A study of scale formed in the Bayer process

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- A Master's Thesis. Submitted in partial fulfilment of the requirements for the award of Master of Philosophy of Loughborough University.

Metadata Record: [https://dspace.lboro.ac.uk/2134/12950](https://dspace.lboro.ac.uk/2134/12950)

Publisher: © H. Chester

Please cite the published version.
This item was submitted to Loughborough University as an MPhil thesis by the author and is made available in the Institutional Repository (https://dspace.lboro.ac.uk/) under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
Please note that fines are charged on ALL overdue items.
A Study of Scale Formed in The Bayer Process.

By

Helen Chester.

A Thesis submitted
in partial fulfilment for the award of

Master of Philosophy of Loughborough University

Department of Chemistry,
Loughborough University,
Loughborough,
Leicestershire,
LE11 3TU.

Dedicated to Mum and Dad.

To aiming high.
Abstract.

This thesis describes an investigation into the problem of aluminosilicate scales formed as a by-product of the industrial extraction of alumina from bauxite ore. Three distinct zeolite scales with different morphologies have been identified; the type of scale depending on the temperature, caustic concentration and type of plant. These scales have been characterised using powder X-ray diffraction, scanning electron microscopy and infra-red spectroscopy.

Synthetic scale was formed at three different temperatures 90, 145 and 220 °C and treated with acid to mimic the behaviour of the three different phases found in the plant during acid cleaning. Mineral acids (sulfuric, nitric and hydrochloric) were added to the three individual scales at 30 and 60 °C for 30 minutes and the amount of scale dissolved was ascertained by back-titration against 2M sodium hydroxide.

The causticity of Bayer liquor varies from plant to plant depending on the composition of the bauxite ore. The effect of the variation from high caustic 300 g/l, through medium causticity 250 g/l to low causticity 210 g/l was investigated, in terms of yield, type of phase formed and rate of phase formation at different temperatures.

The behaviour of the three zeolitic scales varies under dry conditions due to the differing water content of the zeolites. The removal of the water from plant scale resulted in the sample faulting along well-defined planes within the scale, due to incomplete removal of scale and build-up of acid dissolution product. The thermal behaviour of the scales have been investigated by mimicking drying conditions using the HK1200 furnace attached to the Bruker D8 diffractometer.
Acknowledgements.

Firstly I would like to thank Alcan International, without their funding this thesis would not have been possible. I would like to thank my supervisors Sandie Dann for her direction and support, and Robin Furneaux for his knowledge and focus. Thank you both for your encouragement.

I would like to thank my family for their unconditional support and love, thanks Mum, Dad, Tom, Jude, and not forgetting the grandparents. I would especially like to thank David for his support, encouragement and lengthy phone calls, which were a godsend. But more recently your unconditional love and support have aided my completion. Thank you so much!!

To my fellow lab companions Sarah, Julia, The infamous Dr Kelly, Richard, Duncan, Richard, Katie, Jenny, Liam, Martin, Pious, Sean and Sandrine, thank you for the camaraderie and banter it will never be forgotten.

A huge thank you should go to Pauline, your list of talents is endless, so thank you for everything.

