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Investigation of Cryolite Ratio Measurement by Potentiometric Methods

A thesis presented in partial fulfilment of
the requirements for the degree of
Masters of Technology in Chemical Technology
at Massey University, Palmerston North,
New Zealand.

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2002

Abstract

The cryolite ratio of an industrial aluminium electrolyte can effect many variables within the process including the overall energy efficiency. Careful control of the cryolite ratio is therefore very important. Currently no online measurements of the cryolite ratio are used in industry.

The use of potential measurements between a sodium alloy electrode and an aluminium electrode, as a means of cryolite ratio measurement was investigated. The observed potential changes during cryolite ratio step changes were typically of the correct direction and of similar magnitude to the predicted potential changes calculated from activity data.

The cryolite ratio of the electrolyte was found to change continuously during experiments. This was mainly due to the evaporation of $NaAlF_4$, which was identified by X-ray diffraction. This change in the cryolite ratio meant that long term stability of the electrodes was difficult to accurately quantify.

Electrode damage was found to occur after several hours of use and was contributed to the intrusion of electrolyte into the porous boron nitride used as the electrode body. Furthermore the activity of the sodium alloy electrode was found to change significantly during experiments due to the loss of sodium into the electrolyte. This damage to the electrodes is thought to have effected the stability of measurements considerably.

Dropping metal electrodes were investigated as a possible means of overcoming the changes in electrode activity. The overall stability of the potential measured between a dropping Pb-Na electrode and an aluminium electrode was somewhat better than the stability of potentials measured between two static pool electrodes. Operating difficulties with the dropping Pb-Na electrode combined with the short lifetime of these electrodes makes these electrodes unsuitable for industrial use.

Some suggestions have been made for future electrode designs with single use designs recommended as the most viable option especially for industrial use.

Acknowledgements

I would firstly like to thank the relevant people for the following scholarships, which without I would not been able to carry out this work.

- Dick and Mary Earle Scholarship for Technology
- Masters Scholarship (Massey University)
- Massey Scholarship

I would also like to thank my supervisor Dr Richard Haverkamp, who first got me interested in this field and provided a lot of assistance during the project.

I also thank my parents who encouraged my scientific interests and supported me during my undergraduate degree and of course Sonia who has endured my interests and scientific babblings and provided constant love and support.

Aaron Marshall
February 2002

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1 Introduction & Literature Review

1.1 Introduction to the aluminium industry

1.1.1 Aluminium Production

Aluminium is produced by the electrochemical reduction of alumina (Al_2O_3) as shown by Equation 1.1.

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \qquad (1.1)$$

This reaction is performed industrially in the Hall-Héroult cell, named after Hall and Héroult who independently developed the current method of smelting aluminium in 1886. Figure 1.1 shows a schematic of the Hall-Héroult cell.

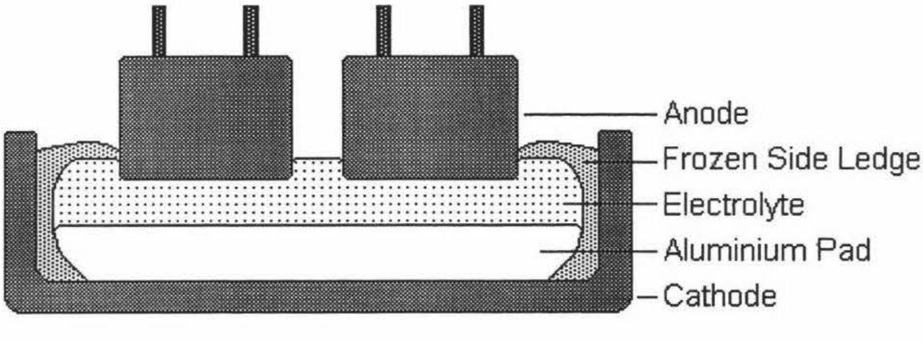

Figure 1.1 Hall-Héroult Cell Schematic

Total annual production of aluminium is reaching close to 24 million tonnes per year [1].

1.1.2 The Hall-Héroult Cell

The Hall-Héroult cell consists of 4 main components, the anode, cathode, aluminium pad, and electrolyte.

The anode is made from a mixture of petroleum coke and coal pitch, and provides the carbon for the reaction, as shown in Equation 1.1. Anodes can either be classified as Prebake or Söderberg anodes depending on their construction method. As the name suggests Prebake anodes are baked into a carbonaceous block before being placed into the cell. Söderberg anodes are baked in position, using waste heat from the cell. The anodes have conducting rods inserted into them, which provides the electrical current to drive the electrochemical reaction. The reaction oxidises carbon from the anode, which means the anodes must be continually lowered into the electrolyte or renewed to maintain the electrical contact with electrolyte.

Like the anode, the cathode is constructed from petroleum coke and coal pitch, also having steel conductor bars inserted through it to carry the electrical current from the cell. The cathode is not used up in the reaction, so it is only replaced once the high temperatures and corrosive electrolyte damage it. Because of the highly corrosive nature of the electrolyte a frozen ledge of electrolyte is allowed to form on the sides of the cathode to reduce the wear and damage.

The aluminium pad is simply the molten aluminium, which is produced during the process. The level of this liquid pad will increase continuously as the aluminium is produced. This means that the aluminium must be siphoned out by vacuum once the level exceeds a set height. Failure to remove the aluminium can result in the anode touching the aluminium pad causing short circuits. Some aluminium should always be present to minimise the wear of the carbon cathode from the corrosive electrolyte.

The electrolyte is where the reaction to reduce alumina takes place. The electrolyte should have the following characteristics to be successful for smelting aluminium.

