The chemical composition of all samples was examined by X-ray powder diffractometer (XRD). A Bruker D8 Advanced diffractometer was operated at 40kA and 40 mA. The patterns were recorded over a range of 20 from 10 to 70 or 80 degree with step size 0.02 degree and counting time 10 seconds per point. Multiphase Rietveld refinements of XRD data were done for all samples using Fullprof software [104].

6.3.2 LECO oxygen analysis

To determine the alumina concentration, the oxygen contents of the samples were quantitatively measured by using a LECO RO-416DR Oxygen Determinator fitted with a model EF-400 Electrode Furnace (LECO Corporation, St. Joseph, MI).

6.4 Thermal analysis methodology

6.4.1 DTA system setup

DTA is widely used for studying the thermal transformation of materials. Commercial DTA apparatus is focused on small, pure samples usually, and is fragile in analysis of crust samples due to their corrosive liquid and vapour. In this study, a multi sample large sample mass DTA system was established. The sketch of this DTA system is shown in Figure 6-7. Laboratory grade alpha alumina powder was used as the reference material. For the alpha alumina powder, the mean particle size is about 100 µm, and the bulk density is 1.02 g/cm³. Four samples and one reference were added into five graphite crucibles (inner diameter Ø20mm). These crucibles were put into a heating furnace. Figure 6-7 b shows the layout of the crucibles with alpha alumina as the reference in the centre crucible, and samples in the four surrounding ones. The DTA tests were conducted under N₂ atmosphere.
A type N class-2 wire thermocouple was inserted into a hole at the bottom of each crucible (see Figure 6-8). The distance between the thermocouple and the inner bottom surface of the crucible is about 3 mm. The thermocouple was directly connected to a Picologger TC-08 data logger which was connected to a computer. The thermocouple has a tolerance of ±2.5 °C or ±0.0075×T between 333 °C and 1200 °C. The data logger has a resolution of 0.01 °C. The samples and the reference were heated to about 1020 °C at a heating rate 1 °C/min, and then cooled to room temperature at a cooling rate -1 °C/min. The temperatures of the samples and the reference were recorded by the data logger. Phase transformation in the sample, either exothermic or endothermic, can be detected relative to the reference.
6.4.2 Calibration of DTA system

Compared with commercial DTA systems, the crucible size is larger, and the distance between crucibles is greater in the DTA system for this study. It is normal that the samples and the reference might not be under the exactly same heating condition. Furthermore, the thermocouple may lead to measurement error as well. Therefore, it is necessary to calibrate the DTA system, as described below. The heating process is discussed below in detail to show the calibration method.

1) By using alpha alumina powder sample

A DTA test was run with 5 g alpha alumina powder in the centre crucible as well as in the surrounding crucibles. Figure 6-9 shows the raw temperature difference curve of the DTA test (sample temperature minus reference temperature, referred to as raw DTA curve below). The DTA test in this study recorded the curve above 400 °C only, where most phase transformations in the crust occur.

Because of slightly uneven heating condition in the furnace, sample 2 was heated fastest, and had about 4 °C increase in temperature difference between 400 and 700 °C. Therefore, the maximum difference in heating rate between the sample and the reference was estimated to be 4/(700-400)×1 °C/min, which is less than 0.015 °C/min. The temperature difference remained relatively stable above 700 °C, which indicated all the samples and the reference had nearly the same heating rate. It is known that pure alpha alumina is inert at the test temperature. As expected, there was no peak detected when alpha alumina sample was used. When other sample is used in the DTA test, any peak detected must relate to the phase transformation or reaction in the sample.
Figure 6-9. Raw DTA curve for alpha alumina samples. Figure adapted from Figure 3, page 592 in TMS Light Metals 2014 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

The raw DTA curve of alpha alumina sample has a slightly random noise (see Figure 6-10). The standard deviation (SD) of the noise is less than 0.07 °C. In addition, the temperature difference varies within a range of 0.2 °C. In order to eliminate the noise, the DTA curve was smoothed by Savitsky-Golay smoothing method (referred to as smoothed DTA curve below). In Figure 6-10, the two nearly straight lines are the temperature curves of the sample and the reference.

Figure 6-10. Example of the random noise of the DTA curve. Figure adapted from
2) By using cryolite sample

Laboratory grade cryolite powder was used to calibrate the DTA system. The cryolite powder has a mean particle size of about 80 µm, and its bulk density is 1.31 g/cm³. The weights of the cryolite powder samples in four crucibles are 2 g, 3 g, 3 g and 5 g respectively.

The alpha↔beta and crystal↔liquid phase transformations of pure cryolite have been widely studied and included in the NIST-JANAF thermochemical tables [80]. The beta↔gamma phase transformation of cryolite at 881 °C was detected by Landon [105]. Table 6-1 shows the temperature and enthalpy of these phase transformations.

Table 6-1. Phase transformations of cryolite [80, 105]

<table>
<thead>
<tr>
<th>Cryolite phase transition</th>
<th>Temperature °C</th>
<th>Enthalpy (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha↔beta</td>
<td>565</td>
<td>45</td>
</tr>
<tr>
<td>beta↔gamma</td>
<td>881</td>
<td>&lt;4</td>
</tr>
<tr>
<td>crystal↔liquid</td>
<td>1011</td>
<td>524</td>
</tr>
</tbody>
</table>

Figure 6-11 presents the temperature curves and DTA curve for a 5 g cryolite powder sample at three representative temperature ranges. The reference temperature curves are nearly straight lines at all temperatures. In contrast, the sample temperature curve has a clear plateau near 1010 °C (see Figure 6-11 (3)), which is close to the theoretical melting temperature of pure cryolite. This slope change is reflected by a strong peak of the DTA curve and at the same time a high SD value 0.66. By contrast, the SD of the DTA curve over temperature range 600~700°C (no phase transformation) is very close to that of the alpha alumina sample. Though there is no clearly visible change of slope at the temperature curve near 570 °C, an evident peak at the DTA curve and relatively high SD still indicate the alpha → beta phase transformation of cryolite.
(1) 500~600 °C (alpha → beta phase transformation)

(2) 600~700 °C (no phase transformation)
Figure 6-11. Detailed temperature and DTA curves of 5 g cryolite powder at three temperature ranges

In general, the melting point is defined as the extrapolated onset temperature (Te), which is the temperature at the intersection of the extrapolated DTA baseline prior to the peak with the extrapolated rising edge of the peak [106]. Figure 6-12 shows the determination of extrapolated onset temperature of the cryolite. More curves with different weights or heating rates contribute to a better determination of the melting point. In many cases, the extrapolated onset temperature is difficult to determine very accurately due to baseline instability or peak broadening. In these circumstances, the melting peak temperature (Tp), which is the clearest characteristic temperature, is used as melting point [107].
Figure 6-12. Determination of melting temperature for cryolite samples (DTA curves were offset to show the intersection with the baseline)

Figure 6-13 shows the smoothed DTA curves of cryolite samples with phase transformations. All alpha ↔ beta and crystal ↔ liquid phase transformations are shown by the curves. No indication of beta ↔ gamma phase transformation in these curves is possibly due to its very low enthalpy.

The liquidus temperature ($T_L$) is determined from the cooling DTA curve, as shown in Figure 6-14. Supercooling is a common phenomenon during homogeneous crystallization, especially for a pure substance [108]. Because of the slight supercooling temperature of 1.5 °C, as shown in Figure 6-14, the peak temperature at point “b” rather than the onset temperature at “a” is taken as the liquidus temperature. To show the supercooling clearly, the cooling DTA curve is plotted in Figure 6-14 differently from the heating DTA curves as shown by Figure 6-13.
Figure 6-13. Phase transformations shown by DTA heating curves (peak is indicated by arrow) (two 3 g cryolite samples are at different positions in the furnace). Figure adapted from Figure 5, page 592 in TMS Light Metals 2014 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

Figure 6-14. Determination of liquidus temperature for 5 g cryolite sample, giving $T_L$ at point b equal to 1009.1 °C
Similarly, the melting/liquidus point of pure NaF sample was measured by the DTA system. The measured results of all above samples are summarized in Table 6-2. Analysed by XRD, the CR of the cryolite sample is 2.94, extremely close to the pure compound. Its theoretical melting temperature is between 1010 and 1011 °C according to Haupin’s measurement [109]. The measurement error of the DTA system is about 4 °C on the low side. The error might be caused by the temperature gradient in the sample and the crucible, and/or the thermocouple tolerance.

Table 6-2. Measured melting/liquidus temperature by the DTA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>DTA measurement temperature</th>
<th>Data from NIST-JANAF Thermochemical Table for pure material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Heating</td>
<td>Cooling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Te (°C)</td>
<td>Tp (°C)</td>
</tr>
<tr>
<td>Na_3AlF_6</td>
<td>2</td>
<td>1006.8</td>
<td>1009.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1006.8</td>
<td>1010.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1006.8</td>
<td>1010.8</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1006.8</td>
<td>1013.2</td>
</tr>
<tr>
<td>NaF</td>
<td>2</td>
<td>992.6</td>
<td>999.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>992.6</td>
<td>998.9</td>
</tr>
</tbody>
</table>

There were two 3 g cryolite samples in crucibles at two different positions in the DTA system. Though the DTA curves are not exactly the same, they give the same measured melting temperature result. The influence of the location of the crucible on the measurement result is thus negligible. For samples of 2 to 5 g, the peak height is clear enough for phase transformation identification. Meanwhile the measurement error is acceptable as shown by the discussion above. Hence, it is reasonable to conclude that the DTA system is validated to acceptable accuracy.

6.4.3 Experimental sample

1) Cryolite/alumina powder mixture samples

Cryolite and alumina are two main components of industrial crust. The binary system cryolite-alumina has been well studied [50]. In this study, the cryolite and alpha alumina powder were mixed together evenly as 5 g samples with various alpha alumina content.
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(0%, 5%, 15%, 25%, 35%, 40%, 45%, 50%, and 60%) respectively. Thermal analyses of the cryolite/alumina mixture samples were carried out using the DTA system as discussed above. The results of these tests were used to verify the phase transformation results of crust samples below.

2) Industrial crust samples

Thermal analyses of the industrial crust samples were performed by using the DTA system. Each sample was the same as the one used for XRD analysis. The weight of each crust sample is 5 g.

6.5 Experimental results

6.5.1 Phases detected by XRD

Three major phases, i.e. alpha alumina, cryolite, and chiolite, were detected in all crusts by XRD. In addition, quite a number of other minor phases were also detected such as AlF₃, K₂NaAlF₆, LiNa₂AlF₆, CaF₂, Na₂LiAlF₆, Na₂Ca₃Al₂F₁₄, Na₂MgAlF₇, NaCaAlF₆, and NaF·1.5CaF₂·AlF₃. K₂NaAlF₆ and LiNa₂AlF₆ in particular existed in most of the present samples.

6.5.2 DTA curve and phase transformation

1) Heating DTA curve

The smoothed heating DTA curves of four cryolite/alumina mixture samples and eight representative crust samples are shown in Figure 6-15 and Figure 6-16, respectively. Peaks below 600 °C can be attributed to alpha ↔ beta phase transformation of cryolite. In the temperature range of 600–1020 °C, one or two distinct peaks at the DTA curve of each sample were detected. In the case of crust sample B1, a very small peak was detected before the main peak (see Figure 6-16).
Figure 6-15. Heating DTA curve of 5g cryolite/alumina mixture. Figure adapted from Figure 7, page 593 in TMS Light Metals 2014 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

Figure 6-16. Heating DTA curves of some crust samples (For the sample name on the
2) Cooling DTA curve

Figure 6-17 shows an example of the cooling DTA curve for sample A2. Compared to pure cryolite which has about 1.5 °C supercooling, most industrial crust samples don’t show obvious supercooling (see Figure 6-17). According to the crystallization theory, homogeneous crystallization requires high supercooling whereas heterogeneous crystallization does not [68]. In the cases of the crust samples, some alumina is solid phase, and may act as crystal nuclei for the heterogeneous crystallization. Thus no supercooling exists in the cooling DTA curve.

![Figure 6-17. An example of cooling DTA curve](image)

3) Summary for phase transformation investigation of crust samples

The phase transformations of crust samples shown by the DTA curves are summarized below:

(1) Crystallisation ↔ liquid transformation of cryolite was detected for most samples,
although several samples had no crystallisation ↔ liquid transformation detected.

(2) Incongruent melting of chiolite (Na₅Al₃F₁₄(s) + Al₂O₃(s) = Na₃AlF₆(s) + Liquid) around 725 °C [60] was detected from the heating curve, while the peak for the eutectic reaction (Lₑ = Na₅Al₃F₁₄(s) + Al₂O₃(s) + AlF₃(s)) around 685 °C [60] was detected from the cooling curves of chiolite enriched samples G1 and G2.

(3) Alpha ↔ beta solid phase transformation of cryolite around 530 to 580 °C was detected, although the decomposition of Na₂LiAlF₆ to Na₃AlF₆, LiF, and AlF₃ at 543 °C might be detected as well [60, 110]. However, these reactions are not critical to the present study because they do not affect the thermochemical stability of the crust.

6.5.3 Chemical composition and melting/liquidus temperature

The chemical compositions and phase transformation temperatures of all samples are given in Table 6-3. The crust samples are further categorized according to their distance to the bottom surface of the sintered crust. For simplicity, the concentrations of NaF, AlF₃, LiF, KF, MgF₂, and CaF₂ have been calculated where necessary from the stoichiometry of the phases.
Chapter 6. Experimental