Finally, thanks also goes to Frank Page for SEM micrographs of outstanding quality and enlightening conversations that I will never forget.
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title Page.</td>
<td>i.</td>
</tr>
<tr>
<td>Declaration.</td>
<td>ii.</td>
</tr>
<tr>
<td>Dedication.</td>
<td>iii.</td>
</tr>
<tr>
<td>Abstract.</td>
<td>iv.</td>
</tr>
<tr>
<td>Acknowledgements.</td>
<td>v.</td>
</tr>
<tr>
<td>Contents.</td>
<td>vi.</td>
</tr>
<tr>
<td>List of Figures.</td>
<td>vii.</td>
</tr>
<tr>
<td>List of Tables.</td>
<td>ix.</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>x.</td>
</tr>
<tr>
<td>Chapter One: Introduction.</td>
<td>1.</td>
</tr>
<tr>
<td>Chapter Two: Methodology.</td>
<td>19.</td>
</tr>
<tr>
<td>Chapter Three: Synthesis and Characterisation of model scale compounds.</td>
<td>26.</td>
</tr>
<tr>
<td>Chapter Four: Acid Dissolution.</td>
<td>33.</td>
</tr>
<tr>
<td>Chapter Five: The Effect of Liquor Causticity on Scale Formation.</td>
<td>46.</td>
</tr>
<tr>
<td>Chapter Six: Variable Temperature XRD Study.</td>
<td>55.</td>
</tr>
<tr>
<td>References.</td>
<td>70.</td>
</tr>
</tbody>
</table>
List of Figures.

1.1. Schematic Diagram of a Zeolite. 2.
1.2. The Sodalite Cage. 3.
1.3. Zeolite A Containing the Sodalite Cage as a Building Block. 3.
1.4. Schematic Representation of the Bayer process. 7.
1.5. The Structure of Cancrinite. 11.
1.6. The Effect Sodium Carbonate Concentration on Scale Formation 14.
2.1. Slice through a Hydrothermal Bomb. 20.
2.2. Output from an X-ray tube. 21.
2.3. Schematic Diagram of a Powder X-ray diffractometer. 22.
2.4. Diagram showing Some Different Stretching Modes for an Angular Triatomic Molecule. 24.
3.1. FT-IR spectra of the Three Aluminosilicate Phases formed at Different Temperatures using NaOH Solution. 28.
3.2. Powder XRD patterns of the Aluminosilicate Scales formed at Different Temperatures using NaOH Solution. 29.
3.4. SEM Micrograph of Cancrinite. 31.
3.5. SEM Micrograph of the Intermediate phase. 31.
3.6. SEM Micrograph of Sodalite. 32.
4.1. Moles of Scale Dissolved in 10% (1.8M) Sulfuric Acid at Different Temperatures. 35.
4.2. Moles of Scale Dissolved in 10% (1.1M) Nitric Acid at Different Temperatures. 36.
4.3. Moles of Scale Dissolved in 10% (1.2M) Hydrochloric Acid at Different Temperatures. 37.
4.4. Comparison of Scale Dissolved at Different Temperatures using 10% (1.8M) Sulfuric Acid by Chester (Set A) and Riley (Set B) 38.
4.5. Comparison of Scale Dissolved at Different Temperatures using 10% (1.1M) Nitric Acid by Chester (Set A) and Riley (Set B) 39.
4.6. Moles of Scale dissolved at Different Temperatures in Sulfuric Acid
using the Batch Scale (method 1) and Cone and Quarter (method 2) Methods.

4.7. Moles of Scale dissolved at Different Temperatures in Nitric Acid using the Batch Scale (method 1) and Cone and Quarter (method 2) Methods.