- High alumina solubility
- Low aluminium solubility
- High electrical conduction
- Low raw material cost
- Higher decomposition voltage than alumina

Currently, only cryolite (Na_3AlF_6) based electrolytes are used for industrial aluminium electrolysis. Further detail on the electrolyte will be given in the following sections.

1.2 Electrolyte Composition

1.2.1 Industrial Electrolytes

As mentioned in the previous section the electrolyte is made up principally of cryolite (Na_3AlF_6). Most industrial smelter cells operate with the addition of aluminium fluoride (AlF_3), as well as calcium fluoride (CaF_2), and occasionally magnesium fluoride (MgF_2), sodium chloride (NaCl), and lithium fluoride (LiF) to improve cell performance. The electrolyte will also contain dissolved alumina (Al_2O_3) that undergoes reduction to produce aluminium.

1.2.2 Cryolite and Bath Ratio

The cryolite ratio (CR) is used to describe the composition of the electrolyte within the smelter cell. It is defined as the molar ratio of sodium fluoride to aluminium fluoride. For pure cryolite the cryolite ratio is equal to 3.

$$\mathrm{CR} = \frac{\text{moles NaF}}{\text{moles AlF}_3} \qquad (1.2)$$

Another term that is often used, is the bath ratio (BR). This is simply the mass ratio of sodium fluoride to aluminium fluoride. Due to the molecular masses of sodium fluoride and aluminium fluoride, the bath ratio is approximately half the cryolite ratio.

$$\mathrm{BR} = \frac{\text{mass NaF}}{\text{mass AlF}_3} \approx \frac{1}{2}\mathrm{CR} \qquad (1.3)$$

Because most cells operate with additions of AlF_3, excess AlF_3 weight percentages are often quoted.

1.2.3 Typical Composition of an Industrial Electrolyte

Typically, an industrial electrolyte consists of cryolite, 5-15 wt% AlF_3 [2,3], 2-5 wt% Al_2O_3 [2,3], and 3-8 wt% CaF_2 [3]. This corresponds to a cryolite ratio of approximately 2.1-2.65. Other additives, such as MgF_2, LiF, and NaCl [4] have also been used in industrial electrolytes

1.3 Effect of Electrolyte Composition on Smelter Cell Variables

The aim of this section is to show how the electrolyte composition can affect many important variables within an aluminium smelter cell. Due to the nature of this work the emphasis will be placed on how the cryolite ratio or excess AlF_3 concentration affects these variables.

As aluminium production has relatively low energy efficiency, the goal should be to maximise the overall energy efficiency of the process by careful selection and control of the electrolyte composition. This discussion will also consider how each variable can affect the energy efficiency of the overall process. It should be noted that many of the variables within a smelter cell are highly correlated and it is often difficult to accurately determine the effect of a single variable.

1.3.1 Liquidus, Superheat, and Bath Temperature

Due to the high temperatures used during aluminium smelting, this variable should be examined to some degree. There are three temperatures within a smelter cell that can be considered: Liquidus, Bath, and Superheat Temperature.

The liquidus temperature is simply the temperature at which the electrolyte melts. As Figure 1.2 shows, there is considerable variance in the liquidus temperature over the NaF-AlF_3 system. Typical industrial electrolytes have liquidus temperatures ranging from 930 to 985 °C (based on 1.2.3 and [5]).

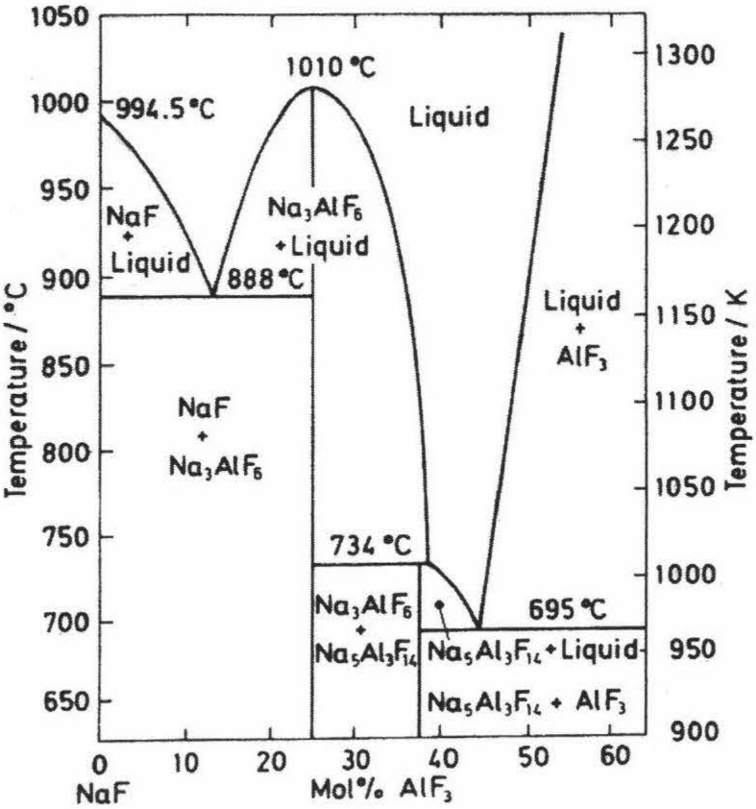

Figure 1.2 NaF-AlF$_3$ Phase Diagram [6]

The bath temperature is the actual temperature of the electolyte within the cell and is a result of the bath composition and thermal balance of the cell [7]. The bath temperature must be above the liquidus temperature for the electrolyte to be in a liquid state. The superheat temperature is the difference between the bath and liquidus temperatures. The superheat of the electrolyte is important when considering the thermal balance and therefore the side ledge of the cell [2,7-9].