Table 6-3. Results of chemical composition and phase transformation temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>From bottom surface of sintered crust (cm)</th>
<th>Chemical composition by XRD Rietveld refinement (wt %)</th>
<th>Stoichiometry concentration</th>
<th>CR from XRD result</th>
<th>wt % Li2O3 by LECO</th>
<th>Phase Transformation temperature by DTA</th>
<th>Calculated liquidus by equation from Solheim</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Major phases</td>
<td>Minor phases</td>
<td>Al2O3</td>
<td>Cryolite</td>
<td>Chiolite</td>
<td>AlF3</td>
<td>LiF</td>
</tr>
<tr>
<td>A1</td>
<td>1.0</td>
<td>48.9</td>
<td>5.2</td>
<td>19.9</td>
<td>52.1</td>
<td>40.2</td>
<td>0.3</td>
</tr>
<tr>
<td>A2</td>
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<td>15.5</td>
<td>57.4</td>
<td>6.7</td>
<td>20.4</td>
<td>43.3</td>
<td>34.6</td>
</tr>
<tr>
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<td>50.8</td>
<td>6.7</td>
<td>13.7</td>
<td>37.2</td>
<td>29.4</td>
</tr>
<tr>
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<td>6.4</td>
<td>33.4</td>
<td>36.8</td>
<td>31.5</td>
</tr>
<tr>
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<td>30.2</td>
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<td>4.2</td>
<td>30.8</td>
<td>33.8</td>
<td>28.4</td>
</tr>
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<td>29.0</td>
</tr>
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<td>41.3</td>
<td>34.4</td>
<td>33.2</td>
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<td>53.3</td>
<td>40.4</td>
<td>1.5</td>
</tr>
<tr>
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<td>3.3</td>
<td>29.5</td>
<td>50.3</td>
<td>39.3</td>
<td>1.6</td>
</tr>
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<td>19.0</td>
<td>51.8</td>
<td>39.6</td>
<td>1.0</td>
</tr>
<tr>
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<td>4.8</td>
<td>31.3</td>
<td>48.4</td>
<td>38.2</td>
<td>1.7</td>
</tr>
<tr>
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<td>7.9</td>
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<td>35.3</td>
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<td>0.4</td>
</tr>
<tr>
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</tr>
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<td>51.7</td>
<td>40.2</td>
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<td>6.1</td>
<td>27.4</td>
<td>33.6</td>
<td>27.9</td>
<td>0.7</td>
</tr>
<tr>
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</tr>
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<td>0.8</td>
</tr>
<tr>
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<td>28.2</td>
<td>19.7</td>
<td>22.5</td>
</tr>
<tr>
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<td>0.0</td>
<td>22.5</td>
<td>54.7</td>
<td>5.0</td>
<td>17.8</td>
<td>40.5</td>
<td>31.4</td>
</tr>
<tr>
<td>D2</td>
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<td>26.8</td>
<td>39.9</td>
<td>3.2</td>
<td>30.2</td>
<td>53.7</td>
<td>27.9</td>
</tr>
<tr>
<td>D3</td>
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<td>26.3</td>
<td>3.6</td>
<td>30.9</td>
<td>35.2</td>
<td>28.2</td>
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<td>D4</td>
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<td>24.5</td>
<td>33.3</td>
<td>6.4</td>
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<td>33.3</td>
<td>30.2</td>
</tr>
<tr>
<td>D5</td>
<td>6.0</td>
<td>24.9</td>
<td>25.5</td>
<td>9.4</td>
<td>36.1</td>
<td>32.6</td>
<td>31.1</td>
</tr>
<tr>
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<td>2.5</td>
<td>35.6</td>
<td>5.5</td>
<td>35.6</td>
<td>47.6</td>
<td>38.3</td>
<td>2.3</td>
</tr>
<tr>
<td>E2</td>
<td>3.0</td>
<td>67.6</td>
<td>6.6</td>
<td>23.9</td>
<td>50.6</td>
<td>39.9</td>
<td>0.4</td>
</tr>
<tr>
<td>F1</td>
<td>3.1</td>
<td>49.7</td>
<td>5.4</td>
<td>41.8</td>
<td>45.5</td>
<td>37.7</td>
<td>3.1</td>
</tr>
<tr>
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<td>1.7</td>
<td>37.4</td>
<td>41.6</td>
<td>19.6</td>
<td>47.7</td>
<td>45.3</td>
<td>0.8</td>
</tr>
<tr>
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<td>80.1</td>
<td>13.5</td>
<td>44.4</td>
<td>51.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The chemical composition in the crust sample is complex, and is difficult to be determined very accurately by XRD. For instance, the phases of Li2NaAlF6 and LiNa2AlF6 have very similar XRD peaks. Though multiphase Rietveld refinements have been carried out for the XRD data analysis, the chemical composition result may still be semi-quantitative.

Nevertheless, XRD analysis has higher relative accuracy for the main phases with higher concentrations. These phases are crucial to the thermochemical stability of the crust because they determine the proportions of liquid and solid material present at each crust location – as will be demonstrated later in section 6.7.2.

Measured alumina content by XRD is compared with the quantitative data measured by...
LECO Oxygen Analyzer, as shown in Figure 6-18. There is 2~3 wt% measurement error for the alumina concentration by the XRD.

![Graph showing Al<sub>2</sub>O<sub>3</sub> wt% by XRD vs. by LECO](image)

Figure 6-18. Measured Al<sub>2</sub>O<sub>3</sub> wt% by XRD vs. by LECO

The CR of each sample is calculated based on the stoichiometric concentration of AlF<sub>3</sub> and NaF measured by the XRD. Like the chemical composition, the CR is semi-quantitative as well.

As quantified by Solheim et al. [61], the liquidus temperature of cryolite based system is a function of the chemical composition. In addition to the data measured by DTA, the liquidus temperatures were also calculated from the chemical compositions measured by XRD. For the alumina enriched crust, only part of the alumina dissolves in the liquid bath, and the saturation solubility is calculated by the empirical equation according to Skybakmoen et al. [50].

The comparisons between calculated and measured liquidus temperature are shown in Figure 6-19. As discussed above, the XRD measured concentration might have a deviation of up to 2~3 wt% from the LECO measured results. Small variations in the additive concentrations results in a few degrees of liquidus temperature change. For instance, when Al<sub>2</sub>O<sub>3</sub> and LiF concentration both vary by 1 wt%, liquidus temperature
will be depressed by about 7 °C and 9 °C, respectively. Despite these limitations, the liquidus temperature calculated using the chemical composition is in reasonable agreement with the results measured by the DTA system. Thus the chemical composition distribution trend in the crust is confirmed.

It was noticed that for each sample the melting temperature is generally higher than the liquidus temperature. The reason for this difference is that the crust becomes more homogeneous after a major part of it melts as liquid phase.

![Comparison of liquidus temperature between results measured by DTA and calculated using the chemical composition measured by XRD](image)

Figure 6-19. Comparison of liquidus temperature between results measured by DTA and calculated using the chemical composition measured by XRD

### 6.5.4 Chemical composition distribution

Figure 6-20 and Figure 6-21 show the vertical distribution of cryolite concentration and CR respectively. The lower sections of the crusts have higher cryolite concentration and CR than the upper sections. Especially in the crystalline crust (the lower section under sintered crust, see section 6.2), this higher cryolite concentration and higher CR is even more pronounced. Similar trends of vertical cryolite concentration and CR distributions have been reported by Liu et al. [14] and Groutzo et al. [32].
6.5.5 Melting/liquidus temperature distribution and depression

Figure 6-22 shows the liquidus temperature distribution in the crust. Generally, the crust bottom has higher liquidus temperature than the crust top. The melting/liquidus temperature of the crust samples decreases with the decrease of CR in general, as shown in Figure 6-23. The melting/liquidus temperature is depressed to about 900 °C in some crusts with low CR.
Figure 6-22. Measured liquidus temperature in the crust (-1 cm denotes crystalline crust)

Figure 6-23. The influence of CR on measured melting and liquidus temperature (the sample with CR near 2.0 has less fluoride additives than other samples, which resulting relatively high liquidus and melting temperature)

It has been found that alumina and fluoride additives depress the liquidus temperature of molten cryolite [61], as shown in Figure 6-24. It is certain that they depress the melting temperature of the crust as well.
6.6 Hypotheses for crust formation

According to the foregoing observations and analysis, there are many differences in visual features, chemical compositions and melting/liquidus temperature among these industrial crusts. These differences can be explained by their formation process and raw anode cover properties, as discussed below.

6.6.1 Feasible mechanisms for crystalline crust formation

It is evident that the crystalline crust was crystallized from the bulk bath. Crystalline crust is more likely formed where insulation is poor. It might not exist in some cells at all, or only exist at localised positions where crust has become thin. These observations will be explained by the lifecycle as discussed below.

(1) Type I crystalline (Macrocrystalline) crust formation

During the later stage of an anode’s life, the bottom of the sintered crust melts and its thickness is reduced. If the bath has a level high enough to make full contact with the crust and superheat low enough at the same time, the formation of type I crystalline crust is likely to be triggered by a low energy deficit across the molten bath-sintered crust boundary.
Under the condition that the bulk bath is in full contact with the thin crust, heat will transfer from the bath and into the crust by convection and conduction rather than radiation. At the beginning of its full contact with the crust, the bulk bath usually has 5~15 °C superheat and will penetrate into the crust. As more and more heat is dispersed to the surroundings, a temperature gradient will exist in the penetrating bath while its local superheat decreases adjacent to the solid boundary. The macrocrystalline crystal is then expected to form slowly by fractional crystallization when the bath temperature is only a few degrees below the liquidus point.

The formation of macrocrystalline crystal is illustrated in Figure 6-25. It starts from the bulk bath/crust boundary where the temperature is lower than the bulk bath. The boundary moves downwards, and the crystalline crust increases its thickness with time. The formation of crystalline crust will cease when the crust provides sufficient insulation to the flow of heat.

![Figure 6-25. Type I crystalline crust formation. 1~2) Crust melted. 3) Bath level increased. 4~5) Type I crystalline crust was formed. (Note that the crystalline crust sample represented by pictures 4-5 here are formed in Figure 6-4)](image)

According to the mechanism proposed in chapter 4, only cryolite crystallizes at the liquidus temperature during cooling process. However, the chemical composition of the Type I crystalline shows that even though it has high cryolite content it is not pure cryolite. Some liquid bath is evidently trapped between the cryolite crystals [111], and consequently the Type I crystalline is not pure cryolite. This phenomenon has also been observed with sidewall ledge analyses [112].
(2) Type II crust (Microcrystalline) formation

When the bulk bath surface fluctuates significantly as shown in Figure 6-26, the liquid bath gets splashed on to the bottom surface of the crust where there was previously a small gap (less than 10 cm). The splashed liquid bath cools down quickly and forms a microcrystalline texture. Eventually, some crystals might melt and begin to drip, or liquid within the crust itself percolates under gravity, resulting in the formation of the crystals of stalactitic shape. The continuous splashing and dripping process made the stalactitic crystal grow gradually. The gap between the bulk bath and the crust may increase with time.

![Figure 6-26. Type II crystalline crust formation. 1) Bulk bath surface fluctuation, 2~3) Type II crystalline crust grew. (Note that the crystalline crust sample represented by pictures 3 here are formed in Figure 6-5)](image)

(3) Type III crust (Microaphanitic) formation

As shown in Figure 6-6, the bottom surface of each crystalline crust layer is covered with carbon dust, while there is not much carbon dust on the top surface. This implies that type II crystalline crust layers were formed intermittently. The details are discussed below.

In some situations, a cell’s temperature may drop quickly. The most likely cause of this sudden temperature drop is due to abnormal feeding of a large amount of alumina, as depicted in Figure 6-28 (e.g. after an anode effect termination, or after a new anode is set). Large amounts of alumina have been observed to accumulate on the anode cover near feeder holes due to feeder hole blockages, as shown in Figure 6-27.
The large dissolution enthalpy required as this alumina finally falls into the bath, leads to a significant local bath temperature and superheat depression. The bath near the crust is cooled rapidly to below the liquidus point, causing the microphanitic crystals to form onto the crust through rapid solid fraction of the bath. The bath temperature recovers soon after alumina dissolution.

As long as such an alumina feeding problem remains, alumina accumulation near feeder holes will continue and the above accumulation and overfeeding can be repeated many times. Crystalline crust may then be formed over time in distinctive layers.

**Figure 6-28. Type III crystalline crust formation.** 1) Bath temperature dropped quickly. 2) Type III crystalline crust layer was formed. 3) Anode was moved up by cell control system. 4–6) Another cycle repeated. (Note that the crystalline crust samples represented by pictures 4–6 here are formed in Figure 6-6 )

### 6.6.2 Sintered crust formation

(1) Effect of pore size
Crusts A, C, and D have no macro pores observed by naked eyes. The raw anode cover material for them was either alumina or typical crushed bath/alumina mixture. Their formation can be illustrated by the sintered crust formation process as proposed in chapter 4.

The top part of Crust B is observed to be macro porous, below which there is no such pore, as shown in Figure 6-29. In addition, Crust B has much less alumina content than Crusts A, C, and D. One possible formation process for Crust B is that the original chiolite and/or cryolite components melt and percolate down into the bulk bath, leaving macro pores there at an early stage in the crust development, similar to the bottom of Crust G. Once the bulk bath contacts the bottom of Crust B, the liquid bath penetrates rapidly and freely from the bottom filling these new macro pores. The crystallization of the liquid bath penetrating the hot crust could be slow, or could even result in the solid cryolite melting into the liquid bath if the liquid bath had high superheat. Crust B is likely to have started crystallizing downwards from the top after liquid stopped moving upwards, as in the formation of the crystalline crust discussed in 6.6.1. Crust B has the features of both the crystalline and sintered crust. Therefore, there is a relatively even CR distribution in the lower part of Crust B.

Figure 6-29. View of Crust B. Figure adapted from Figure 3, page 677 in TMS Light Metals 2013 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)
(2) Bulk bath/crust full contact

In Crust A, B, C and D, the crystalline crust locates exactly below the sintered crust, which indicates that the bulk bath has been in full contact with the bottom surface of the sintered crust.

A possible consequence for the formation of this type of crust is proposed as follows. The anode cover is initially porous and insulating. As the liquid bath penetrates, the sintered crust is formed, and its thermal conductivity increases at the same time. As a result, a crystalline crust is formed beneath it as the heat loss into the crust increases.

The macrocrystalline texture is caused by a very slow crystallization rate which means that the bulk bath temperature cools very slowly. This also indicates that there is likely to be sufficient time for the penetration of liquid bath before the formation of the crystalline crust.

(3) The effects of bath fume

In addition to liquid bath penetration, the decomposition of the bath fume into chiolite and AlF₃ may also result in very high chiolite content and low CR in the top part of a crust, as reported in the study by Groutso et al [32]. However, in the case of the industrial crusts of this study, since most open pores have already filled by the liquid bath through its
penetration, the bath fume penetration is suppressed greatly. Another evidence for the contribution of the liquid bath penetration is the considerable amount of fluoride additives detected in the crust, especially in the top part of the crust. The reason is that the fluoride additives are readily transported by the liquid bath while hardly transported by the bath fume. Therefore, the bath fume penetration is neglected compared with the liquid bath penetration in this study.

6.7 Melting behaviour of the crust

6.7.1 Melting temperature range

Peak shape is an important feature of DTA curve for studying the dynamics of the phase transformation. It has been used for studying both phase diagrams [113] and actual reaction kinetics [114, 115]. Kissinger [114] studied the effect of order of reaction on the peak shape of DTA curve. He applied curves of reaction rate vs. temperature to demonstrate the effect of vary order of reaction, and found that “the dominant factor controlling the shape and position of the differential thermal analysis peak is the nature of the reaction itself” [114].

For a DTA system, the peak shape relates to the heat release and phase transformation rate as well as sample properties such as thermal conductivity, granular size, etc. [116]. Figure 6-31 shows the peak shapes of the cryolite and cryolite/alumina mixture samples. The sample weight seems to have little impact on the peak shape. All cryolite samples have similar sharp peaks when the weight of them decreases from 5 g to 2 g in spite of the decreasing of the peak height.
Figure 6-31. Peak shapes of the cryolite and cryolite/alumina mixture samples. Figure adapted from Figure 11, page 594 in TMS Light Metals 2014 (Copyright © ___ by The Minerals, Metals & Materials Society. Reprinted with permission.)

Compared with the nearly pure cryolite, the 5 wt% alumina mixture has a much broader peak in Figure 6-31. However, the peak becomes narrower when alumina content increases to 15 wt%. Though the slight difference of the physical properties between the samples may contribute to the peak shape difference, the melting behaviour is very likely the dominant cause, as explained below.

It is assumed that the sample is heated/cooled slowly enough to reach phase equilibrium during the DTA test. Thus the melting behaviour follows the phase diagram as shown in Figure 6-32. Solheim et al. [50, 61] have proposed empirical expressions for the two lines ‘EA’ and ‘EB’ in the phase diagram.
NOTE: Due to copyright reasons, this figure has been removed. Please refer to the original source:


Alternatively, refer to a hard copy of this thesis, as deposited in The University of Auckland Library.

Figure 6-32. The liquidus diagram for the binary system Na\textsubscript{3}AlF\textsubscript{6}-Al\textsubscript{2}O\textsubscript{3} [50] (E is the eutectic point).