5.1 Powder XRD Patterns showing the Loss of Kaolinite from the Reaction Product with Time.

5.2. Graph to show the Yield of Scale at 220 °C as a Function of Time

5.3. Graph to show the Yield of Scale at 145 °C as a Function of Time.

5.4. Graph to show the Yield of Scale at 90 °C as a Function of Time.

5.5. Yield of Scale at High Caustic Concentration as a Function of Time

5.6. Yield of Scale at Medium Caustic Concentration as a Function of Time

5.7. Yield of Scale at Low Caustic Concentration as a Function of Time

6.1. XRD patterns of Cancrinite with Increasing Temperature.

6.2. XRD patterns of Intermediate Phase with Increasing Temperature.

6.3. XRD patterns of Sodalite with Increasing Temperature.

6.4. XRD patterns of High Temperature Scale with Increasing Temperature.

6.5. XRD patterns of 39c Kirkvipe Works Heater Scale with Increasing Temperature.

6.6. XRD patterns of AAL 9c scale with Increasing Temperature.

6.7. XRD pattern Comparison of Cancrinite and Plant Scales at 27 °C.

6.8. XRD pattern Comparison of Cancrinite and Plant Scales (High Temperature)


6.10. Identification of Decomposition Product from the Thermal Treatment of Sodalite.
List of Tables.

1.1. Typical Composition of Bayer Plant Spent Liquor. 13.
2.1. IR data for Aluminosilicate Scales / cm$^{-1}$. 25.
3.1. IR data for Aluminosilicate Scales / cm$^{-1}$. 27.
3.2. Positions of the Major Reflections for the Aluminosilicate Scales. 30.
4.1. Moles of Aluminosilicate Scale Dissolved in 10% (1.8M) Sulfuric Acid. 34.
4.2. Moles of Aluminosilicate Scale Dissolved in 10% (1.1M) Nitric Acid. 36.
4.4. Moles of Aluminosilicate Scale Dissolved in 10% (1.2M) Hydrochloric Acid. 37.
4.5. Moles of Aluminosilicate Scales Dissolved in 10% (1.8M) Sulfuric Acid Reported by Riley. 38.
4.5. Moles of Aluminosilicate Scales Dissolved in 10% (1.1M) Nitric Acid Reported by Riley. 39.
4.6. Moles of Aluminosilicate Scales Dissolved in 10% (1.8M) Sulfuric Acid Using the Cone and Quarter Method. 40.
4.7. Moles of Aluminosilicate Scales Dissolved in 10% (1.8 M) Nitric Acid Using the Cone and Quarter Method. 41.
4.8 Formation of a Gel from a Cancrinite and Acid Solution. 43.
4.9 Formation of a Gel from Intermediate Phase and Acid Solution. 44.
4.10 Formation of a Gel from a Cancrinite and Acid Solution. 44.
5.1. The Yield of Precipitate at 220 °C. 45.
5.2. The Yield of Precipitate at 145 °C. 46.
5.3. The Yield of precipitate at 90 °C. 46.
## Abbreviations

The following abbreviations are used throughout this thesis.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom Unit, $10^{-10}$ m</td>
</tr>
<tr>
<td>cm$^{-1}$</td>
<td>wavenumber</td>
</tr>
<tr>
<td>°</td>
<td>degrees</td>
</tr>
<tr>
<td>°C</td>
<td>degrees centigrade</td>
</tr>
<tr>
<td>cm/week</td>
<td>centimetre per week</td>
</tr>
<tr>
<td>DSP</td>
<td>De-silication product</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transform</td>
</tr>
<tr>
<td>g/l</td>
<td>grams per litre</td>
</tr>
<tr>
<td>IR</td>
<td>infra-red</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>mm/week</td>
<td>Millimetre per week</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>wt/vol</td>
<td>Weight per volume</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction.</td>
</tr>
<tr>
<td>PSD</td>
<td>Position Sensitive Detector</td>
</tr>
</tbody>
</table>
Chapter One

Introduction

1.1 Zeolites

Zeolites are a major group of inorganic materials, many of which are naturally occurring. They are named after their capacity to evolve water when heated; the Greek zeo 'to boil' and lith meaning 'stone' giving 'zeolite'. These materials are widely used for their ion exchange, absorption and catalytic properties. Zeolites have been recognised for several centuries, but it was due to the work of J M Barrer\(^1\) in the late 1940's that they first came to prominence.