Temperature of the bath has been shown to affect many other variables within the cell such as electrical conductivity [10], density of aluminium and electrolyte [11], and alumina dissolution rate [12,13]. It has also been shown that decreasing the cryolite ratio to lower the liquidus and bath temperatures, results in an increase of the current efficiency [14,15].

1.3.2 Alumina Solubility and Dissolution Rate

As the goal of the Hall-Héroult process is to produce aluminium, alumina must be dissolved into the electrolyte to enable the reaction shown by Equation 1.1 to proceed. This indicates that alumina solubility and dissolution rate are important variables when operating a smelter cell. It has been shown that the composition of the bath is an important factor in the dissolution rate of alumina [12,13] and alumina solubility [16]. Temperature has also been found to affect the dissolution rate of alumina [12,13]. Maintaining and controlling the dissolved alumina concentration is also important in reducing the occurrence of anode effects in the cell [17], which are characterised by rapid increases in the cell voltage and emission of greenhouse gases such as CF_4 and C_2F_6.

1.3.3 Aluminium Solubility and Re-oxidation

One disadvantage of cryolite based electrolytes, is the solubility of aluminium metal. The loss of aluminium by dissolution and then re-oxidation in the electrolyte melt corresponds to a significant loss in the current efficiency [4] (see 1.3.7). The re-oxidation of dissolved aluminium can occur via the following reactions (referred to as back reactions).

$$2Al + 3CO_2 \rightarrow Al_2O_3 + 2CO \qquad (1.4)$$

$$2Al + 3CO \rightarrow Al_2O_3 + 2C \qquad (1.5)$$

It has been shown that the cryolite ratio and the temperature [18] can affect the solubility of aluminium, and ultimately the current efficiency.

Equation 1.6 shows a correlation for the aluminium solubility as a function of bath composition and temperature [19].

$$\begin{aligned} DM = & -0.288 + 0.0003\,t + 0.027\,BR - 0.0019[CaF_2] \\ & -0.0036[LiF] - 0.0029[NaCl] \end{aligned} \qquad (1.6)$$

where: concentrations e.g. $[CaF_2]$ are in wt%

BR = Bath ratio

T = Temperature (°C)

DM =Dissolved Aluminium concentration (wt%)

1.3.4 Heat Balance and Side Ledge

The heat balance of the cell is a very important factor when both designing and operating a Hall-Héroult cell. Because of the highly corrosive nature of the cryolite based electrolyte a frozen side ledge must be formed to protect the side lining of the cell. This frozen side ledge is formed when the electrolyte temperature at the sides is below the liquidus temperature causing the electrolyte to solidify. This side ledge is rich in cryolite (CR = 3) so changes in the size of the side ledge effects the bulk composition of the bath. The heat balance of the cell (i.e. the balance between the heat loss and heat gain) affects the size of this side ledge.

To illustrate the effect which bath composition has on the side ledge and heat balance, the effect of an AlF_3 addition can be examined [7]. Upon an AlF_3 addition, the liquidus temperature of the electrolyte decreases. This will result in the superheat of the bath increasing, as initially the bath temperature will not decrease. This increase in superheat will cause some of the side ledge to be re-melted, resulting in the cryolite ratio of the electrolyte being higher than expected after the AlF_3 addition. The smaller side ledge will allow higher heat loss through the side lining eventually lowering the bath temperature and reforming more side ledge. During this change in the cells heat balance there will also be a number of other variable changes such as electrical resistance, aluminium solubility, density, and of course current and energy efficiency [7]. If the heat balance of the cell is not managed correctly, cell failure can arise from corrosion and thermal damage of the side lining.

1.3.5 Electrical Conductivity

As the reduction of alumina to aluminium is carried out electrochemically, the electrical conduction of the cell is very important in minimising the total electricity consumption. There has been much work carried out in this area with some very comprehensive reviews available [20]. The widely accepted Choudhary model for the electrical conductivity of cryolite-based electrolytes was developed over 25 years ago [21] (Equation 1.7).

$$\begin{aligned}\ln\kappa = {} & 2.0156 - 0.0207[\mathrm{Al_2O_3}] - 0.005[\mathrm{CaF_2}] - 0.0166[\mathrm{MgF_2}] \\ & + 0.0178[\mathrm{LiF}] + 0.0063[\mathrm{NaCl}] + 0.2175\mathrm{CR} - \frac{2068.4}{\mathrm{T}}\end{aligned} \qquad (1.7)$$

where: concentrations e.g. $[\mathrm{Al_2O_3}]$ are in wt%

CR = cryolite ratio

T = Temperature (K)

κ =electrical conductivity ($\mathrm{S.cm^{-1}}$)

There have been other models suggested [22], which also show that the cryolite ratio and concentration of other additives effect the electrical conductivity of the electrolyte.

1.3.6 Density

The density is a vital factor that can affect the performance of the Hall-Héroult cell [11]. The density of $\mathrm{NaF_3}$-$\mathrm{AlF_3}$ melts is shown at various temperatures (Figure 1.3).

The difference in density between the electrolyte and the aluminium pad has a major effect on the stability of the bath-metal interface [11]. At fixed bath compositions, the density difference increases with increasing temperature [11]. Bath composition also contributes to the density induced flow patterns found close to the side ledge [11].