The way that fusion enthalpy is absorbed during the phase transformation may be the reason for the difference in peak shapes between the cryolite, 5 wt% and 15 wt% alumina mixtures. When pure cryolite melts, all fusion enthalpy is absorbed at an almost fixed temperature, and a very sharp peak forms. In the case of the 5 wt% alumina mixture, from Figure 6-31, it can be seen that 5 wt% alumina + 45 wt% cryolite melts at eutectic temperature, and the remaining 50 wt% cryolite melts into the liquid between the eutectic temperature and 985 °C, which is explained by the line ‘EA’ in the phase diagram (see Figure 6-32). The melting rate of cryolite is calculated to be 2.63 wt%/°C. For the 15 wt% alumina mixture, 9.44 wt% alumina + 85 wt% cryolite melts at the eutectic temperature, and then the composition of the liquid moves along the line ‘EB’ in the phase diagram (see Figure 6-32). The dissolving rate of alumina is about 0.053 wt%/°C.

The fusion enthalpy of cryolite is 524 kJ/kg [80]. According to Phan-Xuan’s measurement [117], the partial enthalpy of the dissolution of alumina in liquid bath was 1431 kJ/kg when the alumina concentration was more than 6 wt%. The corresponding endothermic enthalpy changes (equal to melting/dissolving rate times enthalpy) along line ‘EA’ (5 wt% alumina mixture) and ‘EB’ (15 wt% alumina mixture) are 1378 kJ/(kg°C) and 76 kJ/(kg°C) respectively.

The melting behaviour of 15 wt% alumina mixture follows closely that of pure cryolite,
and most fusion enthalpy is absorbed at the eutectic temperature. Whereas for the 5 wt% alumina mixture, only about half of the fusion enthalpy is absorbed at the eutectic temperature, and other half fusion enthalpy is absorbed between the eutectic temperature and 985 °C.

Figure 6-33 shows peak shapes of some crust samples. The peak becomes broader when the CR decreases. For instance, crust samples C3 and G1 have similar original cryolite content, but the latter has much higher chiolite content. Because chiolite incongruently melts to solid cryolite and liquid, crust sample G1 contains more solid cryolite and also liquid above 725 °C. According to the phase equilibria, solid cryolite continuously melts in the liquid over a very wide temperature range (from 725 °C to the melting temperature). Other fluoride additives may also dissolve in the liquid. For the crust sample with lower chiolite content, less liquid comes from chiolite leading to less solid cryolite melting in the liquid. This may explain why the peak of sample G1 is distinctly broader than that of sample C3. Conversely the compositions of crust sample B1 is dominated by the mixture of cryolite, alumina and additives, hence melts in a relative narrow temperature range.

![Figure 6-33. Peak shape of the crust samples. Figure adapted from Figure 13, page 595 in TMS Light Metals 2014 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)](image)

### 6.7.2 Crust thermal stability

Liu [14] measured the crust temperature in two industrial cells, as shown in Figure 6-34. The measurement started from the time when the anode cover was added into the cells. The heating rate of the anode cover was below 1.6 °C/min. The measured chiolite content
in the bottom 2-3 cm of the crust in Cell A and B were 20.4 wt% and 38.7 wt%, respectively. The crust in Cell B seemed to have lower temperature but melted and collapsed faster than that in Cell A (see Figure 6-34). According to the present study, higher chiolite content results in more liquid above 725 °C, which then melts more cryolite. This probably explains the faster melting of crust in Cell B.

Figure 6-34. Crust isotherm measured by Liu [14]. Figure adapted from Figure 4, page 491, Liu [14] in TMS Light Metals 1992 (Copyright © ____ by The Minerals, Metals & Materials Society. Reprinted with permission.)

In addition, Liu [14] observed that the occurrence of anode effect (AE) in the cell broke the bottom crust. The loss of large amounts of the crust bottom occurred after the AE in Cell A. It is known that a large amount of energy is released quickly during the AE, and a considerable portion of it is likely to be transferred to the crust via the overheated liquid bath below. The energy in the crust which cannot be conducted to the surroundings in time turns into sensible and latent heat. When the absorbed latent heat exceeds the fusion enthalpy of the crust, at least the bottom part of it will melt and collapse. Termination of the AE involves movement of the anodes up and down, displacing the crust, and this is equally likely to have led to mechanical loss of crust material.
The analysis in this study shows that the melting of the crust with high CR is energy intensive in a narrow temperature range. Whereas, the chiolite enriched crust melts continuously over a broad temperature range. The crust with lower chiolite content and higher CR has higher mechanical strength (less liquid) and better thermal stability. High alumina content in crust would also contribute to good thermal stability. However, unfortunately high alumina content (>20 wt% in the anode cover) also reduces the thermal conductivity of the original anode cover [37] and causes rapid overheating of the material followed by accelerated melting as found by Liu [14]. Reducing anode movements (e.g., reduced AE frequency) is another way to avoid the collapse of the crust. However, metal tapping can still trigger crust collapse for thermally unstable anode cover.

6.8 Summary

In this chapter, experimental analyses of XRD, LECO and DTA methods are carried out to measure the chemical composition, as well as the liquidus and melting temperatures of the crust samples taken from the industrial cells.

The measurement results of chemical composition and liquidus temperature are consistent with each other, and show that cryolite content and CR decreases from the bottom (60~70 wt% and approximately 2.6, respectively) to the top part (20~30 wt% and approximately 2.0, respectively) of the crust.

The different crystal textures of the crystalline crusts observed support the hypothesized formation of these crystalline crusts. The macrocrystalline crust forms from the bulk bath under very slow cooling rate. This indicates that there was physical contact between the bulk bath and the sintered crust, and thus the liquid bath penetrated into the sintered crust.

Microphananitic crust is possibly the result of rapid temperature drop of the bulk bath, whereas microcrystalline crust may form from the fluctuating bulk bath, as well as the percolating liquid bath melting from the crust.

The melting behaviour of the crust sample was studied. The heating curves of the crust sample detected by the DTA test have different melting peak shapes dependent on the
chemical composition. The crust samples with high chiolite content have broader peak shape with smaller total energy requirements than the samples with high cryolite content and CR. This indicates that chiolite enriched crust not only has a lower melting temperature and wider melting temperature range, but also melts less energy intensively.

Verified by using the measured data in industrial cells by Liu [14], the melting and thinning of the crust are caused by the high chiolite content and the consequent high liquid bath content in the crust.
7 Thermochemical model validation

This chapter aims to validate the thermochemical model developed in Chapter 4, and thus test the central hypothesis of the thesis, namely the thermochemical behaviour of the sintered crust formation. A computational prediction of crust evolution by the present model is compared with the physical and experimental observations of Chapter 6, as well as experimental data from literatures.

The major variables of the present model include temperature, chemical composition, and volume fraction of liquid bath and solid phase (directly relating to bulk density). The comparisons of these properties between the simulation results from the present model and the experimental data are carried out in this section to test the thermochemical evolution hypothesis.

In this study, the available experimental data include:

1) The data from the synthetic crust formation experiments carried out by Eggen, Rye et al. [13, 17, 18], as reviewed in Chapter 3.3, including (a) a number of cover/crust temperature evolution curves, (b) the liquid bath front position curve, and (c) the bulk density distributions in the crust; (The comparisons between the simulation results from the present model and experimental data from the synthetic crust formation experiments are discussed in section 7.1.)

2) The measured chemical composition distributions in the industrial crusts as reported in Chapter 6. (The comparisons between the simulation results from the present model and measured chemical compositions from the industrial crusts are discussed in section 7.2.)

7.1 Simulation of synthetic crust formation

In this section, experimental data are from the synthetic crust formation experiment carried out by Eggen, Rye et al. [13, 17, 18], as reviewed in Chapter 3.2. The physical and chemical parameters refer to Appendix A.14.
7.1.1 Comparison of temperature evolution

As discussed in Chapter 4, three processes are taken into account in the present model, i.e. heat conduction, liquid bath penetration with liquid solid phase transformation, and transition alpha alumina phase transformation. All three processes have impact on the temperature evolution of the cover/crust. To identify the impact of each process, three simple models are now applied. Compared with the present model, these simple models ignore the liquid bath penetration, the transition alpha alumina phase transformation or crystal liquid phase transformation. These models are described by using the heat conservation equation. The contrast between them is discussed below.

(1) TC model: Only transient heat conduction is taken into account

The liquid bath penetration and phase transformation are not included in TC model. The heat conservation equation for TC model is given in equation (7.1),

\[ C \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) \]  

(7.1)

where \( T \) is the temperature, \( C \) is the specific heat capacity, \( \rho \) is the density, and \( k \) is the thermal conductivity.

(2) TCP model: Transient heat conduction and transition alpha alumina phase transformation are taken into account

The liquid bath penetration is not included in TCP model, and thus the liquid solid phase transformation caused by the liquid bath penetration is also not included. The heat conservation equation for TCP model is given in equation (7.2),

\[ C \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + q \]  

(7.2)

where \( q \) is the heat generation rate due to the transition alpha alumina phase transformation. For detailed calculation of \( q \), refer to equation (4.36) in Chapter 4.2.4.

(3) Simple TCAP model: Transient heat conduction, advection and transition alpha alumina phase transformation are taken into account
As for the simple TCAP model, it is assumed that in the crust there is liquid bath penetration without crystal liquid phase transformation above the minimum freezing temperature. The heat conservation equation in the crust for the simple TCAP model is given below,

\[
CP \frac{\partial T}{\partial t} + C\rho u \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + q
\]  
(7.3)

where \( u \) is the superficial velocity of the fluid in the crust.

In this case, the liquid solid phase transformation during the liquid bath penetrations is not taken into account.

The equation (7.3) is usually referred to as an advection-diffusion problem. The term “advection” here refers to heat transfer upwards with the fluid as it travels through the porous media.

4. Enhanced TCAP model which is used in the present work: Transient heat conduction, advection and all phase transformation are taken into account

The heat conservation equation in the crust for the enhanced TCAP model is given below (all equations listed in section 4.5 are included in enhanced TCAP model but not listed here, the solution of these equations refers to section 5.4),

\[
C_E \rho \frac{\partial T}{\partial t} + C_E \rho u \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} (k \frac{\partial T}{\partial x}) + q
\]  
(7.4)

where \( C_E \) is the effective specific heat capacity combining the inherent sensible specific heat capacity and effective latent heat released from the liquid solid phase transformation during the liquid bath penetrations, \( u \) is the superficial velocity of the liquid bath penetration. For detailed explanation of the equation, refer to Chapter 4.

The value of \( C_E \) refers to Appendix A.12, and is estimated to be in range of 2000 to 10000 J/kgK. Thus, the average value of \( C_E \rho u \) is in range of 20 and 100 W/m²K.

The governing equations, boundary conditions for above models are summarized in
Figure 7-1. Summary of the three simple models and the present model

These models are applied to simulate the temperature evolution during the synthetic crust formation experiment reviewed in Chapter 3.2. The physical and chemical parameters
Chapter 7. Thermochemical model validation

refer to Appendix A.14.

The thermal conductivity in these three models is predicted by Zehner-Schlunder-Laubitz model (see Chapter 4) and verified in Appendix A.11. The simulation results are compared with the experimental data, as discussed below.

(1) Comparison between \( TC \) model simulation results and the experimental data

Figure 7-2 shows the experimental data and \( TC \) model simulation results for cover/crust temperature evolution curves at different measurement positions. For positions greater than 48 mm height (distance from the crust bottom surface), there is about 200 °C temperature gap between the simulation results and the experimental data. The \( TC \) model does not predict well the temperature evolution during the crust formation.

![Figure 7-2. Comparison of temperature evolution between \( TC \) model simulation results and experimental data from Eggen, Rye et al. [17] (see Chapter 3.2)](image)

For the synthetic crust formation experiment, the moisture content in the cover was not given. In addition, the heat transfer by moisture vapour is very complicated and not within the scope of this study, and thus is not taken into account in the present model. In view of the contribution of the moisture vapour, it is assumed that the anode cover has initial temperature of 100 °C though the actual initial temperature is room temperature (i.e. about 25 °C).
(2) Comparison between TCP model simulation results and the experimental data

Figure 7-3 shows TCP model simulation results and the experimental data. Compared with TC model, there is only a slight improvement in the agreement between the simulation results and the experimental data.

![Figure 7-3. Comparison of temperature evolution between the TCP model simulation results and the experimental data from Eggen, Rye et al. [17] (see Chapter 3.2)](image)

(3) Comparison between the simple TCAP model simulation results and the experimental data

Figure 7-4 shows the simple TCAP model simulation results and the experimental data. Though the agreement between the simulation results and the experimental data is improved to a certain degree, there is still considerable gap between them.
Figure 7-4. Comparison of temperature evolution between the simple TCAP model simulation results and the experimental data from Eggen, Rye et al. [17] (see Chapter 3.2).

(4) Comparison between the enhanced TCAP model simulation results and the experimental data

Figure 7-5 shows comparison between the enhanced TCAP model simulation results and the experimental data. Of all four models and experimental data, the temperature distributions in the cover/crust at time 240 minutes are shown in Figure 7-6. Comparing with other three models, the enhanced TCAP model has considerable improvement in the agreement with the experimental data.
Figure 7-5. Comparison of temperature evolution between the enhanced TCAP model simulation results and the experimental data from Eggen, Rye et al. [17] (see Chapter 3.2).

Figure 7-6. Comparison of temperature distribution at time 240 minutes between simulation results and experimental data from Eggen, Rye et al. [17] (see Chapter 3.2).

However, there are still slight deviations in temperature evolution curves between the enhanced TCAP model simulation results and the experimental data as shown in Figure...
7-5, which may be due to:

1. **Experimental limitations:**
   The crucible was adjusted slightly and manually at the time of one hour during the experiment leading to temperature increase in the cover/crust. The affected area is labelled with ‘a’ and ‘c’ in Figure 7-5.

2. **Simplifications and limitations of the present model:**
   As noted earlier, the present model has limitation in simulating the heat transfer by moisture vapour. It is assumed that the anode cover has initial temperature of 100 °C. The mainly affected area is labelled with ‘b’ in Figure 7-5. Other simplifications, limitations and model solution error might also affect the accuracy of the simulation results in all areas (i.e. ‘a’, ‘b’ and ‘c’ in Figure 7-5).

Among these four models, the enhanced TCAP model (i.e. the model developed in Chapter 4) gives the best prediction for the experimental temperature evolution curves. The reason is that the heating of the cover/crust is not merely a result of heat conduction, but also the liquid bath penetration and phase transformation.

Because the liquid bath is migrating from the bulk bath into the crust, both the sensible heat of the liquid bath and the latent heat (released during the crystallization of cryolite and alumina from the liquid bath) accelerate the heating rate of the cover/crust.

The distribution of superficial fluid velocity $u$ in the crust is shown in Figure 7-7. Even though the flow velocity of the liquid bath is as low as the order of $10^{-6}$ m/s, the value of advection component $C_{epu}$ can reach 20 – 100 W/m$^2$K (for more details, see Appendix A.12).
Chapter 7. Thermochemical model validation

Figure 7-7. The distribution of superficial fluid velocity $u$ in the crust

To confirm the impact of advection component $C_\rho \rho u$ of 20 W/m³K on heat transfer, Figure 7-8 shows case studies of simple TC model and TCA model in semi-infinite region (for more details, see Appendix A.10). Apart from the advection component, same values are assigned to the parameters $C$, $\rho$ and $k$ of the TCA model and TC model. The analytic solutions of TC model and TCA model are shown in Figure 7-9.