The zeolitic structure consists of a framework that can form channels or cavities, which are large enough to incorporate small inorganic and organic molecules. The framework is constructed from linked tetrahedra, the most common examples of which are \(\text{AlO}_4\), \(\text{SiO}_4\), \(\text{BO}_4\), \(\text{PO}_4\) and \(\text{GaO}_4\). However, most zeolite materials are solely based on silicon and aluminium \(\text{MO}_4\) units. At present over 200 aluminosilicate framework structures are known, with approximately forty naturally occurring. The general formula may be derived from silica in which all the silicon atoms are vertex-linked. If some of the \(\text{SiO}_4\) tetrahedra are replaced with \(\text{AlO}_4\) tetrahedra, the charge balance must be maintained by the incorporation of cations into the structure. These neutral structures are frequently hydrated leading to the formula given in the expression below.

\[
\{\left[\text{M}^{n+}\right]_{x/n} [\text{mH}_2\text{O}]\} \{\left[\text{AlO}_2\right]_x \left[\text{SiO}_2\right]_{1-x}\}
\]

A schematic diagram of a zeolite structure with cavities and cations is shown in Figure 1.1. If the zeolite is dehydrated, the cations migrate to the edges of the channels and this achieves better co-ordination to the framework oxygen atoms. This means that dehydrated zeolites can absorb small molecules as well as the water. The larger the pores, the larger a molecule it can absorb.
1.2.1 Absorption

The open framework of the structure allows molecules to be absorbed into their structure. The size and shape of the molecules absorbed depends on the pore size of the zeolite. The ability of the zeolite to absorb water depends on the Al:Si ratio. When the ratio is 1:1 (the highest possible for zeolites synthesised hydrothermally) water is absorbed readily. However as the silicon content increases, the pores become hydrophobic and start to absorb non-polar solvents preferentially.

1.2.2 Löwenstein’s Rule

Löwenstein’s Rule states that the formation of Al-O-Al links is thermodynamically un-favoured. This means that, because the majority of zeolites are formed using low temperature hydrothermal methods, they have ordered frameworks with no Al-O-Al link and the highest Si:Al ratio is 1:1.
1.2.3 Structure

The tetrahedral MO₄ units link together in numerous ways to form different sized rings, which then form the 3D framework structures. The flexibility of the M-O-M links allow tilting of the framework tetrahedra in order to incorporate cations of different sizes inside the zeolite framework. The most common zeolite structural unit is composed of 4 and 6 membered rings and is called the sodalite cage as shown in Figure 1.2. This β cage is the building block of other zeolites, for example Zeolite A (see Figure 1.3).

Figure 1.2: The Sodalite Cage.

Open circles are tetrahedral framework atoms and the lines between them represent T-O-T links

Figure 1.3: Zeolite A Containing the Sodalite Cage as a Building Block.
1.2.4 Ion Exchange

Approximately 60% of commercially utilized zeolites are used for ion exchange. An example of this is clinoptilolite, which is used by BNFL in radioactive water treatment. Sodium zeolites are used in washing powders as they rapidly exchange their sodium ions with the divalent hard water ions at room temperature. This is shown in Equation 1.1.

\[
\text{Na}^-\text{-Zeolite A} + \frac{1}{2}\text{Ca}^{2+} \rightarrow \text{Ca}_{3.5}^-\text{-Zeolite A} + \text{Na}^+
\]

\textit{Equation 1.1.}

1.2.5 Catalysis

H-zeolites, are acid derivatives of zeolites, which are excellent catalysts widely used in industry. The H-zeolites can be formed by ion exchange with weak acids, but since strong acids can cause the zeolite framework to breakdown, acidic zeolites are often formed by ion exchange with an ammonium salt followed by thermal degradation. Heating the ammonium zeolite at 500 °C results in decomposition of the ammonium cation, where ammonia gas is lost and a proton remains; this is shown in Equation 1.2.

\[
\text{Na-zeolite} \xrightarrow{\text{NH}_4^+} \text{NH}_4^-\text{-zeolite} \xrightarrow{500^\circ\text{C}} \text{H-zeolite}
\]

\textit{Equation 1.2.}

This catalytically active zeolite can either be Brønsted or Lewis acidic. Once generated the acidic zeolites can absorb molecules into the cavities and behave like a strong acid. H-zeolites are typically used in rearrangement and dehydration reactions.