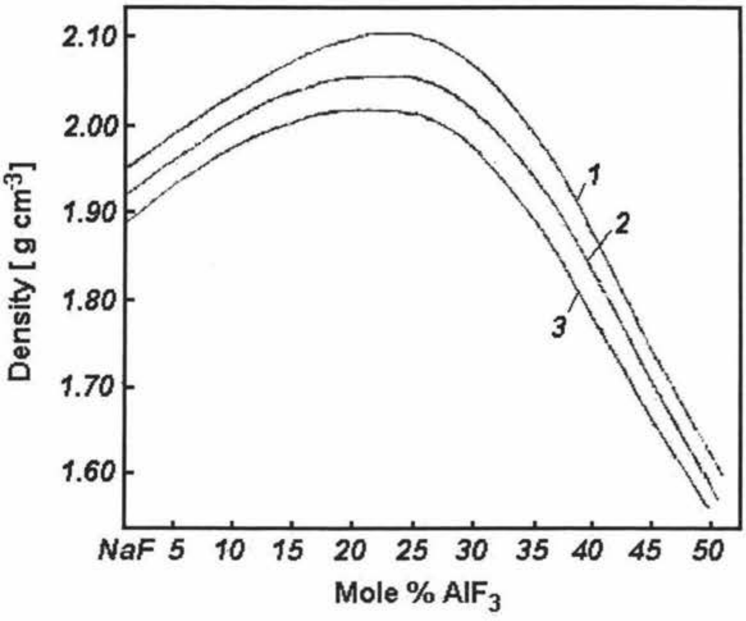

Figure 1.3 Densities of NaF-AlF$_3$ Mixtures [23], (1) 1000 °C, (2) 1050 °C, (3) 1100 °C

1.3.7 Current and Energy Efficiency

The previous sections have looked at how the bath composition, in particular the cryolite ratio, can affect many chemical and physical properties of the electrolyte. These properties are important when considering the current and energy efficiency of the process.

The current efficiency is defined as the ratio between the actual metal output (kg/Amp) and the theoretical aluminium output (kg/Amp). According to Faraday's law, the theoretical output of aluminium is calculated at 0.3354 g/Amp. Most industrial cells operate with high current efficiency values of between 85 % and 95% [24].

The energy efficiency is simply defined as the ratio of actual energy input (kWh/kg Al) and the theoretical energy required (kWh/kg Al). Using the thermodynamics for the reduction of alumina to aluminium it is found that the theoretical energy requirements are 5.64 kWh/kg Al for an isothermal process. Currently all industrial smelters operate with energy efficiencies below 50%.

Equation 1.8 gives the overall specific energy consumption.

$$E = \frac{2.980 * V}{x} \quad (1.8)$$

where: E = Specific energy consumption [kWh/kg Al]

V = Cell voltage

x = Current efficiency

As discussed in section 1.3.3, the current efficiency is primarily affected by the re-oxidation of dissolved aluminium. Bath temperature is considered to be one of the most influential variables that can be used to increase the current efficiency by reducing this re-oxidation rate [25]. Operating at low cryolite ratios, by the addition of AlF_3, is one way of reducing the liquidus temperature of the melt.

The cell voltage, which appears in Equation 1.8, is the result of three different contributions:

- The decomposition voltage which provides the energy for Equation 1.1
- Polarisation voltage at the electrode-electrolyte interfaces
- Voltage drops due to the resistance of cell components (electrodes, electrolyte etc.)

Section 1.3.5 described how the electrical conductivity of the electrolyte and therefore voltage drop, is affected by the bath composition and temperature. Improving the electrical conductivity can reduce the voltage drop and therefore increase the overall energy efficiency.

Bath composition, namely the cryolite ratio, is therefore a vital variable that can be used to maximise the current and energy efficiency of the smelting process.

1.4 Changes in the Cryolite Ratio

As shown in the previous sections the bath composition, especially the cryolite ratio, influences many variables within the Hall-Héroult cell. Therefore it is important to select an electrolyte composition that will optimise the process, to give high aluminium production rates with low operating and capital costs. However this selection of bath composition is not the end of the problem: the bath composition in industrial smelter cells continuously changes with time. Generally there is a net decrease in the AlF_3 concentration (i.e. a net increase in CR) with approximately 20 kg of AlF_3 consumed per tonne of aluminium produced [25]. Reasons for this change are given in the following sections.

1.4.1 Reactions of Electrolyte with Impurities

There are many impurities that enter the cell during the process of producing aluminium. These impurities include various metals oxides and usually enter the cell during the addition of alumina. The following equation shows how these impurities can react with the electrolyte to change the composition of the bath. This leads to a net decrease in the AlF_3 concentration.

$$6NaF.2AlF_3 + 3MO \rightarrow 3MF_2 + Al_2O_3 + 6NaF \qquad (1.9)$$

where: M is a divalent metal such as Ca or Mg

1.4.2 Reaction of Electrolyte with Moisture

Moisture can also enter the cell and react with the electrolyte. Equation 1.10 shows the reaction between cryolite and water, leading to a decrease in the AlF_3 concentration. Hydrogen fluoride is also released adding to the fluoride loss from the cell.

$$6NaF.2AlF_3 + 3H_2O \rightarrow 6HF + Al_2O_3 + 6NaF \qquad (1.10)$$

1.4.3 Side Ledge Changes

As discussed in paragraph 1.3.4, side ledge changes can effect the composition of the electrolyte, as the side ledge is rich cryolite. When this frozen ledge is re-melted or dissolved into the bulk of the electrolyte, it will increase the overall cryolite ratio of the cell. Likewise there will be a decrease in the cryolite ratio during the formation of the side ledge. It has been estimated that a change of ± 20% in the side ledge mass can effect the AlF_3 concentration by ± 2% for a certain cell type [26]. Side ledge changes occur when the heat balance of the cell is disrupted by events such as the anode effect, material addition to the cell, or cell voltage changes.

1.4.4 Evaporation and Dusting of Electrolyte Species

The evaporation of various electrolyte species can also change the composition of the bath. The major vapour species is considered to be $NaAlF_4$ [27], which will cause an increase in the cryolite ratio of industrial electrolytes. Hydrogen fluoride gas is another component found in the exhaust gas. This gas originates from the reaction between the electrolyte and water (Equation 1.10). Entrainment of electrolytic species in the anode gas is the other contributor to fluoride loss in industrial cells [27]. These entrained species may either be in a liquid or solid state.