Figure 7-8. Case studies of TC model and TCA model in semi-infinite region

TC

Transient heat conduction

$$C\rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}(k \frac{\partial T}{\partial x})$$

$C = 2000, \rho = 2000, k = 0.5, T_0 = 100, T_i = 950$

$\alpha = \frac{k}{C\rho}$

Analytical solution:

$$T = (T_0 - T_i) \text{erf}\left(\frac{x}{2\sqrt{\alpha \cdot t}}\right) + T_i$$

TCA

Transient heat conduction & advection

$$C\rho \frac{\partial T}{\partial t} + C\rho u \frac{\partial T}{\partial x} = \frac{\partial}{\partial x}(k \frac{\partial T}{\partial x})$$

$C = 2000, \rho = 2000, k = 0.5, u = 5 \times 10^6, C\rho u = 20$

$T_0 = 100, T_i = 950, \alpha = \frac{k}{C\rho}$

Analytical solution:

$$T(x,t) = (T_0 - T_i) f(x,t) + T_0$$

$$f(x,t) = \frac{1}{2} \text{erfc}\left(\frac{x}{2\sqrt{\alpha t}}\right) + \frac{1}{2} \exp\left(\frac{u \cdot x}{\alpha}\right) \text{erfc}\left(\frac{x + u \cdot t}{2\sqrt{\alpha \cdot t}}\right)$$
In these case studies, despite that $u$ is as low as $5 \times 10^{-6}$ m/s (i.e. $C_\rho u$ is 20 W/m²K), it still has great impact on the temperature evolution (i.e. heat transfer), as shown in Figure 7-9. Therefore, it is reasonable to conclude that the advection component $C_\rho u$ of 20 ~ 100 W/m²K contributes greatly to the improvement of the agreement between the present model simulation results and the experimental data, as shown in Figure 7-5 and Figure 7-6.

The validation provided here clearly shows that the enhanced TCAP model is capable of reproducing the experimental temperature behaviour, while the TC, TCP and simple TCAP models do not.

### 7.1.2 Comparison of liquid bath front position

In the experiments done by Eggen and Rye et al. [13, 17, 18] reviewed in Chapter 3.2, there was liquid bath penetrating in the crust, and the liquid bath front is moving boundary which were detected using an electrical detecting device (see the symbols $\bullet$ in Figure 3-1 in Chapter 3.2).

In the present model, the liquid bath front position is predicted by applying Stefan Condition and assuming that the minimum freezing temperature of the liquid bath (i.e. $T_f$)
685 °C) is the temperature at the liquid bath front (for more details, see Chapter 4.2.5).

Figure 7-10 shows the simulation results from the present model and the experimental data from Rye [18], which indicates that the present model also gives reasonable prediction of the liquid bath front. In fact this is an essential component in the overall energy and liquid/solid phase balance within the crust, both from a thermal and a mechanical property prediction viewpoint.

Figure 7-10. Comparison of liquid bath front position (distance from the bottom surface of the crust) between experimental data from Rye [18] and simulation results from the present model

7.1.3 Comparison of the bulk density

The bulk density of the crust is dependent on the volume fraction of the liquid bath and the solid phase. As reviewed in Chapter 3.3.3, Rye [18] measured the vertical distributions of the bulk density in the crust of two experiment cases in which the superheat of the bulk bath are 55 °C and 10 °C respectively. Figure 7-11 compares the bulk density predicted by the present model with the experimental data in the case of superheat 55 °C.
Figure 7-11. The bulk density distribution in the crust (vertically from the bottom to the top, the bath superheat is 55 °C, the experimental data is from Rye [18])

The bulk density increase with height in the lower part might be related to the superheat of the liquid bath. As the liquid bath penetrates upward in the crust, no cryolite solid phase crystallises until the liquid bath cools down and reaches its liquidus temperature. The rate of crystallization decreases with the decrease of the temperature below the liquidus temperature (see Appendix A.12).

Thus, more solid phase precipitates near the liquidus isotherm. At the same time, the liquidus isotherm in the crust moves upwards with time as the whole crust is heating up. Consequently, the vertical distribution of the bulk density in the crust at any time will have a maximum in the electrolyte penetrated and partially solidified interior, with lower densities above and below this region due to liquid phase at the bottom and high solid porosity at the top. The particular curve in Figure 7-11 is influenced by the initially very high superheat (55 °C) of the molten bulk bath in this case and is well predicted by the model.

For a case with lower superheat of 10 °C which is much more common in industrial cells, the vertical distribution of the bulk density is closer to a declining trend, as shown in
Figure 7-12 because the liquidus temperature is reached faster and lower in the crust. In this case, the simulation results have a good agreement with the experimental data as well.

The comparisons of the bulk density indicate that the present model predicts the volume fraction of the liquid bath and solid phase well since these relate directly to the bulk density of the crust.

7.2 Simulation of industrial sintered crust formation

In addition to temperature and bulk density, chemical composition is another important property predicted by the present model. As reported in Chapter 6, chemical compositions of several crusts taken from industrial cells were analyzed by XRD. Among these crusts (only sintered crust is taken into account in this section), Crust C is alumina based crust, and Crust A and D are crushed bath crusts (for more details, see Chapter 6). Each of Crusts A, C, and D has 3 to 6 cm of well-formed sintered crust whereas others do not.
In this section, the measured chemical compositions of Crusts A, C, and D are selected to compare with the simulation results from the present model. For more detailed simplifications and initial conditions of the simulations, see Appendix A.13. The physical and chemical parameters refer to Appendix A.14.

The thermochemical model (namely enhanced TCAP model, see the equations listed in section 4.5) is applied here. The solution of the thermochemical model refers to section 5.4.

(1) Comparison of chemical composition in Crust C (the raw anode cover material is alumina)

(1.1) Simulation condition

Crust C was taken from the place near the feeding hole where the alumina accumulated from the feeder. The composition of the raw anode cover material was 100% alumina. According to the average measured data from the industrial reduction cells where crust pieces were taken from, the average chemical composition of the bulk bath is: CR = 2.3, CaF$_2$ wt% = 5, Al$_2$O$_3$ wt% = 3, LiF wt% = 3, MgF$_2$ wt% = 1, KF wt% = 1. The average bath temperature is 950 °C.

(1.2) Simulation result

Figure 7-13, Figure 7-14, and Figure 7-15 show the comparisons between the predicted and measured chemical composition distributions in Crust C, which compares the trends in actual and predicted chemical composition distributions in Crust C.
Chapter 7. Thermochemical model validation

Figure 7-13. Comparison of CR distribution in Crust C

Figure 7-14. Comparison of cryolite content distribution in Crust C
(2) Comparison of chemical composition in Crust A and D (raw anode cover material is crushed bath/alumina mixture)

(2.1) Simulation condition

The raw anode cover material for industrial Crusts A and D is a mixture of crushed bath and alumina. In practice, the initial raw material for crushed bath cover is inevitably heterogeneous in chemical composition in industrial cells.

To simplify the simulation, average values of chemical composition of the raw crushed bath cover material are applied to the simulation condition. The raw anode cover material is made of 60 wt% crushed bath and 40 wt% alumina, and the crushed bath composition is 30 wt% alumina, 40 wt% cryolite, 10 wt% chiolite, and 20% fluoride additives compounds consisting of CaF₂, MgF₂, KF and LiF. The density is 1.5 g/cm³. The porosity is 0.5 [20].

The chemical composition and temperature of the bulk bath are the same as that for the alumina based crust.

(2.2) Simulation result
The comparisons between measured chemical composition and simulation results are shown in Figure 7-16 and Figure 7-17.

(1) Comparison of cryolite content in Crust A
Chapter 7. Thermochemical model validation

(2) Comparison of CR in Crust A

(3) Comparison of alumina content in Crust A

Figure 7-16. Comparison of chemical composition in Crust A
(1) Comparison of cryolite content in Crust D

(2) Comparison of CR in Crust D
(3) Comparison of alumina content in Crust D

Figure 7-17. Comparison of cryolite content distribution in Crust D

The comparisons between the predicted and measured results for Crust A, C and D are summarized in Table 7-1. Generally, the simulated composition trends have acceptable agreement with the experimental data considering the complicated practical situation in the industrial crust. At the lower part of the Crust A and D, the simulation results of cryolite content and CR are slightly higher than the experimental data. In the case of alumina content in Crust A, at the bottom part and top part of the crust, the experimental data deviates from the simulation results to some extent.
Table 7-1. Summary of the comparisons between measured and predicted results

<table>
<thead>
<tr>
<th>Height (cm)</th>
<th>Cryolite content wt%</th>
<th>Alumina content wt%</th>
<th>CR</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Predicted</td>
<td>Error</td>
</tr>
<tr>
<td>Crust A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>57.4</td>
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<td>1</td>
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</tr>
<tr>
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<td>33.6</td>
<td>-1.2</td>
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</tr>
<tr>
<td>3</td>
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</tr>
<tr>
<td>Crust C</td>
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<td></td>
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</tr>
<tr>
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<td>38.2</td>
<td>-1.9</td>
</tr>
<tr>
<td>2</td>
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<tr>
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<td>9.4</td>
<td>13.8</td>
<td>4.4</td>
</tr>
<tr>
<td>Crust D</td>
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<td></td>
<td></td>
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<tr>
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<td>54.7</td>
<td>62.5</td>
<td>7.8</td>
</tr>
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<tr>
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<td>25.5</td>
<td>23.4</td>
<td>-2.2</td>
</tr>
</tbody>
</table>

These deviations might be caused by the following factors:

1. The chemical composition for the raw crushed bath cover is an assumed average value in the present model. As noted above, the actual initial chemical composition is inevitably heterogeneous.

2. At the start of the simulation, the bottom part of the crushed bath crust may shrink after sintering. The fact that the present model predicted a higher value of cryolite and CR at the bottom part of the Crust A and D might be because of a higher assumed, initial porosity which has led to higher volume fraction filled by the liquid bath.

7.3 Summary

In this chapter, some particular ideal benchmark cases for which the analytical solutions are known have been used to verify the computational code. These particular cases use the same system of partial differential equations (PDEs) as the present model developed in Chapter 4. The simulation results for these cases are calculated by the same present TCAP computational code, with good agreement observed between the numerical results and the analytical solutions.

To test the hypothesis of the thermochemical mechanism proposed in this thesis, several sets of experimental data is compared with the simulation results from the present model. The comparisons between the simulation results and the experimental data show that:
1) The present model which takes into account two components, the liquid bath penetration and phase transformation, can predict the temperature evolution curves of the cover/crust with much better confidence than simple models which do not contain both of these mechanisms.

2) The present model simulates the moving position of the liquid bath front with reasonable accuracy in the only case known where the movement of this interface has actually been measured inside the crust.

3) The bulk density distribution in the crust is also predicted well by the present model, showing that the liquid phase distribution in the crust is determined correctly. This has previously been shown to be crucial to the hot strength of aluminium smelting crusts [14].

4) There is acceptable agreement on the chemical composition distribution in the industrial crust between the simulation results and the experimental data, given the inhomogeneity of the industrial cover materials in terms of composition and density.
Chapter 8. Conclusions and suggestions for future work

This study focuses on the thermochemical behaviour and stability of the crust. It aims to answer two questions: (1) What is the mechanism of the thermochemical behaviour in the crust? (2) What impacts do the chemical compositions have on the thermal stability of the crust?

8.1 Theoretical model development

A mechanism is proposed for the thermochemical behaviour during the sintered crust formations and aging process, as summarised below.

Crushed bath and alumina are the raw materials used for the anode cover of industrial aluminium reduction cells. Added to a reduction cell, the loose anode cover is heated by the heat flux from the hot bulk bath underneath and forms a sintered crust at its bottom part. When the anode cover makes contact with the bulk bath, the latter is driven upwards through the porous cover/crust by capillary pressure and continues to move, limited by the isotherm of the minimum freezing temperature, namely the eutectic point of 685 °C.

The liquid bath is cooled down during its penetration upwards. As defined by the phase diagram, the solid phases of cryolite and alumina crystallize out of the liquid bath above the peritectic point of 725 °C. The remaining liquid bath penetrates upward through the crust with decreasing CR. All components of the liquid bath can be considered to freeze between 685 °C and 725 °C. Under conditions of high liquid bath content, the crust bottom melts/falls under gravity resulting in the weakening and thinning of the crust.

A theoretical thermochemical model has been developed to simulate the above thermochemical evolution process, including the sintered crust formation and ageing stages. The model was constructed by assuming that the porous anode cover/crust consists of a group of parallel cylindrical pores. The relationships between phase transformation rate and chemical composition, as well as phase transformation rate and temperature were theoretically deduced from the conservation equations of mass, momentum and energy. The temperature and chemical composition variables were
coupled together using an effective specific heat capacity in the conservation equation of energy to take account of the latent heat transfers due to freezing and melting of the bath phases. The liquid bath front is represented as a moving boundary in the anode cover/crust. The Stefan condition was applied to predict the liquid bath front movement.

8.2 Numerical solution of the model

Complexities in the model are due to the moving boundary problem and non-linear partial differential equations, along with the sensitivity of properties such as the thermal conductivity of the cover and crust to the phase composition and temperature of the material.

The moving boundary condition partitions the regions of the crust and the loose cover into different zones over time, as reflected in the physical appearance and phases of the industrial crust samples in Chapter 6. Using the coordinate transformation technique [83, 87], the regions are transferred to three fixed zones which simplify the solution of the model.

The partial differential equations were converted to discrete equations using finite element method (FEM) and Galerkin approach [88-90], and then solved by MATLAB® software. An iterative method was used to solve the thermochemical model in each time step.

8.3 Experimental

8.3.1 Industrial crust samples

Seven clean crust pieces taken from industrial reduction cells were investigated in this study. These crust pieces represent the most common crust types found in industrial cells, i.e. crushed bath sintered crust (upper part of Crust A and D), alumina base sintered crust (upper part of Crust C), chiolite enriched crust (Crust G), crystalline crust (lower part below sintered crust), and macro porous crust (the top of Crust B and bottom of Crust G), respectively.

8.3.2 Optical microscope observation of crystalline crust

Crystalline crust was classed into three types (i.e. macrocrystalline, microcrystalline, and
According to the crystal texture observed with an optical microscope. The cooling rate during the crystalline crust formation accounts for the different crystal morphologies.

8.3.3 Experimental analysis

Experimental analyses of XRD, LECO and DTA were carried out on the crust samples which were vertically sampled from the industrial crust pieces.

The XRD analysis reveals the chemical compositions of these crust samples. Three major phases detected are cryolite, alumina and chiolite. Other minor phases detected are fluoride additives including KF, LiF, MgF₂ and CaF₂.

A non-commercial DTA system was constructed, and calibrated using pure cryolite and NaF. The phase transformations from 400 to 1020 °C were analysed by the DTA system. The crystal ↔ liquid phase transformation of cryolite was detected in most crust samples over temperature range from 900 to 990 °C. In chiolite enriched crust samples, the chiolite incongruent melting at 725 °C and eutectic reaction of chiolite at 685 °C were detected from the heating curves and cooling curves respectively.

There are decreasing trends for cryolite content, CR and liquidus temperature distributions from the bottom to the top of the industrial crusts, which are consistent with earlier studies of Liu et al. [14] and Groutso et al.[32]. At the lower part of the crust, the cryolite content reaches as high as 60~70 wt%, and the CR is approximately 2.6, which contributes to the high liquidus and melting temperatures of 980~990 °C. At the top part of the crust, the cryolite content and CR decrease considerably to approximately 30 wt% and 2.0, respectively. As a result, the liquidus and melting temperatures are depressed to 900 °C. In addition to CR, fluoride additives depress the liquidus and melting temperatures of the crust samples as well.

8.3.4 Crystalline crust formation hypothesis

A hypothesis for the crystalline crust formation was proposed. The macrocrystalline crust material crystallizes from the bulk bath under very slow cooling rates. Under this condition, the liquid bath is able to penetrate into the sintered crust from the bulk bath.
Microphanitic crust may form due to rapid temperature drops in the bulk bath. In contrast, microcrystalline crust is likely to be the result of the splashed liquid bath from the fluctuating level of bulk bath, as well as the percolating liquid bath melting from the crust above.