1.3 Zeolites as by-products in Chemical Processes

Zeolites are unwanted by-products in several industrial chemical processes. During the production of alumina from aluminium ore (bauxite), aluminosilicate zeolites are produced as by-products of the Bayer Process (the production of alumina) in the process plant. The work in this thesis attempts to address this problem by investigating methods to reduce and remove these zeolitic scales.
1.3.1 Aluminium

Aluminium is the second most abundant metal in the earth's crust and is generally found deposited as the mineral, bauxite. The commercial production of aluminium metal is comprised of two processes. The first process was developed by Bayer, and involves the extraction of gibbsite or boehmite in bauxite ore, followed by its conversion to alumina by calcination; this is the Bayer process. The second is the electrolytic reduction of alumina to aluminium metal.

Aluminium has mechanical, physical and chemical properties, which makes it the material of choice for many products and industry sectors. Not only is it ductile and malleable, but also has excellent corrosion resistance and remains versatile when alloyed with other metals. Aluminium is also a good thermal and electrical conductor. When aluminium is recycled, it retains its metal quality in terms of ductility and strength. The aluminium industry initiated the recycling of aluminium primarily because it requires five percent of the energy costs to produce secondary aluminium compared to the energy required to produce molten aluminium from bauxite.

All commercial production of aluminium is based on the Hall-Heroult smelting process. An electrical current is passed through a molten solution of alumina and cryolite (sodium aluminium fluoride) in a series of reduction cells that are lined at the bottom with carbon cathodes. The carbon anodes are partially immersed into the molten solution. The electric current causes the oxygen from the alumina to combine with the carbon of the anode forming carbon dioxide gas. The molten aluminium settles, and is drawn off by a vacuum crucible into the furnaces where it is often alloyed and cast.

1.3.2 Bauxite

Bauxite is largely composed of a mixture of hydrous aluminium oxides and many impurities including iron oxides, silicates and clay minerals. The component aluminium-containing minerals of bauxite are very stable oxides, gibbsite Al(OH)₃, boehmite AIO(OH) and diaspore (which has the same composition as boehmite but is denser and harder), alone or in mixtures. Common mineral impurities are clays, haematite, goethite and quartz. The average grade of bauxite mined contains approximately 45% available alumina and 1.5% reactive silica.
The composition of bauxite varies depending on its country of origin. It can be found in most countries, but the largest deposits occur in the tropics. In 1994, three countries accounted for 60% of the world output of bauxite; Australia, Guinea and Jamaica. Of these, Australia is the World's largest producer of bauxite and alumina. Bauxite ores can vary enormously in their texture, where some can be soft, easily crushed and structureless, others can be hard, dense, and porous. Colour variation of the ore is largely dependent on the iron oxide content. They range from white, for pure hydrated alumina, through cream to dark brown, when the iron mineral content is higher.

1.3.3 The Bayer process

The Bayer process was patented by Bayer in 1887 and has become the main method for extracting gibbsite and boehmite from bauxite. This multiple stage process is shown schematically in Figure 1.4.