1.4.5 Time Lag and Overfeeding

It has been reported that there is a time lag between the addition of AlF_3 and the resulting change in the AlF_3 concentration [28]. This time lag can be anywhere between several hours and several days in length [28,29]. Because of this time lag, cell operators can overreact to AlF_3 concentration measurements, resulting in excessive AlF_3 addition and eventually a lower than expected cryolite ratio [28]. This overreaction may also occur when the cryolite ratio gets to low and soda is added to correct the baths composition.

1.5 Electrolyte Composition Measurement

As discussed is section 1.4, the cryolite ratio of industrial electrolytes, continuously changes with time. Currently there is no in situ method for accurately measuring the cryolite ratio. As seen in section 1.3, the cryolite ratio affects many bath variables, so fast and accurate measurement of the cryolite ratio is important in order to control these variables. A brief description of various techniques used for cryolite ratio and bath composition measurements is given below.

1.5.1 Traditional Wet Chemical Analysis

There are many chemical methods that can be used to determine the cryolite ratio of the electrolyte. Typical methods include:

- Pyro-titration [30]
- Titration with $AlCl_3$ [31,32]
- Titration with $Th(NO_3)_4$ [31,32]

Pyro-titration is performed on acidic electrolyte samples (i.e. $CR< 3$) by first adding a known quantity of NaF to a molten sample. The excess AlF_3 present in the sample reacts with the newly added NaF, forming cryolite. The neutralisation point of the titration can be determined by dripping an indicator such as phenolphthalein or bromothymole blue on to a cooled portion of the sample. Once this neutralisation point is reached, the mass of NaF used in the pyro-titration can be used to calculate the excess AlF_3 percentage or cryolite ratio.

Volumetric titration of the cryolite ratio firstly involves the selective dissolution of NaF and AlF_3 containing compounds in a NaOH solution. A known excess of standardised NaF solution is added and the solution neutralised with HCl, followed by saturation with NaCl. The aluminium present in the solution forms cryolite, and the remaining excess F^- is titrated with an $AlCl_3$ solution while boiling, using eriochrome cyanamide as the indicator. This method is used for AlF_3 rich samples typically giving the cryolite ratio with an accuracy of ± 0.4 - 0.6 units [32].

The titration of excess F^- using thorium nitrate is another method of determining the cryolite ratio of an electrolyte sample. For samples rich in AlF_3, the sample is first sintered with a measured quantity of NaF at 600-800 °C for at least 20 minutes. During this process the excess AlF_3 is converted to cryolite. Depending on the cryolite ratio, the excess AlF_3 can be in the form of chiolite ($Na_5Al_3F_{14}$) ($1.65 < CR < 3$) or both chiolite and AlF_3 ($CR < 1.65$) [6]. If the electrolyte sample is basic ($CR > 3$) no sintering step is needed.

$$2Na_5Al_3F_{14} + 8NaF \rightarrow 6Na_3AlF_6 \qquad (1.11)$$

$$AlF_3 + 3NaF \rightarrow Na_3AlF_6 \qquad (1.12)$$

The sinter is finely ground and leached with water to dissolve the remaining NaF. The excess of F^- is titrated with $Th(NO_3)_4$, using sodium alizarin sulphonate as the indicator. This method gives highly reproducible results with a typical accuracy of ± 0.1 units [31,32]. The problems with this method arises from the sintering reaction which is required when analysing acidic electrolytes. At the high temperatures used in this sintering step, AlF_3 rich species such as $NaAlF_4$ can be lost as a vapour. This loss results in the measured cryolite ratio being overestimated.

These traditional chemical methods are generally time consuming and labour intensive due to the nature of the reactions involved, and can suffer from lack of reproducibility [32].

1.5.2 Instrumental Analysis

There are several instrumental techniques, which can determine the composition of the electrolyte. These include atomic absorption spectroscopy, x-ray diffraction, and x-ray fluorescence and Fluoride selective electrodes.

Atomic absorption spectroscopy is a very common technique of determining the concentrations of a wide range of elements in a solution, providing a relatively quick analysis of a sample using instruments that are relatively common in most laboratories. The benefit of atomic absorption spectroscopy is that no sintering or melting the sample is required.

Provided that the alumina content of a sample is known, the cryolite ratio could be calculated simply by analysing a solution containing the dissolved electrolyte sample, for both sodium and aluminium. Other compounds including calcium, magnesium and lithium fluoride could also be measured this way.

A method has also been described where by the excess aluminium fluoride is first reacted with potassium chloride in the presence of fluoride ions, as shown by Equation 1.13 [33].

$$\mathrm{AlF_3 + KCL_{excess} + F^- \rightarrow K_3AlF_6 + KCl} \qquad (1.13)$$

Once the reaction is complete, the remaining potassium chloride is determined by flame atomic absorption spectroscopy. This method enabled cryolite ratios between 2.4 and 3 to be determined, with a standard deviation of ± 0.9-3.4% [33]. This method may be considered simpler than other atomic absorption techniques as only potassium needs to be analysed and the alumina content does not need to be known.

X-ray diffraction and x-ray fluorescence are considered more useful than the other instrument techniques as the analysis can be performed directly on solidified samples taken from the bath [32]. X-ray diffraction identifies compounds from characteristic diffraction patterns each compound produces. The intensity of the peaks within the diffraction pattern is related to the amount of that particular compound present in the sample. When a sample of electrolyte is taken from the bath, a range of crystalline compounds form upon cooling, as shown below [32].