### 8.3.5 Melting behaviour

The melting behaviour of the crust is studied based on the shape analysis of the DTA melting peak. The analysis of the well-studied cryolite-alumina system and pure cryolite shows that the melting peak shape relates to the phase diagram. Crust with a high CR has a sharp peak shape because the latent energy is released over a narrow temperature range. In contrast, crust with a low CR melts over a broad depressed temperature range. Especially for the chiolite enriched crust, a substantial amount of liquid bath is generated from 725 °C due to the incongruent melting of the high chiolite fraction, and this liquid melts the remaining solid cryolite over a very wide temperature range from 725 to 950 °C, as the broad DTA peaks measured for these crusts demonstrate.

High chiolite content leads to the high liquid content of bath with low CR in the crust above 725 °C, and the continuous melting of solid cryolite with lower energy absorption. Consequently, high CR and low chiolite content are helpful to achieve a high thermal stability of the crust due to the lower liquid bath fraction, which is in agreement with the in-situ crust temperature measurement in industrial cell carried out by Liu [14].

### 8.4 Model validation

To test the hypothesis of the thermochemical mechanism, the simulation results from the thermochemical model were compared with the experimental data from the synthetic crust formation experiment carried out by Eggen and Rye et al. [13, 17, 18], as well as from industrial crust samples measured in this study.

In addition to the thermochemical model, three more simple models were considered. These simple models ignore the advection effect of the liquid bath penetration, or the transition alpha alumina phase transformation. Over the experimental duration, the temperatures in the upper part of the crust predicted by both simple models are much lower than the experimental data measured. Whereas, in the case of the thermochemical
model which incorporates these factors and especially the energetic effect of the liquid bath penetration and freezing inside the crust, the simulation results of temperature evolution have good agreement with the experimental data.

The position of the liquid bath front, as well as the bulk density distribution in the crust predicted by the thermochemical model are both in good agreement with the experimental data from Rye [17].

For the chemical composition distribution in the industrial crust, there are acceptable agreements between the simulation results and the experimental data measured in this study, given the difficulty of taking representative samples of the rather inhomogeneous crust material in the industrial cells.

8.5 Limitations of the research

The thermochemical model is based on the assumption of local phase equilibrium, and this should hold under slow phase transformation rate conditions no matter whether freezing or melting is occurring. However due to experimental limitations, only a limited amount of experimental data during crust formation is available to validate the model in Chapter 7.

In addition, for the sintered crust formation, it is assumed that the solid phase is dominant, and the liquid bath is trapped inside the crust without dripping down by gravity. In the case of high liquid bath fraction in the crust, the thermochemical model is not capable of simulating the thinning of the crust which is dependent on the mechanical separation of liquid or liquid/solid mixture from the crust.

However, the qualitative laboratory study in Chapter 6 shows that local phase equilibrium assumption also applies during crust melting, indicating that the thermochemical model can predict the liquid bath fraction during crust melting, although another mechanical model is still required alongside it to better predict the liquid separation and thinning process of the crust.

8.6 Recommendations for future work

More experimental and measurement work on industrial crusts are necessary to
thoroughly validate the model in future research.

To quantitatively predict the thinning rate of the crust, it is relevant to investigate the mechanism of how the ‘soft’ lower part (i.e. where the liquid bath fraction is high) is separated from the ‘hard’ upper part (i.e. where the liquid bath fraction is low) under mechanical disturbances and gravity, as well as the mechanism of the liquid bath percolation through the crust and then dripping down into the bulk bath underneath under gravity, since the appearance of stalactites of frozen bath under many industrial crusts does indicate this is part of the main melting mechanism.
Appendices

A.1. Easy-filling porosity

(1) Alumina based cover

In the case of alumina base cover, it is difficult to calculate the easy-filling porosity theoretically. Experimental measurement is an alternative way to estimate the value of it. In Townsend’s [36] measurement, about 35% of the liquid bath volume was soaked up immediately by industrial alumina. This value is in agreement with the measured primary sandy alumina macro porosity (>6.8 µm) by Coque [19], which is mostly about 30%~40%.

(2) Crushed bath based cover

As noted earlier, the crushed bath cover is usually crushed from recycled crust material. If the recycled crust has high bulk density, it is very likely that most internal open pores have already been filled. As measured by Shen [10], though crushed bath based cover may have high alumina content, the porosity is only 0.35~0.48, which is much less than that of primary alumina. It is reasonable to assume that the overall porosity is the sum of the open porosity (i.e. inter-particle porosity) and the closed porosity.

Based on these facts, the open porosity of the crushed bath based cover is taken as the easy-filling porosity of it. The closed porosity of single crushed bath particle is estimated to be the total porosity ($\varepsilon_{\text{crust}}$) of the recycled crust before crushing.

For the crushed bath based cover with overall porosity $\varepsilon_{\text{cover}}$ and open porosity $\varepsilon_{\text{open}}$, the volume fraction of dense solid phase is $1 - \varepsilon_{\text{cover}}$, the volume fraction of particles is $1 - \varepsilon_{\text{open}}$. The following equation is therefore satisfied:

$$1 - \varepsilon_{\text{cover}} = (1 - \varepsilon_{\text{open}})(1 - \varepsilon_{\text{crust}})$$  \hspace{5cm} (9.1)
According to the assumption, the easy-filling porosity $\varepsilon_{L0}$ is equal to the open porosity $\varepsilon_{open}$. Thus, $\varepsilon_{L0}$ can be estimated by:

$$\varepsilon_{L0} = 1 - \frac{1 - \varepsilon_{cover}}{1 - \varepsilon_{crust}}$$  \hspace{1cm} (9.2)

(3) Crushed bath/alumina mixture cover

An anode cover is mixed by $W_c$ wt% crushed bath and $W_a$ wt% primary alumina. The crushed bath has overall porosity $\varepsilon_{c\_cover}$, open porosity $\varepsilon_{c\_open}$ and bulk density $\rho_c$. The alumina has inter-particle open porosity $\varepsilon_{a\_open}$, internal open porosity $\varepsilon_{a\_iopen}$, closed porosity $\varepsilon_{a\_close}$ and bulk density $\rho_a$. The crushed bath/alumina mixture cover has overall porosity $\varepsilon_{cover}$ and bulk density $\rho_w$.

The internal open porosity of the mixture cover $\varepsilon_{m\_iopen}$ is

$$\varepsilon_{m\_iopen} = \frac{\rho_w}{\rho_a} \times W_c \% \times \varepsilon_{a\_iopen}$$  \hspace{1cm} (9.3)

The closed porosity of the mixture cover $\varepsilon_{m\_close}$ is

$$\varepsilon_{m\_close} = \frac{\rho_w}{\rho_a} \times W_c \% \times \varepsilon_{a\_close} + \frac{\rho_w}{\rho_c} \times W_a \% \times (\varepsilon_{c\_cover} - \varepsilon_{c\_open})$$  \hspace{1cm} (9.4)

Hence, the easy-filling porosity $\varepsilon_{L0}$ of the mixture cover is,

$$\varepsilon_{L0} = \varepsilon_{cover} - \varepsilon_{m\_iopen} - \varepsilon_{m\_close}$$  \hspace{1cm} (9.5)
A.2. **Effective capillary radius**

The porous anode cover can be described as a group of parallel cylindrical pores (the amount is $n$) with equally radius $R$. The axis direction of these cylindrical pores is parallel with the liquid bath flow direction ($x$ axis), which is from the bottom surface to the top surface of the anode cover. The radius $R$ satisfying that the pore volume/surface area ratio is equal to that of the porous material is called the effective capillary or hydraulic radius [118].

![Figure A-1. Schematic diagram showing fluid in cylindrical pores](image)

The effective capillary radius satisfies

\[ n \cdot 2\pi R \cdot l = l^3 S \]  \hspace{1cm} (9.6)

\[ n \cdot \pi R^2 \cdot l = l^3 \varepsilon_L \]  \hspace{1cm} (9.7)

\[ R = \frac{2\varepsilon_L}{S} \]  \hspace{1cm} (9.8)

\[ \frac{4\pi n}{l^2} = \frac{S^2}{\varepsilon_L} \]  \hspace{1cm} (9.9)

where $\varepsilon_L$ is the volume fraction of the liquid bath, $S$ is the surface area of the interface between the liquid bath and the solid phase.
A.3. Surface tension and capillary pressure

Literatures [119-122] give a measured surface tension for the molten cryolite system. Surface tension of the liquid bath is given in following equation [122],

\[
\gamma_L / (\text{mN m}^{-1}) = 264.3 - 0.1318 \times t / ^\circ \text{C} - 4.6 \log (c_{al2o3} / \text{wt}) - (3.29 - 0.00329t / ^\circ \text{C}) \times c_{al2o3} / \text{wt}
\] (9.10)

The surface tension of the liquid bath is about 0.1 Nm\(^{-1}\). Surface tension of solid alumina is about 1 Nm\(^{-1}\).

Interfacial tension between liquid and solid phase can be estimated by an expression proposed by Turnbull [123]:

\[
\gamma_{Sl} \approx \frac{kT \Delta H_M}{V S N_A^{1/3}}
\] (9.11)

Where \(V_S\) is the molar volume of primary solid phase, \(\Delta H_M\) is the molar latent heat of fusion (or enthalpy of solid dissolution in the liquid), \(N_A\) is Avogadro’s number and the coefficient \(k_T\) is 0.45 for metals and 0.34 for non-metallic systems.

The relationship between surface tension and contact angle \(\theta\) is known as the Laplace-Young equation [124].

\[
\cos \theta = \frac{\gamma_S - \gamma_{Sl}}{\gamma_L}
\] (9.12)

For the surface tension between the liquid bath and the alumina crystal, calculated \(\gamma_{Sl} \approx 0.89\) Nm\(^{-1}\), \(\cos \theta \approx 0.84\). For surface tension between the liquid bath and cryolite crystal, calculated \(\gamma_{Sl} \approx 0.34\) Nm\(^{-1}\). Assuming that the liquid bath can complete wet the cryolite crystal, thus \(\cos \theta = 1\);

Capillary pressure \(P_c\) in cylindrical tube is given by [124],

\[
...
\[ \Delta P_c = \frac{2\gamma_L \cos \theta}{R} = \frac{S\gamma_L \cos \theta}{\varepsilon_L} \]  

(9.13)

where \( \gamma_L \) is the surface tension of the liquid bath, \( \theta \) is the contact angle. \( R \) is the radius of cylindrical tube, \( \rho_L \) is the density of the liquid bath.
A.4. Surface area

For a cylindrical pore with radius $R$, after infinite time $\Delta t$, there are $\Delta m$ liquid solid phase transformations, and radius changes to $R - \Delta R$, then

$$\pi [R^2 - (R - \Delta R)^2] \rho_s = \pi [2R\Delta R - \Delta R^2] \rho_s = \pi 2R\Delta R \rho_s = \Delta m$$  \hspace{1cm} (9.14)

The change of surface area is

$$\pi 2\Delta R \rho_s = \Delta S$$  \hspace{1cm} (9.15)

In terms of time differential

$$\frac{dS}{dt} = \frac{1}{R} \frac{m}{\rho_s} = \frac{S}{2\varepsilon_L} \times \frac{d\varepsilon_L}{dt}$$  \hspace{1cm} (9.16)

$$\frac{dS}{S} = \frac{1}{2} \frac{d\varepsilon_L}{\varepsilon_L} \rightarrow \ln S = \frac{1}{2} \ln \varepsilon_L + a \rightarrow \frac{S^2}{\varepsilon_L} = \frac{S_0^2}{\varepsilon_{L0}}$$  \hspace{1cm} (9.17)

where $S_0$ is initial surface area, $\varepsilon_{L0}$ is initial porosity.

The anode cover is initially in packed powder condition. The BET surface area involves the internal surface area inside the particles. Since the liquid bath does not go into the particles immediately, the external surface area of the particles are more relevant for the estimation of $S_0$. The relationship between the radius of solid particles and the surface area is

$$n4\pi R_p^2 = VS_0$$

$$n4\pi R_p^3 = 3V \varepsilon_s$$  \hspace{1cm} (9.18)

Initial surface area $S_0$ is given by,

$$S_0 = \frac{3\varepsilon_s}{R_p}$$  \hspace{1cm} (9.19)

where $n$ is particles number in volume $V$, $\varepsilon_s$ is the volume fraction of the solid particle, $R_p$ is the mean particle radius.
A.5. Liquid bath flow velocity

A flow with very low velocity can be considered as a laminar flow. Interstitial fluid velocity $v$ is

$$
v = \frac{Q}{A\varepsilon} \text{ [m / s]} \tag{9.20}
$$

where $\varepsilon$ is the volume fraction of liquid bath, $Q$ is volumetric flow rate, $A$ is cross section area.

Superficial fluid velocity $u$ is

$$
u = \frac{Q}{A} = v\varepsilon \text{ [m / s]} \tag{9.21}
$$

The kinetic energy, accelerated speed and inertia force can be ignored when the packed bed Reynolds number, $Re_p$ is below 2 [41].

$$
Re_p = \frac{\rho_u u}{(1 - \varepsilon)S_p \mu} \tag{9.22}
$$

where $\mu$ is viscosity of the liquid bath, about 2.3 mPa·s [109].

For liquid bath penetration in the porous alumina cover, the measured interstitial fluid velocity $v$ is less than 1 mm/min [125], $Re_p$ is about $1.65 \times 10^{-7} << 2$. The viscous pressure drop for laminar flow of fluid through the cylindrical pore is given by the Hagen-Poiseuille equation [41] (the effect of phase transformation is ignored),

$$
\Delta P_v = \frac{8L_u \mu \nu_i}{R^2} \tag{9.23}
$$

where $L_u$ is the total pore length along the flow channel in the packed bed, $\nu_i$ is the interstitial velocity along the flow channel as shown in Figure A-2, is given by equation (9.24).
NOTE: Due to copyright reasons, this figure has been removed. Please refer to the original source:


Alternatively, refer to a hard copy of this thesis, as deposited in The University of Auckland Library.

Figure A.2. Schematic diagram showing interstitial velocity [41]

\[ v_i = \frac{L_a}{H} \frac{u}{\varepsilon_L} \]  
\[ \tau = \left( \frac{L_a}{H} \right)^2 \]  

\( \tau = (L_a / H)^2 \) is defined as the tortuosity, where \( H \) is the packed bed depth.

According to (9.23) and (9.24),

\[ \Delta P_v = \frac{8L_a \mu}{R^2} \frac{L_a}{H} \frac{u}{\varepsilon_L} = \frac{8 \mu H}{R^2 \varepsilon_L} \left( \frac{L_a}{H} \right)^2 u \]

(9.25)

Substituting \( \tau = (L_a / H)^2 \) and \( R = 2 \varepsilon_L / S \) (equation (9.8), see Appendix A.2) in above equation,

\[ \Delta P_v = \frac{2 \tau H \mu S^2}{\varepsilon_L^2} u = \frac{K_h H \mu S^2}{\varepsilon_L^3} u, K_2 = 2 \tau \]

(9.26)

Taken \( K_2 = 5 \), equation (9.25) is known as the Carman-Kozeny equation [41].

According to Darcy’s law [41] and equation (9.25), the hydraulic conductivity \( K_h \) is given by

\[ K_h = \frac{\rho \mu S^3}{5 \varepsilon_L^3} \]

(9.27)
A.6. Correlation between phase transformation rate and concentration

The liquid/solid phase transformation is related to the concentration. In this Appendix, the correlation between phase transformation rate and concentration is deduced.