The bauxite is initially crushed into a fine powder in preparation for alumina leaching in the digesters. Bauxite ores are digested in sodium hydroxide at elevated temperatures of 150 – 255 °C. The digestion conditions vary to assist the optimum extraction of the alumina, depending on the mineralogical composition of the ore. The greater the amount of boehmite present, the higher the causticity and temperature needed to effectively digest the ore. Gibbsite requires a digestion temperature of ~140 °C, whereas the less soluble boehmite requires a higher digestion temperature. Silicate impurities also dissolve in the sodium hydroxide solution whilst the ore resides in the digesters. The rate of dissolution of the reactive silicon oxides is dependant on the temperature and increases as the temperature rises. The source of silicate is important; clay minerals are soluble throughout the digestion temperature range, whilst quartz only shows notable solubility at the higher temperatures.
Silicon-rich impurities, derived from the clay minerals and to a lesser extent quartz, are the most undesirable impurities in bauxite and must be removed by desilication. This process involves the formation of desilication product, (DSP) by the reaction of sodium hydroxide with silicate and aluminate species in solution to form sodium aluminosilicate. The need for desilication means that the material must be held at the digestion temperature long enough to allow the silicate impurities to react and hence precipitate the DSP. After digestion, the slurry is quickly cooled to 100 °C to allow DSP to precipitate. The DSP precipitate is removed, with a number of other impurities, as a red mud (named as a consequence of the colour imparted by the iron oxide impurities), before the remaining solution is cooled further and seeded to precipitate the gibbsite. The amount of DSP that precipitates, as part of the red mud, depends on the digestion temperature, since a higher digestion temperature increases the concentration of the silicate species in solution. In addition, titanate scales may also be produced at this point depending on the quantity of titanium in the bauxite ore.

Chapter One: Introduction.
Any undissolved bauxite residue remaining after digestion is also removed from the hydrate-rich solution by settling in the red mud. The red mud is filtered and washed to recover as much sodium hydroxide and gibbsite as possible for returning to the Bayer liquor.

After removal of the red mud, the resulting liquor, termed 'pregnant' as precipitation of alumina has not yet occurred, is cooled further to 60 – 80 °C to increase the supersaturation of gibbsite. It is then seeded with alumina and cooled again in the stirred tanks to initiate secondary isothermal nucleation. Precipitation is very slow, taking 24-60 hours to produce commercially acceptable crystals of gibbsite. This process is carried out in stages to precipitate the alumina hydrate \((\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O})\) that is separated by filtration and washed to remove the final traces of caustic soda and other impurities. The alumina hydrate produced is then calcined to remove the water by passing the solid through rotary kilns at ~ 1100 °C to convert to alumina. The final product, a fine white powder, is in excess of 99 % pure alumina. The caustic soda solution remaining (termed 'spent liquor') is recycled to be reused with fresh bauxite. Carbon dioxide is readily absorbed from the air into the caustic solution to form carbonate by reaction with hydroxide. The reaction is shown in Equation 1.3. Carbonate is also generated by the aerial oxidation of humic material that is often present in bauxite ore. The spent Bayer liquor is causticised by the addition of calcium oxide (lime) to convert as much of the sodium carbonate to sodium hydroxide as possible, to improve the digestion of bauxite.

\[
2\text{OH}^- + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_3^{2-}
\]

*Equation 1.3*

The spent liquor is recycled through the heat exchangers to reheat the liquor to the temperature required for bauxite extraction.

1.3.4 The Formation of Scale.

Spent Bayer liquor is reheated to the bauxite digestion temperature by passing through heat exchangers (mild steel pipes). This reheating results in the formation of the sodium aluminosilicate scale (essentially DSP) in the heat exchangers by the same reaction as observed during desilication, where the silicate and aluminate species in
solution react with sodium hydroxide and precipitate. There are two stages to scale formation

1. The scale forms by nucleation and growth from the solution, termed the ‘growth scale’
2. The scale forms by settling and sedimentation of slurry particles.

Nucleation can be the slow step in scale growth, however once the nuclei have formed, growth is very predictable and governed by kinetic factors. The cooler pipes and tank walls are favourable sites for nucleation. Growth scale is normally hard, brittle, highly crystalline and non-porous with developed crystal faces. The growth rate is in the range of 0.1 – 1.0 mm/week, and is readily predicted by the knowledge of temperature and liquor composition. The flow rate in the pipes promotes a denser uniform scale. The scale in the digestion tanks is frequently more porous and soft, however this scale forms more rapidly at a rate ~1.0 cm/week.