• Cryolite	(Na_3AlF_6)
• Chiolite	($Na_5Al_3F_{14}$)
• Calcium Cryolite	($NaF.CaF_2.AlF_3$)
• Fluorite	(CaF_2)
• Sodium Fluoride	(NaF)
• Alumina	(Al_2O_3)
• Lithium Cryolite	(Li_3ALF_6)
• Aluminium Fluoride	(AlF_3) at CR < 1.65 [6]

The cryolite ratio can be determined by comparing the intensities of a certain cryolite peak and a peak from chiolite, as the majority of excess AlF_3 crystallises as chiolite [32]. An internal standard method of determining the cryolite ratio by x-ray diffraction has also been discussed and showed good agreement with a titration technique [34]. However when electrolytes with high AlF_3 concentrations (above 24wt%), are solidified, AlF_3 is also crystallised, making this method unsuitable these electrolytes [35].

X-ray fluorescence may be used to determine the concentration of elements within the electrolyte. Like x-ray diffraction the solid sample must be prepared in a consistent way to ensure results are comparable. There are also some inter-elemental effects, which must be considered when analysing the result. X-ray fluorescence has been successful in determining the cryolite ratio, CaF_2, and Al_2O_3 concentration of low temperature electrolytes [35].

Fluoride selective electrodes are another way that the cryolite ratio of an electrolyte sample can be determined [30,36]. Fluoride selective electrodes provide a potential response to the free F^- present in a solution, which is typically logarithmic in respect to concentration.

For acidic ($CR<3$) samples, the excess AlF_3 is reacted with NaF to produce cryolite before the remaining sodium fluoride is determined using the fluoride selective electrode. This reaction can be performed in aqueous solutions [36] or by sintering the sample with the sodium fluoride at high temperature as shown by equations 1.11 and

1.12 [30]. Sintering at high temperature can result in the volatilisation of AlF_3 rich species, so this needs to be considered. Once the excess AlF_3 has reacted, the potential of the solution is measured using a fluoride selective electrode. The potential is compared to a standard curve to determine the quantity of NaF remaining, allowing the cryolite ratio to be calculated. This method has been found to give results in good correspondence to other methods such as X-ray diffraction [36], pyro-titration and the thorium nitrate titration [30].

1.5.3 Using other Bath Variables

From measurements of bath and liquidus temperature, it is be possible to calculate the cryolite ratio provided the content of alumina and other additives is known. Temperature measurements have been used for calculating the excess AlF_3 concentration in industrial cells [25,37-39]. There are probes available for liquidus temperature [40] and alumina content [41] measurement in industrial cells. This method of cryolite ratio measurements could be developed further although currently liquidus temperature and alumina content measurements are not widely performed in industrial cells. A method utilising differential temperature measurement has also been suggested as a method by which the cryolite ratio or alumina content can be measured [42]. Bath resistance has also been used in a model to control the AlF_3 content of industrial electrolytes [25].

1.5.4 Electrochemical Measurement

Electrochemical measurements of cryolite ratio changes, have been made in cryolite-alumina melts using liquid aluminium and sodium alloy electrodes [3]. The galvanic cell used for measuring the cryolite ratio is shown below.

$$\mathrm{Al} / \mathrm{NaF} - \mathrm{AlF_3} - \mathrm{Al_2O_{3(sat)}} / \mathrm{Pb} - \mathrm{Na}_{(xNa\approx 0.05)} \qquad (1.14)$$

This corresponds to the following overall cell reaction:

$$3\text{NaF} + \text{Al} \rightarrow 3\text{Na} + \text{AlF}_3 \qquad (1.15)$$

with the following Equation describing to potential between the electrodes:

$$E = E^0 - \left(\frac{RT}{nF}\right)\ln\left(\frac{(a_{\text{AlF3}})(a_{\text{Na}})^3}{(a_{\text{NaF}})^3(a_{\text{Al}})}\right) \qquad (1.16)$$

where: E = Potential difference between electrodes [V]
E^0= Standard Potential of the cell [V]
R = Gas constant, 8.314 [J/mol.K]
T = Temperature [K]
n = Number of electrodes involved
F = Faraday constant, 96490 [C/mol]
a_x = activity of species x

Assuming the activities of the aluminium and sodium electrodes remain constant this equation simplifies to:

$$E = E_c - \left(\frac{RT}{nF}\right)\ln\left(\frac{(a_{\text{AlF3}})}{(a_{\text{NaF}})^3}\right) \qquad (1.17)$$

where: E_c is a constant potential term

This shows that a change in the ratio of the AlF_3 and NaF activities (i.e. a change in the cryolite ratio) will correspond to a change in the measured potential between an aluminium and sodium alloy electrode.

The basic equipment set-up used for these electrochemical measurements is shown in Figure 1.4.

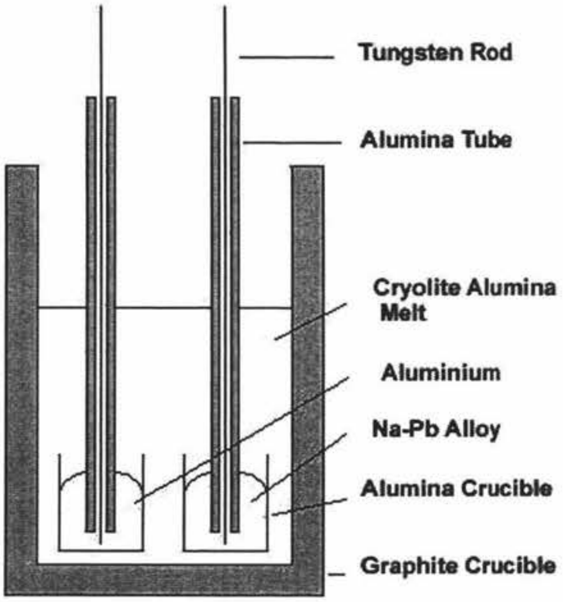

Figure 1.4 EMF cell set-up [3].