1) Uniform cylindrical pores

It is assumed that all cylindrical pores have same temperature and concentration distribution. One cubic section is taken here for derivation. The length \( l \) of the cubic is sufficiently small, and the radius \( R \) is kept constant in this region. Variable \( r \) is the radial coordinate of the cylindrical pore, defined as 0 at the centre axis of the cylindrical pore, and \( R \) at the interface between the fluid and the solid. The radial direction (\( r \) axis) is perpendicular to the axial direction (\( x \) axis).

![Schematic diagram showing phase transformation and fluid in cylindrical pores](image)

(1) The diffusion process

The two major models of the mechanism of mass transfer between two phases are the penetration model and the film model. Experimental results show that they are limiting cases of a real situation [126].

\( \phi_i \) denotes the overall volumetric concentration. \( \phi'_i \) denotes concentration at the solid-liquid interface. \( \phi_i^* \) denotes saturation concentration. \( m_i, \phi_i, \phi'_i, \) and \( \phi_i^* \) are functions of \( x \) and \( t \) (time).
(i) the penetration model

The relationship between the phase transformation rate $m_i$ and the concentration $\phi_i$ is given by (see Appendix A.7).

$$\phi_i = \phi_i' - K_{D,i}m_i$$  \hspace{1cm} (9.28)

$$K_{D,i} = \frac{\varepsilon_L}{2D_iS^i\rho_L}$$  \hspace{1cm} (9.29)

where $D_i$ is diffusion coefficient of $i$th species in the liquid bath.

(ii) the film model

Another possibility is that the thickness $\delta$ of the concentration boundary layer (film) between the fluid and the solid is much smaller than the pore radius. The typical value of $\delta$ is about $10^{-9}$m [127].

$$\frac{\delta}{4} < \frac{\varepsilon_L}{2S}$$  \hspace{1cm} (9.30)

The phase transformation rate is given by

$$m_i(x,t) = \frac{D_i}{\delta} S[c'_i(x,t) - c_i(x,t)]$$  \hspace{1cm} (9.31)

Therefore,

$$\phi_i = \phi_i' - K_{D,i}m_i$$  \hspace{1cm} (9.32)

Therefore $K_{D,i}$ can be written as,

$$K_{D,i} = \frac{\delta}{D_iS^i\rho_L}$$  \hspace{1cm} (9.33)

By comparing the two models, the range of the $K_{D,i}$ is given by,
(2) Interfacial reaction process

Assume that the interfacial reaction process is a first order reaction. The phase transformation rate in the interfacial reaction process is given by [68, 128],

$$m_i = K_{R_i}S(c_i^* - c'_i) = K_{R_i}S(\phi_i^* - \phi'_i)\rho_L$$  \hspace{1cm} (9.35)

where $K_{R_i}$ is the interfacial reaction rate constant.

(3) Overall solid liquid phase transformation process

The overall solid liquid phase transformation process equation may be written as:

$$\phi_i = \phi_i^* - K_i m_i$$  \hspace{1cm} (9.36)

$$K_i = K_{D,i} + \frac{1}{K_{R_i}\rho_L S}$$  \hspace{1cm} (9.37)

The average concentration $\phi_i$ is related to the saturation concentration $\phi_i^*$ and phase transformation rate $m_i$.

2) Cylindrical pores with various radiiuses

For more general situation, the porous anode cover is made of a group of parallel cylindrical pores (the amount is $n$) with various radius $R_j (j=1,2,…,n)$. 

\[ \frac{\varepsilon_i}{2D_i S^2 \rho_L} \geq K_{D,i} \geq \frac{\delta}{D_i S \rho_L} \]  \hspace{1cm} (9.34)
Figure A-4. Schematic diagram showing phase transformation and fluid in cylindrical pores with various radiiuses

The relationships between pore radius and surface area, pore radius and porosity are

\[ 2\pi (R_1 + R_2 + \ldots + R_n) \cdot l = l^3 S \quad (9.38) \]
\[ \pi (R_1^2 + R_2^2 + \ldots + R_n^2) \cdot l = l^3 \varepsilon_L \quad (9.39) \]

The following derivation is similar to the one in the case of uniform cylindrical pore.

(i) The penetration model

The range of the \( K_i \) is (see Appendix A.8),

\[ \frac{\varepsilon_i}{2D_i\rho_L S^2} + \frac{1}{K_{R,i}\rho_L S} \leq K_i < \frac{R_{\text{max}}}{4D_i\rho_L S} + \frac{1}{K_{R,i}\rho_L S} \quad (9.40) \]

\( K_i \) are related to the size of largest pores. In the case of maximum pore radius of 50 µm,

\[ K_i < \frac{5 \times 10^{-5}}{4D_i\rho_L S} + \frac{1}{K_{R,i}\rho_L S} \cdot \]

(ii) The film model

Under the possibility that the concentration boundary layer (film) is much less than the pore radius, \( K_{Di} \) is not related to \( R_j \).

\[ K_i = \frac{\delta}{D_i S \rho_L} + \frac{1}{K_{R,i}\rho_L S} \quad (9.41) \]
Combining the two possibilities, the range of $K_i$ is estimated as

$$\frac{\delta}{D_i \rho_L S} + \frac{1}{K_{R_i} \rho_L S} \leq K_i < \frac{R_{\text{max}}}{4D_i \rho_L S} + \frac{1}{K_{R_i} \rho_L S} \quad (9.42)$$

This estimated inequation is important for the simplification of the model.
A.7. Concentration in the case of uniform pores

It is assumed that crystallization is dominated by heterogeneous nucleation, which means crystal grows on the surface of an existing solid phase without a new crystal nucleus generated. There is concentration gradient between a point in the fluid and the fluid/solid interface (crystal surface), which drives mass transfer between them.

\( T_L(x,t) \) denotes the one dimensional temperature distribution in the fluid (\( x \) and \( t \) denote location of coordinate \( x \) and time respectively ). \( \bar{c}_i(x,r,t) \) and \( c_i(x,t) \) denotes the two and one dimensional concentration distribution for the \( i \)th solute in the fluid. The concentration value of \( c_i(x,t) \) is defined as the average value of concentration \( \bar{c}_i(x,r,t) \) of all point in the fluid at the same \( x \) location.

\[
\begin{align*}
  c_i(x,t) &= \frac{\int_0^R \bar{c}_i(r,x,t) \cdot 2\pi r dr}{\pi R^2} \quad (9.43) \\
  c_i(x,t) &= \phi_i(x,t)\rho_L \quad (9.44)
\end{align*}
\]

\( c_i^*(x,t) \), \( \phi_i^*(x,t) \) and \( c_i'(x,t) \), \( \phi_i'(x,t) \) denote saturation concentration and concentration at the fluid/solid interface, respectively.

At the interface of the fluid and solid phase, the Fick’s first law gives,

\[
m_i(x,t) = D_i S \left. \frac{\partial \bar{c}_i(r,x,t)}{\partial r} \right|_{r=R} \quad (9.45)
\]

Where \( D_i \) is diffusion coefficient of the \( i \)th phase in the fluid.

According to the definition of \( c_i'(x,t) \),

\[
\bar{c}_i(r,x,t) \bigg|_{r=R} = c_i'(x,t) \quad (9.46)
\]

According to symmetry condition and continuity of derivative,

\[
\left. \frac{\partial \bar{c}_i(r,x,t)}{\partial r} \right|_{r=0} = 0 \quad (9.47)
\]
The fitting function \( \bar{c}_i(r, x, t) \) which satisfies equations (9.46), (9.45) and (9.47) is used to approximate the real function \( \bar{C}_i(r, x, t) \).

\[
\bar{c}_i(r, x, t) = c'_i(x,t) - \frac{m_i(x, t)}{D_i S} (R - r) + \frac{m_i(x, t)}{2 D_i S \cdot R} (R - r)^2
\]

The average concentration \( c_i(x, t) \) is given by,

\[
c_i(x, t) = \frac{\int_0^R \left[ c'_i(x, t) - \frac{m_i(x, t)}{D_i S} (R - r) + \frac{m_i(x, t)}{2 D_i S \cdot R} (R - r)^2 \right] \cdot 2 \pi r dr}{\pi R^2}
\]

\[
= c'_i(x, t) - \frac{m_i(x, t)}{D_i S} \frac{R}{4}
\]

According to (9.44),

\[
\phi_i(x, t) = \phi'_i(x, t) - \frac{\varepsilon_i}{2 \rho_i D_i S^2} m_i(x, t)
\]
A.8. Concentration in the case of various pores

According to Cauchy inequality and equation (9.38) and (9.39),

\[
\frac{1}{n} \sum_{j=1}^{n} R_j^2 \leq \frac{\sum_{j=1}^{n} R_j^2}{\sum_{j=1}^{n} R_j} = \frac{2\varepsilon_L}{S} \quad (9.51)
\]

\(\nu\) denotes phase transformation interface moving velocity, m/s. \(m_{s,j}\) denotes area phase transformation rate, kg/(m²s).

\[
m_{s,j} = \rho_{s,j}\nu \quad (9.52)
\]

Assume the area phase transformation rate \(m_{s,j}\) in all pores are the same. \(\phi_{i,j}\) denotes the average concentration of the \(i\)th phase in the \(j\)th pore with radius \(R_j\). According to the penetration model (similar derivation with Appendix A.7),

\[
m_{s,j} = D_i \left. \frac{\partial c_{i,j}}{\partial r} \right|_{r=R_j} \quad (9.53)
\]

\[
\left. \frac{\partial c_{i,j}}{\partial r} \right|_{r=0} = 0 \quad (9.54)
\]

\[
\phi_{i,j} = \phi_{i,j}^* - \frac{m_{s,j} R_j}{4D_i \rho_L} \quad (9.55)
\]

\[
m_{s,j} = K_{R_j}(c_{i,j}^* - c_{i,j}^{'*}) = K_{R_j}(\phi_{i,j}^* - \phi_{i,j}^{*'})\rho_L \quad (9.56)
\]

\[
\phi_{i,j}^* = \phi_{i,j}^{*'} - \frac{m_{s,j}}{K_{R_j}\rho_L} \quad (9.57)
\]

\[
\phi_{i,j} = \phi_{i,j}^* - m_{s,j} \left( \frac{R_j}{4D_i \rho_L} + \frac{1}{K_{R_j}\rho_L} \right) \quad (9.58)
\]

The overall concentration \(\phi_i\) is the average value of all the \(\phi_{i,j}\), thus
According to Chebyshev’s inequation,

\[ \sum_{j=1}^{n} (\pi R_j^2 \phi_{j,L}) = \phi^* \frac{1}{\sum_{j=1}^{n} (\pi R_j^2)} \frac{\sum_{j=1}^{n} \left[ m_{i,j} \left( \frac{1}{4D_j \rho_L \pi R_j^3 + \pi R_j^2} \frac{1}{K_{R,j} \rho_L} \right) \right]}{\sum_{j=1}^{n} (\pi R_j^2)} \]

(9.59)

\[ = \phi^* - \frac{m_i}{S} \left( \sum_{j=1}^{n} (R_j^3) \cdot \frac{\pi}{4D_j \rho_L} \varepsilon_L l^2 + \frac{1}{K_{R,j} \rho_L} \right) \]

According to Chebyshev’s inequation,

\[ \sum_{j=1}^{n} (R_j^3) \geq \frac{1}{n} \sum_{j=1}^{n} (R_j^3) \cdot \sum_{j=1}^{n} (R_j) = \frac{\varepsilon_L S \cdot l^2}{2\pi^2 n} \]

(9.60)

When \( R_1 = R_2 = \ldots = R_n \) (the uniform pore situation), above inequation reaches minimum value, and \( \frac{l^2}{n \pi} = \frac{4\varepsilon_L}{S^2} \) (equation (9.9)).

The upper limiting case is,

\[ \sum_{j=1}^{n} (R_j^3) < \sum_{j=1}^{n} (R_j^2) \cdot R_{\max} = \frac{\varepsilon_L \cdot l^2}{\pi} \cdot R_{\max} \]

(9.61)

where \( R_{\max} \) is the maximum radius among \( R_j \).

According to equation (9.59),

\[ |m_i| \left( \frac{\varepsilon_L}{2D_j \rho_L S^2} + \frac{1}{K_{R,j} \rho_L S^2} \right) \leq |\phi^* - \phi| < |m_i| \left( \frac{R_{\max}}{4D_j \rho_L S} + \frac{1}{K_{R,j} \rho_L S} \right) \]

(9.62)

\( K_i \) satisfies following inequation relationship,

\[ \frac{\varepsilon_L}{2D_j \rho_L S^2} + \frac{1}{K_{R,j} \rho_L S} \leq K_i < \frac{R_{\max}}{4D_j \rho_L S} + \frac{1}{K_{R,j} \rho_L S} \]

(9.63)
A.9. Simplification of differential equations

For a given differential equation,

\[ y' = ay^2 + by + bf(x), b \gg a, b \gg 1, b \gg f(x), b \gg 4a^2 f(x)^2 \]  \hspace{1cm} (9.64)

It is known as a Riccati equation, where the solution is:

\[ y = -\frac{u'}{au} \]  \hspace{1cm} (9.65)

\[ u = (c_1 + c_2 \int e^{-2rx-bx} dx)e^{rx} \]  \hspace{1cm} (9.66)

\[ r = \frac{b - \sqrt{b^2 - 4abf(x)}}{2} \]  \hspace{1cm} (9.67)

Since \( b \gg a, b \gg 1, b \gg f(x), b \gg 4a^2 f(x)^2 \), \( r \) is simplified as

\[ r \approx \frac{b - \sqrt{b^2 - 4abf(x) + 4a^2 f(x)^2}}{2} = af(x) \]  \hspace{1cm} (9.68)

\[ u \approx c_1 \times e^{af(x)} \]  \hspace{1cm} (9.69)

The approximate solution \( y \) is

\[ y \approx -f(x) \]  \hspace{1cm} (9.70)
A.10. Numerical correctness of the present model

As discussed in Chapter 4, the present model includes three types of partial differential equations (PDEs), i.e. transient heat conduction equation, transient heat conduction & advection equation, and Stefan boundary condition equation (for more details, see section 4.2 and section 4.4).

In Chapter 5, these PDEs were solved by a computational code applying the numerical method of FEM. The numerical correctness of the present model is firstly established through verification of the computational code. In this section, the numerical results are compared with the exact analytical solutions of some case studies.

The numerical result is an approximate solution calculated by the computational code, while the analytical solution is exact solution based on mathematical theory.

The domain of a practical problem is usually limited to a finite space. For instance it is about \(0 \leq x \leq 12\) cm in this study (\(x\) is dimensional coordinate). Usually the exact analytical solution for this finite situation is not readily available. However, in some particular cases such as semi-infinite domain \((0 \leq x \leq \infty)\) with constant boundary condition, exact analytical solutions can be given. Even though these particular situations in some details differ from the crust formation situation studied in this thesis, they can still be used to verify the computational code.

(1) Transient heat conduction

It is assumed there is a semi-infinite plate for the discussion below. Set coordinate \(x\) as the distance from the position in the plate to the end. Its initial temperature is \(T_0\). The end of this plate \((x=0)\) is suddenly brought to the temperature \(T_I\) at time \(t=0\). The temperature inside the plate will increase with time. Thus, temperature \(T(t,x)\) is the function of time \(t\) and position \(x\), as shown in Figure A-5.
The transient heat transfer equation (one dimensional, the same below) for heat diffusion problem in the plate can be defined as equation (9.71) [129],

$$\rho C \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2}$$  \hspace{1cm} (9.71)

where $\rho$ is the density of the plate, $C$ is the specific heat capacity of the plate, and $k$ is the thermal conductivity of the plate. $T$ is the temperature, $t$ is the time, $x$ is the coordinate position.