The scale forms in specific areas of the plant due to the change in the process conditions. High temperature and liquor supersaturation are model conditions for scale formation. The scale forms on the liquor side of the heat exchangers; although most of the DSP is removed in the red mud, the spent Bayer liquor is still supersaturated with residual silicon oxides. The reduction in dissolved gibbsite concentration of the liquor during gibbsite precipitation results in a decrease in silicon oxide solubility thus causing a rise in supersaturation. Higher temperatures increase the kinetics of scale formation; hence at the higher temperature end of the heat exchangers the scale formation becomes more of a problem. The sodium aluminosilicate scale formation on the heat exchanger surfaces causes restriction of liquor flow in the process vessels and pipes, loss of heater exchange efficiency and increased energy consumption. Due to this build up, the process usually has to be stopped for the heat exchangers to be cleaned. This represents a large percentage loss of production, the cleaning process also uses 10% wt/vol sulfuric acid which corrodes the mild steel pipes of the heat exchangers, lessening their life.
1.4 Types of zeolitic scale

1.4.1 Sodalite
Of all the known zeolites, the sodalite family is the largest and includes many subgroups such as hauynes \([M^{2+}]_2[M^+]_6[SiAlO_4]_6(SO_4^{2-})\) and noseans \([M^+]_8[SiAlO_4]_6(SO_4^{2-})\) which form naturally. The general formula of an aluminosilicate sodalite is \([M^+]_n[SiAlO_4]_6[X_m^x]^+\), where M and X are a wide range of cations and anions including \(M = Ca^{2+}, Na^+, Li^+\) and \(K^+\) and \(X = Cl^-, SO_4^{2-}\) and \(OH^-\). The sodalite structure consists of an aluminosilicate cage, constructed from four and six membered rings of vertex-linked tetrahedral aluminium and silicon atoms.\(^{12}\) The anion is placed centrally in the cage and is coordinated to four cations that are situated close to the six membered rings to allow coordination of the occluded cations to the oxygen atoms in the framework. For the majority of systems prepared at low temperature, the aluminium:silicon ratio is 1:1 and the framework is ordered. Such sodalites crystallise in the space group P-43n with a unit cell parameter, a \(> 8.9\) Å. Hassan\(^{13}\) explained that the network of large cages observed in sodalite based systems is due to an AB-BA-AB packing arrangement.

Gerson\(^{14}\) reported that precipitated scale analysed from low temperature Bayer plants operating at 150 °C was a sodalite-based system.

1.4.2 Cancrinite
Gerson\(^{14}\) also reported that the scale analysed from the higher temperature Bayer plants, operating at 255 °C, was cancrinite. Edgar\(^{15}\) stated that when cancrinite was prepared at temperatures \(\sim 200 \) °C it was hexagonal with unit cell dimensions of a = 12.69 ± 0.02 Å and c = 5.18 ± 0.02 Å and crystallised in the space group P6\(_3\). It was also reported that by looking down the c axis it was composed of identical layers of 12 atom rings stacked in an AB-AB packing arrangement. An example of this is shown in Figure 1.5. Zheng\(^{16}\) reported that the Bayer plant scale was similar to the precipitate formed in the synthetic reaction temperatures of \(>180 \) °C. In contrast, Barnes\(^{17}\) reported forming synthetic cancrinite at 90 °C using the same methodology as for producing synthetic sodalite. However, in this case reaction times were increased from 24 hours to 336 hours for this to occur which is very different from the
operating conditions in the Bayer plant. The likely cause of this reaction may be the absorption of significant quantities of carbon dioxide due to prolonged exposure to the air. Buhl reported that cancrinite can have stacking faults in the ABC sequence, and positional disorder with regards to the hexagonal translation. These faults result in a variation in the content of enclathrated carbonate and water molecules and slightly alters the structure.

Figure 1.5: The Structure of Cancrinite.
Projection down the c axis in cancrinite showing the hexagonal structure. Small open spheres are the tetrahedral framework atoms. Black spheres are oxygen framework atoms. The larger grey spheres are the sodium cations.