The results from this work showed that the potential could indeed be used to measure the cryolite ratio changes, however problems with the stability of the electrodes were found [3]. The activities of the electrodes, in particular the sodium alloy electrode, were found to change with time [3]. This was suggested to be due to the dissolution of sodium into the molten electrolyte [3]. Aluminium was also found within the sodium alloy electrode and is believed to be due to the reaction shown by Equation 1.18 [3].

$$3\text{Na} + \text{AlF}_3 \rightarrow 3\text{NaF} + \text{Al} \qquad (1.18)$$

Although the liquid pool electrodes have stability problems in cryolite-based melts, it is believed that electrochemical measurement of the cryolite ratio is possible, provided that stable electrodes can be constructed. The benefit of an electrochemical method to determine the cryolite ratio would be the speed and ease of obtaining the results.

Several other workers [43] have carried out other electrochemical measurements in cryolite-based melts using galvanic cells. One such cell as shown below was used to measure the activity data for the NaF-AlF_3-Al_2O_3 system [44].

$$\text{Pb-Na} / \text{Na}_3\text{AlF}_{6\,(l)}\ \alpha\text{-Al}_2\text{O}_{3\,(sat)} / \alpha\text{-Al}_2\text{O}_3 / \text{NaF}_{(l)}\ \text{AlF}_{3\,(diss)}\ \alpha\text{-Al}_2\text{O}_{3\,(sat)} / \text{Pb-Na} \qquad (1.19)$$

The cell shown in Equation 1.19 gave quite stable potential measurements for cryolite ratios above 2, and the potential was found to be a linear function of the cryolite ratio [44]. The sodium-lead alloy used was found to be a reliable sodium electrode with the relative change of the measured potential being typically ±0.1 mV/hr [44].

Activity data for AlF_3 and NaF in cryolite based melts have been reported in literature to some degree [44-47]. These activity measurements will enable the theoretical potentials or potential changes to be calculated, for cells similar to those shown by equation 1.14. The activity of NaF and AlF_3 has been calculated as a function of the cryolite ratio (Figure 1.5).

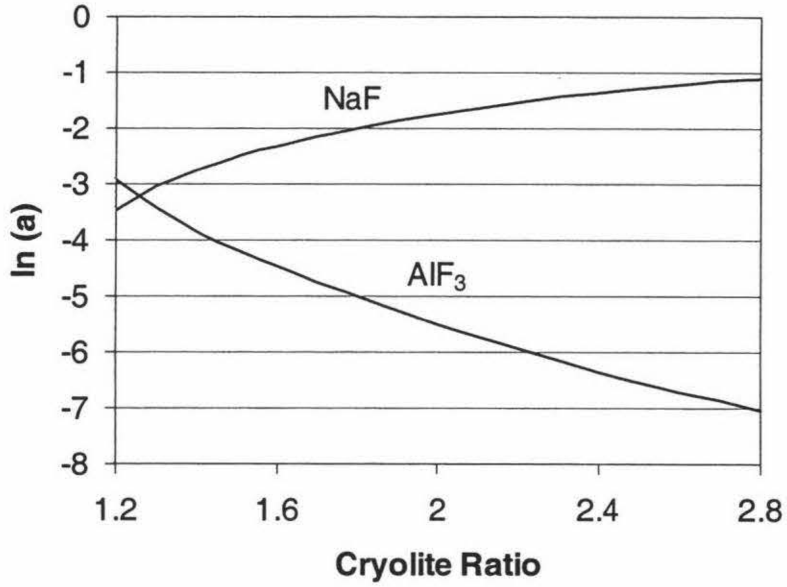

Figure 1.5 Activity of NaF and AlF_3 in the NaF-AlF_3 system, as a function of CR at 1300 K [46]

1.6 Electrodes for Electrochemical Sensors

As discussed above, it is critical that stable electrodes are used when constructing a system to make potentiometric measurements of the cryolite ratio. In order to test electrode stability the potential between the electrode in question, and an electrode that is known to be stable must be measured. Provided that this measured potential is stable over some period the electrode can be considered stable. If a stable test electrode does not exist, the electrode in question should be compared to another identical electrode [48]. Variation from a potential difference of zero indicates a lack of stability.

1.6.1 Liquid Metal Electrodes

As discussed in section 1.5.4, electrodes constructed using static pools of liquid metal have been partly successful for electrochemical measurements in laboratory cells [3]. These can suffer from dissolution and contamination reactions (Equation 1.18), which prevents these electrodes, particularly liquid sodium alloy electrodes, from remaining stable over any extended period in cryolite melts. It has been shown that aluminium electrodes constructed using a wetted molybdenum hook design, have good stability in cryolite melts [48]. Several authors [48,49] have also described liquid aluminium electrodes where the aluminium is allowed to sit above a density-modified bath containing high levels of BaF_2.

1.6.2 Gas Electrodes

Gas electrodes have been successfully used to determine the activity of species within a cryolite melt [43]. These electrodes usually incorporate a platinum wire or carbon rod, over which a gas such as oxygen, carbon monoxide, or carbon dioxide is flushed. It is felt that these electrodes should be avoided due to difficulties when used in industrial cells [3].

1.6.3 Solid Electrodes

There are some solid electrodes that have been used for electrochemical measurements in cryolite based melts [43]. These electrodes can be constructed from various metal oxides and aluminium alloys [43]. These electrodes are reported to suffer from corrosion and stability problems, due to the extreme conditions found in industrial electrolytes.