The boundary and initial conditions are given as,

$$t = 0, T(x,0) = T_0$$
$$x = 0, T(0,t) = T_i$$
$$x \to \infty, T(x,t) = T_0$$  \hspace{1cm} (9.72)

The analytical solution for the above problem is shown as [129]:

$$T = (T_0 - T_i) \text{erf} \left( \frac{x}{2\sqrt{\alpha t}} \right) + T_i$$  \hspace{1cm} (9.73)

where $a = \frac{k}{\rho C}$ is the thermal diffusion coefficient of the plate.

The mesh size strategy is 0.1 mm at domain of [0,1], 0.1 m at domain of [1,2], 1 m at
domain of \([2,10]\). The domain near the end of the plate is fine meshed because there is high temperature gradient. The boundary condition is \( T = T_0 \), at \( x=10 \) m (approximation as \( \infty \)). The time step is 5 seconds.

A particular case of \( \rho = 1000, C=1000, k=0.5, T_0=25, T_1=950 \) is applied here.

Figure A-6 gives the distribution of temperature along position \( x \) at a series of time \( t \), and Figure A-7 gives the distribution of temperature along time \( t \) at a series of position \( x \).

![Figure A-6. Distribution of temperature along position \( x \) at a series of time \( t \)](image)

\[
\text{Figure A-6. Distribution of temperature along position } x \text{ at a series of time } t
\]
Figure A-7. Distribution of temperature along time $t$ at a series position $x$

(2) Transient heat conduction and advection (advection-diffusion)

It is assumed that there is a pipe with a semi-infinite length. The pipe is filled with fluid. Set coordinate $x$ as the distance from the position in the pipe to the end. The superficial velocity of the fluid is $u$. The initial temperature of the fluid is $T_0$. The pipe wall is adiabatic. The temperature of the fluid entering the pipe is suddenly brought to $T_1$ at time $t=0$. The temperature inside the pipe will increase with time. Thus, temperature $T(t,x)$ is the function of time $t$ and position $x$, as shown in Figure A-8.

Figure A-8. Transient heat transfer by fluid in a semi-infinite pipe
The governing equation for the above problem is shown below in equation (9.74) [70].

\[
\rho C \frac{\partial T}{\partial t} + \rho C u \frac{\partial T}{\partial x} = k \frac{\partial^2 T}{\partial x^2}
\] (9.74)

where \( \rho \) is the density of the fluid, \( C \) is the specific heat capacity of the fluid, \( u \) is the fluid velocity of the fluid, and \( k \) is the thermal conductivity of the fluid.

An equivalent mathematical form is shown as,

\[
C \rho \frac{dT}{dt} + C \rho u \frac{dT}{dx} = k \frac{d^2T}{dx^2}
\] (9.75)

The initial condition is shown as,

\[ T(0,0) = T_0, T(x,0) = T_0, x > 0 \] (9.76)

The boundary condition are listed in following equations,

\[ x = 0, t > 0, T(0,t) = T_1 \] (9.77)

\[ x \to \infty, T = T_0 \] (9.78)

The analytical solution is as following [130]

\[ T(x,t) = (T_1 - T_0) f(x,t) + T_0 \] (9.79)

\[
f(x,t) = \frac{1}{2} \text{erfc}[\frac{x - ut}{2\sqrt{at}}] + \frac{1}{2} \exp(-\frac{ux}{a}) \text{erfc}[\frac{x + ut}{2\sqrt{at}}]
\] (9.80)

where \( a = \frac{k}{\rho C} \) is the thermal diffusion coefficient of the liquid fluid.

The mesh size strategy is 0.1 mm at domain of [0,1], 0.1 m at domain of [1,2], 1 m at domain of [2,10]. The boundary condition is \( T = T_0 \) at \( x=10 \) m (approximation as \( \infty \)). Time step is 5 seconds.
It has been revealed that high coefficient $C\rho u$ contributes to the difficulty of the numerical solution [131].

A particular case $\rho C = 10^8$, $u = 5 \times 10^{-6}$, $k = 0.5$, $T_0 = 25$, $T_1 = 950$ is applied here.

Figure A-9 gives the distribution of temperature along position $x$ at a series of time $t$, and Figure A-10 gives the distribution of temperature along time $t$ at a series of position $x$.

![Figure A-9. Distribution of temperature along position $x$ at a series of time $t$](image)
Figure A-10. Distribution of temperature along time $t$ at a series position $x$

(3) Stefan boundary condition

It is assumed that there is a semi-infinite solid. Set coordinate $x$ is the distance from the position in the solid to the end. The melting temperature of the solid is fixed at $T_m$. Its initial temperature is $T_0 (T_0 < T_m)$. The end of it ($x=0$) is suddenly brought to temperature $T_1 (T_1 > T_m)$. The temperature inside the solid will increase with time. Thus, temperature $T(t,x)$ is the function of time $t$ and position $x$.

Figure A-11. Melting of semi-infinite solid
This process is governed by the following energy equation with moving boundary,

\[ \rho C_L \frac{\partial T_L}{\partial t} = k_L \frac{\partial^2 T_L}{\partial x^2}, \quad x \leq h \]

\[ \rho C_S \frac{\partial T_S}{\partial t} = k_S \frac{\partial^2 T_S}{\partial x^2}, \quad x \geq h \]

At the boundary between solid and liquid, the heat flux obeys the following equations \((9.83)\) and \((9.84)\),

\[ T_S = T_L = T_m, \quad x = h \]

\[ \rho L \frac{dh}{dt} = k_S \frac{\partial T_S}{\partial x} \bigg|_{x=h^-} - k_L \frac{\partial T_L}{\partial x} \bigg|_{x=h^-} \]

where \(\rho\) is the density of the solid (and the liquid), \(C_L, C_S\) are the specific heat capacities of the liquid and the solid respectively, \(k_L, k_S\) are the thermal conductivities of the liquid and the solid respectively, \(L\) is the latent heat of solid liquid phase transformation, \(h\) is the position of the boundary between the solid and the liquid phase, which is the function of time \(t\).

An equivalent mathematical form is shown in equations \((9.85)\) to \((9.88)\),

\[ \frac{\partial T}{\partial t} = \alpha_L \frac{\partial^2 T}{\partial x^2}, \quad x \leq h \]

\[ \frac{\partial T}{\partial t} = \alpha_S \frac{\partial^2 T}{\partial x^2}, \quad x \geq h \]

\[ T \bigg|_{x=h^-} = T_m \]

\[ \rho L \frac{dh}{dt} = k_S \frac{\partial T}{\partial x} \bigg|_{x=h^-} - k_L \frac{\partial T}{\partial x} \bigg|_{x=h^-} \]

The initial conditions are shown below,

\[ T(x,0) = T_0, \quad 0 < x < \infty \]

\[ h(0) = 0 \]
The boundary conditions are listed below,

\[ T(0, t) = T_1, t > 0 \]  \hspace{1cm} (9.90)

\[ T(+\infty, t) = T_0 \]  \hspace{1cm} (9.91)

The analytical solution is as following: [86]

\[ h(t) = 2\lambda\sqrt{\alpha_t t} \]  \hspace{1cm} (9.92)

\[ T(x, t) = T_1 - (T_1 - T_m)\frac{\text{erf}(\frac{x}{2\sqrt{\alpha_t t}})}{\text{erf}(\lambda)}, 0 < x \leq h(t) \]  \hspace{1cm} (9.93)

\[ T(x, t) = T_0 + (T_m - T_0)\frac{\text{erfc}(\frac{x}{2\sqrt{\alpha_t t}})}{\text{erfc}(\lambda\sqrt{\alpha_L / \alpha_S})}, x > h(t) \]  \hspace{1cm} (9.94)

where \( \lambda \) is the solution of the following transcendental equations,

\[
\frac{St_L}{\exp(\lambda^2)\text{erf}(\lambda) - \frac{\lambda}{2\pi}} - \frac{St_S}{\exp(z^2\lambda^2)\text{erfc}(z\lambda)} = \frac{\lambda}{\sqrt{\pi}}
\]

\[ St_L = \frac{C_L(T_1 - T_m)}{L}, St_S = \frac{C_S(T_m - T_b)}{L}, z = \frac{\alpha_L}{\sqrt{\alpha_S}} \]  \hspace{1cm} (9.95)

Above equations were solved by using a coordinate transformation technique based on a boundary fixing method [83, 87].

In the liquid zone, following coordinate transformation is used,

\[ \eta = \frac{x}{h(t)}, 0 \leq x \leq h(t), 0 \leq \eta \leq 1 \]  \hspace{1cm} (9.96)

The differential operators with the coordinate transformation are mathematically related to the following equations:

\[
\frac{\partial}{\partial t} = \frac{\partial}{\partial t} - \frac{\eta H}{h} \frac{\partial}{\partial \eta}, H = \frac{dh}{dt}
\]  \hspace{1cm} (9.97)
\[
\frac{\partial}{\partial x} = \frac{1}{h} \frac{\partial}{\partial \eta} \tag{9.98}
\]

In the solid zone, the following coordinate transformation is used,

\[
\xi = \frac{x - h(t)}{h_0 - h(t)}, \quad h(t) \leq x \leq h_0, \quad 0 \leq \xi \leq 1 \tag{9.99}
\]

The differential operators with the coordinate transformation are also mathematically related to the following equations:

\[
\frac{\partial}{\partial t} = \frac{\partial}{\partial t} - \frac{(1-\xi)H}{h_0 - h} \frac{\partial}{\partial \xi} \tag{9.100}
\]

\[
\frac{\partial}{\partial x} = \frac{1}{h_0 - h} \frac{\partial}{\partial \xi} \tag{9.101}
\]

Energy equations with moving boundary can be transformed to the following equations, respectively:

\[
\frac{\partial T_L}{\partial t} = \frac{\eta H}{h} \frac{\partial T_L}{\partial \eta} + \frac{1}{h^2} \alpha_L \frac{\partial^2 T_L}{\partial \eta^2}
\]

\[
T_L\big|_{\eta=0} = T_1
\]

\[
T_L\big|_{\eta=1} = T_m
\]

\[
\frac{\partial T_S}{\partial t} = \frac{H(1-\xi)}{h_0 - h} \frac{\partial T_S}{\partial \xi} + \frac{1}{(h_0 - h)^2} \alpha_S \frac{\partial^2 T_S}{\partial \xi^2}, \quad H = \frac{dh}{dt}
\]

\[
T_S\big|_{\xi=0} = T_m
\]

\[
T_S\big|_{\xi=1} = T_0
\]

At moving boundary,

\[
\rho L \frac{dh}{dt} = \frac{k_S}{h_0 - h} \frac{\partial T_S}{\partial \xi}\bigg|_{\xi=h} - \frac{k_L}{h} \frac{\partial T_L}{\partial \eta}\bigg|_{\eta=h} \tag{9.104}
\]

Equations (9.102) and (9.103) are solved by the method of finite element. The numerical differential equation for equation (9.104) is:
\[ \rho L \frac{h^{n+1} - h^n}{2\Delta t} = k_S \frac{-3T_{S,0}^{n+1} + 4T_{S,1}^{n+1} - T_{S,2}^{n+1}}{2(h_t - h^{n+1})\Delta \eta} - k_L \frac{3T_{L,\text{end}}^{n+1} - 4T_{L,\text{end}^{-1}}^{n+1} + T_{L,\text{end}^{-2}}^{n+1}}{2h^{n+1}\Delta \eta} \]  \hspace{1cm} (9.105)

The minimum mesh size is $10^{-5}$ for coordinate $\eta$, and $10^{-5}$ for coordinate $\zeta$ near the boundary. $T$ equals to $T_0$ at 10 m (approximation as $\infty$). Time step is 5 second.

Case 1: $\rho = 1000, C_L = C_S = 4200, k_L = 0.5, k_S = 2, T_0 = 25, T_1 = 1000, T_m = 700, L = 5.24 \times 10^5$.

The moving boundary position is shown in Figure A-12. Figure A-13 gives distribution of temperature along position $x$ at a series of time $t$. Figure A-14 gives distribution of temperature along time $t$ at a series of position $x$.

![Figure A-12. Correlation of moving boundary position $h(t)$ with time](image)
Case 2: $\rho =2000$, $C_L=2000$, $C_S=1000$, $k_L=1$, $k_S=1$, $T_0=25$, $T_1=1000$, $T_m=700$, $L=5.24 \times 10^5$.

The moving boundary position is shown in Figure A-15. Figure A-16 illustrating the distribution of temperature along position $x$ at a series of time $t$. Figure A-17 gives the distribution of temperature along time $t$ at a series of position $x$. 
Figure A-15. Correlation of the moving boundary position $h(t)$ with time

Figure A-16. Distribution of temperature along position $x$ at a series of time $t$
Figure A-17. Distribution of temperature along time $t$ at a series of position $x$

As shown in the above figures, the error of temperature results is less than 1 °C, and that of moving boundary positions is less than 0.5 mm. The numerical results are in good agreement with the analytical solutions. It should be noted that the parameters (i.e. heat capacity and thermal conductivity) in these case studies above are constant which are necessary to get analytical solution, whereas these in the present model are not constant and dependent on temperature and chemical composition.

### A.11. Effective thermal conductivity

Thermal conductivity, an important thermal property of the present model, affects the transmission of heat and consequently the thermochemical behaviour of the cover/crust. In Chapter 4, Zehner-Schlunder-Laubitz (ZSL) model [75, 77, 78] was included in the present model to predict the effective thermal conductivities of the anode cover and the crust.

1. **(1) The effective thermal conductivities of alumina based cover**

   The thermal conductivities of air [132] and dense alumina [133] are applied in the ZSL model to predict the thermal conductivity of the alumina cover.

   As noted earlier, Llavona [23], Hatem *et al.* [24] and Rye *et al.* [13] measured similar
thermal conductivities of smelter grade alumina, which are not consistent with the measured results from Shen [10] and Wijayaratne et al. [20]. Figure A-18 shows predicted and measured thermal conductivity (More detailed comparison is shown in Figure A-19).

As shown in Figure A-18, thermal conductivities of alumina cover measured by Shen [10] and Wijayaratne et al. [20] are considerably higher than that by Hatem et al. [24], Rye et al. [13] and Llavona [23], as well as the predicted results.

Shen [10] and Wijayaratne et al. [20] measured the thermal conductivity by radial steady state method using the same experimental rig in the University of Auckland, whereas the other researchers measured the thermal conductivity independently. The overestimation of the measured data from Shen [10] and Wijayaratne et al. [20] may due to the limitation of the experimental rig.

![Figure A-18. Thermal conductivity of alumina (predicted results by ZSL model and measured data from Shen [10], Wijayaratne et al. [20], Hatem et al. [24], and Llavona [23])](image)

In the study of Llavona [23], the smelter grade alumina used in the measurement had various bulk density between 1.0 and 1.26 g/cm³ with estimated porosity between 0.66 and 0.72. Because of this, these measured data are used for more detailed comparison, as shown in Figure A-19. The deviations between the predicted results and the
experimental data are within ±0.035 W/mK (±15%). The results predicted by ZSL model has reasonable agreement with the experimental data from Llavona [23].

Figure A-19. Comparison of the thermal conductivity of smelter grade alumina between predicted results by ZSL model and measured data from Llavona [23] (mean particle size $d=0.1$ mm, radiant emissivity $e=0.5$ [134, 135])

(2) The effective thermal conductivities of crust

For the crust, average thermal conductivity over a temperature range from 700 to 950 °C was measured in-situ by Rye et al. [13]. The measured thermal conductivity is 0.45–0.7 W/mk for alumina based crust, and 1.05–1.65 W/mk for crushed bath based crust [13]. However, for these crusts, the volume fractions of liquid, solid and air phases were unknown, and they are necessary for the thermal conductivity prediction according to the ZSL model used here.