1.6.4 Dropping Metal Electrodes

Dropping metal electrodes have been used in electrochemical experiments since Kucera first developed them in 1903 [50]. They have traditionally been used for polarography, which was developed by Heyrovsky in 1922 [51]. Polarography is linear sweep voltammetry, carried out at a dropping electrode. This electrode consists of a reservoir and a fine capillary (ID < 1 mm), from which the liquid metal is allowed to drip into the electrolyte (Figure 1.6). The drop of metal provides the electrical contact with the electrolyte.

Polarography allows the changes in current resulting from the electrolysis of a solute, to be followed by a dropping electrode and an increasing applied voltage [52]. As the voltage sweeps, there will be a point at which a metal ion will be reduced. As this occurs the current increases sharply until the diffusion-limited current is reached at which point the current levels off [53]. Small polarographic maxima can also be observed in the polarogram, when the current exceeds the diffusion-limited current for a short period. This is suggested to be due to the streaming or convection of the electrolyte around the growing electrode drop [53]. These polarographic curves have been widely used for quantitative analysis of both inorganic and organic solutes [53] as well as analysis of molten salts [54].

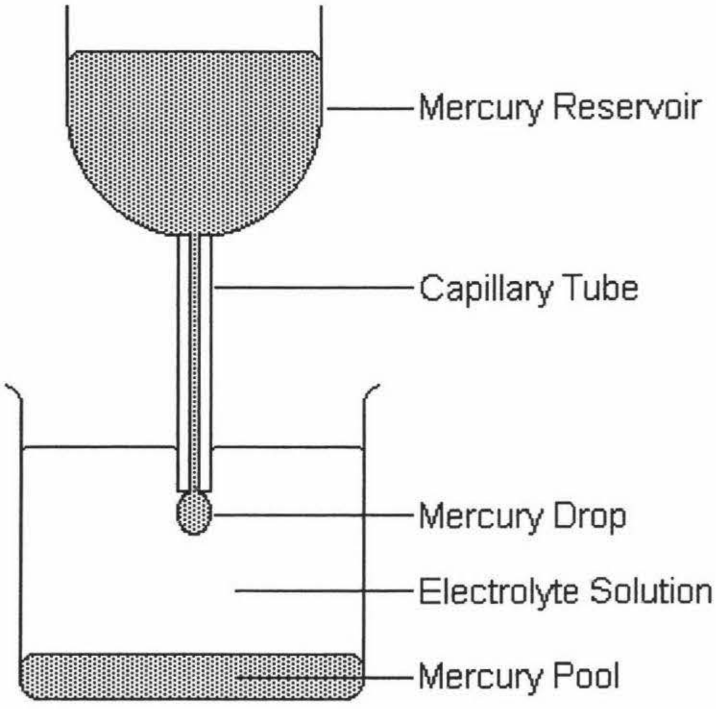
Mercury Reservoir
Capillary Tube
Mercury Drop
Electrolyte Solution
Mercury Pool

Figure 1.6 Dropping Metal Electrode Schematic

Dropping metal electrodes usually use mercury as the electrode metal, as this is liquid at room temperature, although molten metals such as lead [55,56], bismuth [55,57] silver [57,58] and gold [57] have been used at higher temperatures.

The benefit of using dropping metal electrodes is the continuously renewing electrode surface at the drop-electrolyte interface. This means that reactions between the electrolyte and the electrode metal do not affect the activity of the electrode, as any surface contamination or dissolution is lost when the drop falls away from the capillary.

The Hagen-Poiseuille Equation, as shown below, gives the flow rate of liquid metal from the capillary tube.

$$\mathrm{m} = \frac{\pi \mathrm{r}^4 \rho \mathrm{P}}{8 \mathrm{l} \eta} \qquad (1.20)$$

where m = Mass flow rate of liquid metal [kg/s]
r = Internal radius of capillary [m]
ρ = Density of liquid metal [kg/m^3]
P = Pressure of liquid metal head [Pa]
l = Length of capillary [m]
η = Viscosity of liquid metal [Pa.s]

The drop's formation will be restricted due to the surface tension of the electrolyte-metal interface. This is described as the back pressure on the drop, as given by Equation 1.21.

$$\mathrm{P}_{\mathrm{back}} = \frac{2\gamma}{r} \qquad (1.21)$$

where: $\mathrm{P}_{\mathrm{back}}$ = Back pressure on drop [Pa]
r = radius of drop at any time [m]
γ = electrode-metal surface tension [N/m]

In most applications of dropping metal electrodes, the electrode is designed to give 10-60 drops/min [53] at an overall flow rate of 1-4 mg/sec [52]. There are some methods that have been used to control the dropping rate or flow rate of metal, by using mechanical drip dislodges [59], and pressure head control [52,56,57]. There are several texts available that fully cover polarography and polarographic techniques [52,59].

Currently it is believed that dropping metal electrodes have only been used in electroanalytical techniques where a signal such as a voltage is actively applied to the cell in order to measure a response. They have not been utilised in a galvanic or passive cell set-up in order to measure the potential between two electrodes such as in potentiometry.

This type of electrode may be useful in a system to make potentiometric measurements of the cryolite ratio. The discussed activity changes of the sodium electrode could be avoided, if a sodium alloy is used as the metal in the dropping electrode.

1.7 Objectives of Work

As shown by section 1.3 the cryolite ratio, can effect many variables with an industrial smelter cell, including the overall efficiency of the aluminium production process. Currently only laboratory based methods such as X-ray diffraction, are used to measure the cryolite ratio. As these methods have a time lag between sampling and measurement, cryolite ratio control based on these methods is difficult. A sensor that can measure the cryolite ratio in situ would greatly improve the ability for cryolite ratio control.

The Objectives of this work are as follows:

- Develop liquid metal electrodes for electrochemical cells
- Investigate cryolite ratio measurement using electrochemical cells
- Develop dropping metal electrodes for cryolite melts
- Investigate dropping metal electrodes in electrochemical cells