To investigate the boundaries of predicted conductivity for a crust, four typical cases of
the volume fraction composition are selected to predict the thermal conductivity, as shown in Figure A-20. The predicted results are consistent with the measured data from Rye et al. (i.e. 0.45–0.7 W/mk for alumina based crust, and 1.05–1.65 W/mk for crushed bath based crust) [13].

Figure A-20. Predicted thermal conductivity of the crust with four typical volume fraction compositions: (1) alumina based crust 1, Liquid $\epsilon_L=0.5$, Solid $\epsilon_S=0.4$, Air $\epsilon_A=0.1$; (2) alumina based crust 2, $\epsilon_L=0.35$, $\epsilon_S=0.35$, $\epsilon_A=0.3$; (3) crushed bath crust 1, $\epsilon_L=0.55$, $\epsilon_S=0.45$; (4) crushed bath crust 2, $\epsilon_L=0.3$, $\epsilon_S=0.7$ (note: measured data are temperature averaged, and not plotted in this figure)
A.12. The calculation of the effective specific heat capacity

As discussed in Chapter 4, the phase transformation rate \((m)\) relates to \(d\Omega/dT\) (i.e. the change of concentration with temperature), which is dependent on the relevant phase diagrams. Therefore, the chemical composition of the bulk bath (i.e. initial condition of the penetrating liquid bath) impacts the phase transformation rate.

For instance, in the case of \(Na_3AlF_6-AlF_3\) system, the equilibrium composition of the liquid bath can be illustrated by the \(Na_3AlF_6-AlF_3\) phase diagram [38]. Assume the initial point is ‘a’. As noted in Chapter 4, when the liquid bath is cooled down, its composition will keep constant until it reaches the liquidus point ‘b’, then it will change along the liquidus curve (see Figure A-21). The liquidus curve can be approximately determined by the following empirical equation [61].

\[
T = 1011 + 0.5[AlF_3] - 0.13[AlF_3]^{1.2}
\]

\[
[AlF_3] + [Na_3AlF_6] = 100
\]

Thus, the correlation curve between the temperature and cryolite content wt\% is determined and shown in Figure A-21 (b), the slope of which has reciprocal relationship with \(d[Na_3AlF_6]/dT\). Thus the latter can be calculated from the liquidus curve.

![Figure A-21. Phase diagram for the system Na₃AlF₆-AlF₃[38]](image)
For the Na$_3$AlF$_6$-AlF$_3$-Al$_2$O$_3$ system, $d[Na_3AlF_6]/dT$ is determined in a similar way (see Figure A-22).

\[
T = 1011 + 0.5[AlF_3] - 0.13[AlF_3]^2 \\
6.99[Al_2O_3] \\
-1 + 0.0936[Al_2O_3] - 0.0017[Al_2O_3]^2
\]

\[
[AlF_3] = (11.9 - 0.062[AlF_3] - 0.003I[AlF_3]^2)(\frac{T}{1000})^{\frac{4-0.14T}{T-70}}
\]

Figure A-22. Phase diagram for the system Na$_3$AlF$_6$-AlF$_3$-Al$_2$O$_3$[51]

In addition, the other two examples of cryolite based systems with more additives are:

(A) Na$_3$AlF$_6$ + AlF$_3$ + Al$_2$O$_3$ + CaF$_2$ with the initial bath composition of CR = 1.85, CaF$_2$ wt% = 5, Al$_2$O$_3$ wt% = 3. The liquidus temperature is 910 °C.

(B) Na$_3$AlF$_6$ + AlF$_3$ + Al$_2$O$_3$ + CaF$_2$ + LiF + MgF$_2$ + KF with the initial bath composition of CR = 2.3, CaF$_2$ wt% = 5, Al$_2$O$_3$ wt% = 3, LiF wt% = 3, MgF$_2$ wt% = 1, KF wt% = 1. The liquidus temperature is 934 °C.

According to the empirical equations for cryolite liquidus temperature and alumina saturation solubility (see Chapter 4), the equilibrium concentrations of cryolite and alumina in the liquid bath are temperature dependent and shown in Figure A-23 and Figure A-24. Therefore, the change of concentration with temperature can be determined accordingly (see Figure A-25 and Figure A-26). As the crystallization rate directly relates to the $d\phi/dT$, solid cryolite and alumina partially crystallizes faster at higher temperature.
Figure A-23. Equilibrium concentration of cryolite vs temperature

Figure A-24. Equilibrium concentration of alumina vs temperature
As deduced in section 4.4, $C_E$ is calculated from the following equations,
\[ C_E = C_L + F_L, F_L = [F]_{11} L_{alo} + [F]_{21} L_{cry} = [F]_{12} L_{alo} + [F]_{22} L_{cry} \]

\[
[F] = \frac{1}{1 - \phi_{alo} - \phi_{cry}} \begin{bmatrix}
1 - \phi_{cry} & \phi_{alo} & \frac{\partial \phi_{alo}}{\partial T_L} & \frac{\partial \phi_{alo}}{\partial T_L} \\
\phi_{cry} & 1 - \phi_{alo} & \frac{\partial \phi_{cry}}{\partial T_L} & \frac{\partial \phi_{cry}}{\partial T_L}
\end{bmatrix}
\] (9.107)

where \( C_L \) is sensible specific heat capacity of the liquid bath (1880 J/kgK), \( L \) is latent heat of crystal liquid phase transformation.

\[ \phi_{alo} = \frac{[Al_2O_3] \text{wt} \%}{100}, \quad \phi_{cry} = \frac{[Na_3AlF_6] \text{wt} \%}{100}, \quad \frac{d\phi_{alo}}{dt} = \frac{d[Al_2O_3] \text{wt} \%}{dt} \times \frac{1}{100}, \]

\[ \frac{d\phi_{cry}}{dt} = \frac{d[Na_3AlF_6] \text{wt} \%}{dt} \times \frac{1}{100}. \]

\( C_E \) is dependent on temperature, and is shown in Figure A-27.
A.13. Simulation of industrial Crust A, C and D

(1) The initial condition for the simulation

The initial conditions of temperature and chemical composition are important to simulate the industrial Crust A, C and D (for more details, see Chapter 6) using the present model.

Normally the time when raw anode cover is initially added into a cell might be considered as the initial time of the simulation. However, due to the unknown complicated practical situation in the industrial cell, this initial time is not applicable for the simulation. In this section, some simplifications are made to establish another initial time for the simulation, as discussed below.

Figure A-28 shows three stages (i.e. early, middle and later stages) for the whole anode cover rota. Early stage starts from the new anode cover dressing. During the early stage, a crust (referred to as early crust) forms at the bottom part of the anode cover.

Figure A-28. Position where Crust A, C and D taken from (early stage: the initial anode cover → the lower sintered crust starts melting; middle stage: lower part melts; later stage: bulk bath makes contact with crust again)

Generally, the total thickness of the initial anode cover is about 40 ~ 50 cm according to anode height and bath level. Because the anode cover with high thickness has good thermal insulation, the bottom part of the crust is very likely to melt, especially during AE. The stage relating to the melting of the early crust is referred to as middle stage, during which there is an air gap between the bulk bath and the crust. During this stage,
there is thermal radiation heat transfer between the bulk bath and the crust.

Later stage starts from when there is physical contact between the bulk bath and the crust again. This physical contact may be caused by a sudden increase of bath level after manual additions of extra bath into the pot. During the later stage, the bulk bath not only supply more heat transmission to the crust (convective heat transfer rather than radiation heat transfer), but also supply liquid bath to penetrate in the crust. The crust forms further during the later stage.

Taken at the end of the later stage, the industrial Crusts A, C and D, which provide the experimental data of chemical composition, are just the remaining top part of the whole initial anode cover, and have reduced crust thickness of 3 cm and 6 cm.

The evolution of crust formation during whole rota is very complicated and highly related to the operations occurring. The formation and melting of the lower part of the early crust at early and middle stages in Figure A-28 is difficult to predict and is therefore excluded from the present model.

The initial time of the simulation is the beginning of the final contact between the crust and the bulk bath, i.e. the start time of later stage in Figure A-28. One approximation for the initial condition of the simulation is that the temperature distribution in the crust has been at a steady state and there is radiation heat transfer between the bottom surface of the crust and the bulk bath. At the start of the simulation, the radiation heat transfer between the bulk bath and the crust is replaced by a convective heat transfer between them which is dependent on proximity.

At the early stage in Figure A-28, it is also likely that the bulk bath makes contact with the crust, and thus liquid bath penetration occurs. However, this early crust melts later during the anode rota, and the early liquid bath penetration might have little impact on the remaining later crust (i.e. Crusts A, C and D).

During early and middle stages, since the liquid bath penetration is ignored, the chemical composition is determined by phase transformation between solid and liquid phases at the same position. In this case, the initial chemical composition is determined
by the temperature and initial chemical composition through application of the phase diagram. For more details, refer to Chapter 6.

(2) Translation of hot state simulation result to cold state

The evolution of chemical composition is difficult to measure in situ during cell operation or experiment. Therefore, the chemical composition has been measured at the final cold state (e.g. cool to room temperature after the experiment or taking the sample from operating cell). In contrast, the chemical composition at the hot state is simulated by the present model. To make the simulation results comparable to the experimental data reported in Chapter 6, it is necessary to convert the simulation result from the hot state to the cold state.

The crust at hot state consists of solid and liquid phases. It has been assumed here that there is only liquid to solid phase transformation and no spatial mass transfer inside the crust when samples are cooled down. The conversion is therefore as described by the phase equilibrium diagram (for more details, see Chapter 4).

(3) Uncertainty of minor phases

As noted in Chapter 4, at the eutectic temperature, chiolite and fluoride additive compounds crystallize simultaneously. It is difficult to determine the amount of chemical compounds made of fluoride additives because of the complicated phase diagram for this system. For example, CaF$_2$ may exist in compounds including CaF$_2$, NaCaAlF$_6$, NaCaAl$_2$F$_9$, or Na$_2$Ca$_3$Al$_2$F$_{14}$ when it is cooled down. Temperature, the cooling rate, and initial chemical composition all influence the final chemical composition of these minor phases.

Since most fluoride additives compounds and chiolite all contain NaF and AlF$_3$, the chiolite content is also difficult to determine. In addition, the measured result by XRD analysis may give low accuracy for the composition of these phases if there are multiple additives such as Li, K, Mg, and Ca present alongside more well understood additives.

Nevertheless, the total amount of NaF and AlF$_3$ are certain. The ratio between NaF and AlF$_3$ (i.e. CR) does not change after conversion from hot state to cold state no matter
which chemical compound is formed.

Comparisons of cryolite content, alumina content and CR between the experimental data and simulation results are included in this study.
### A.14. Properties and constants used in model

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$</td>
<td>Specific heat capacity (J/kgK)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid electrolyte ($C_{L}$)</td>
<td>1880</td>
</tr>
<tr>
<td></td>
<td>Solid cryolite ($C_{S,2}$)</td>
<td>1100–1660</td>
</tr>
<tr>
<td></td>
<td>Solid alumina ($C_{S,1}$)</td>
<td>900–1260</td>
</tr>
<tr>
<td>$C_E$</td>
<td>Effective specific heat capacity (J/kgK)</td>
<td>$2\times10^3$–$10^4$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient (m$^2$/s)</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>$e$</td>
<td>Emissivity (m$^2$/s)</td>
<td>0.4</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravity acceleration (m$^2$/s)</td>
<td>9.8</td>
</tr>
<tr>
<td>$h_C$</td>
<td>Convective heat transfer coefficient (W/m$^2$K)</td>
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</tr>
<tr>
<td>$h_f$</td>
<td>Convective heat transfer coefficient (W/m$^2$K)</td>
<td>500</td>
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<tr>
<td>$R$</td>
<td>Effective capillary radius (m)</td>
<td>$R=2\varepsilon L/S$</td>
</tr>
<tr>
<td>$k_{eff}$</td>
<td>Effective thermal conductivity (W/mK)</td>
<td>Alumina based crust</td>
</tr>
<tr>
<td>Material</td>
<td>Value</td>
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</tr>
<tr>
<td>--------------------------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Alumina loose cover</td>
<td>0.1~0.3</td>
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</tr>
<tr>
<td>Crushed bath crust</td>
<td>1.0~1.5</td>
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</tr>
<tr>
<td>Crushed bath loose cover</td>
<td>0.2~0.8</td>
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</tr>
<tr>
<td>$K_R$  Reaction rate constant (1/min)</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>$L$  Latent heat(J/kg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eutectic reaction ($L_e$)</td>
<td>$7.56 \times 10^5$</td>
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<tr>
<td>Chiolite melting ($L_p$)</td>
<td>$5.12 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>$S$  Surface area per unit volume (m²/m³)</td>
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<td></td>
</tr>
<tr>
<td>Sandy alumina</td>
<td>$7.7 \times 10^7$</td>
<td></td>
</tr>
<tr>
<td>$\rho$  True density(kg/m³)</td>
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<td></td>
</tr>
<tr>
<td>Liquid electrolyte ($\rho_L$)</td>
<td>2100</td>
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</tr>
<tr>
<td>Solid cryolite ($\rho_{5,2}$)</td>
<td>2970</td>
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</tr>
<tr>
<td>Fluoride additives ($\rho_{5,3,8}$)</td>
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<td></td>
</tr>
<tr>
<td>Solid alumina ($\rho_{5,1}$)</td>
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<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Value</td>
</tr>
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<td>--------</td>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Volume fraction</td>
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<tr>
<td>$\mu$</td>
<td>Viscosity of the liquid electrolyte (mPa·s)</td>
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</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant (kg/s$^3$k$^4$)</td>
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<tr>
<td>$\gamma_L$</td>
<td>Surface tension of the liquid electrolyte (Nm$^{-1}$)</td>
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<tr>
<td>$\theta$</td>
<td>Contact angle between the liquid electrolyte and the solid</td>
<td>$\cos \theta \approx 1$</td>
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</table>
A.15. DTA cooling curve

The DTA cooling curves for the DTA tests mentioned in Chapter 6 are given in following figures.

Figure A-29. DTA cooling curve of crust sample A1

Figure A-30. DTA cooling curve of crust sample A2
Figure A-31. DTA cooling curve of crust sample A3

Figure A-32. DTA cooling curve of crust sample A4
Appendices

Figure A-33. DTA cooling curve of crust sample A5

Figure A-34. DTA cooling curve of crust sample A6
Figure A-35. DTA cooling curve of crust sample B1

Figure A-36. DTA cooling curve of crust sample B2
Figure A-37. DTA cooling curve of crust sample B3

Figure A-38. DTA cooling curve of crust sample B4
Appendices

Figure A-39. DTA cooling curve of crust sample B5

Figure A-40. DTA cooling curve of crust sample B6
Figure A-41. DTA cooling curve of crust sample B7

Figure A-42. DTA cooling curve of crust sample B8
Figure A-43. DTA cooling curve of crust sample C1

Figure A-44. DTA cooling curve of crust sample C2
Figure A-45. DTA cooling curve of crust sample C3

Figure A-46. DTA cooling curve of crust sample C4
Figure A-47. DTA cooling curve of crust sample D1

Figure A-48. DTA cooling curve of crust sample D2
Figure A-49. DTA cooling curve of crust sample D3

Figure A-50. DTA cooling curve of crust sample E1
Figure A-51. DTA cooling curve of crust sample F1

Figure A-52. DTA cooling curve of crust sample F2
Figure A-53. DTA cooling curve of crust sample G1

Figure A-54. DTA cooling curve of crust sample G1
Figure A-55. DTA cooling curve of crust sample G2

Figure A-56. DTA cooling curve of crust sample G2
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