This disordered cancrinite is so named because it shows weak cancrinite reflections in the powder XRD pattern. This phase can be indexed with the typical unit cell of cancrinite, albeit having a smaller unit cell. Buhl found that disordered cancrinite forms at high temperatures (~200 °C) with very low carbonate concentrations. It is very difficult to distinguish between these two phases as they have very similar reflections in their powder XRD patterns. As a mixture, ordered and disordered cancrinite also cannot be successfully distinguished using their IR spectra. In both cases, characteristic absorptions are observed for the enclathrated carbonate species at 1410 and 1455 cm⁻¹, and for occluded water at 1650 cm⁻¹ and 3100-3600 cm⁻¹.

Chapter One: Introduction.
1.4.3 Intermediate phase

Buhl\textsuperscript{19} and Armstrong\textsuperscript{20} have both reported that at intermediate temperatures (135 \degree C), under hydrothermal conditions, an intermediate phase is formed; a different phase from that of the disordered cancrinite. This has a strong one-dimensional stacking disorder of (AlSiO\textsubscript{4}) layers in its crystal structure. This mixed phase is akin to natrodavyne. Its general formula is given in the expression:

\[
\text{Na}_6\text{Al}_8\text{Si}_6\text{O}_{24}\text{CO}_3\cdot n\text{H}_2\text{O}
\]

Buhl\textsuperscript{19} proposed that the X-ray powder pattern of the intermediate phase could be indexed with a hexagonal unit cell, with the small unit cell of one structural aluminosilicate layer. The intermediate phase is a different phase to the disordered cancrinite, as reflections typical for a cancrinite phase are not observed in its powder XRD pattern. In a similar way to ordered and disordered cancrinite, the intermediate and the disordered cancrinite cannot be separated by IR spectroscopy, as they both have characteristic absorptions for enclatharated water and carbonate.

1.5 Spent Bayer Liquor
The chemical composition of Bayer liquor varies from plant to plant. The differences are due to the variation in composition of the bauxite ore used. The concentration of sodium hydroxide needed to dissolve the bauxite is dependent on whether the bauxite is gibbsite or boehmite rich.

1.6 Solubility
Silica solubility has been shown to increase with increasing sodium hydroxide and alumina concentrations, however there are several different views on the effect of temperature on silica solubility. Breuer\textsuperscript{21} and Ostap\textsuperscript{22} reported increasing silica solubility with increasing temperature for synthetic Bayer solutions when sodium aluminosilicate was present. However Oku\textsuperscript{23} reported no temperature dependence up to 150 \degree C in the desilication rate of Bayer liquors.
Table 1.1 Typical Composition of Bayer Plant Spent Liquor.

<table>
<thead>
<tr>
<th>Liquor component</th>
<th>Plant Spent Bayer Liquor High Causticity*</th>
<th>Plant Spent Bayer Liquor Low Causticity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Caustic (g/l)</td>
<td>303</td>
<td>211</td>
</tr>
<tr>
<td>Al₂O₃ (g/l)</td>
<td>130</td>
<td>80</td>
</tr>
<tr>
<td>Na₂CO₃ (g/l)</td>
<td>35</td>
<td>70</td>
</tr>
<tr>
<td>Na₂C₃O₄ (g/l)</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Na₂SO₄ (g/l)</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Na₃PO₄ (g/l)</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>NaCl (g/l)</td>
<td>6.6</td>
<td>5.0</td>
</tr>
<tr>
<td>SiO₂ (g/l)</td>
<td>1.5</td>
<td>N/A</td>
</tr>
<tr>
<td>TOC (g/l)</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Total Titratable Soda</td>
<td>337</td>
<td>280</td>
</tr>
<tr>
<td>Causticity %</td>
<td>89</td>
<td>75</td>
</tr>
<tr>
<td>A/C ratio§</td>
<td>0.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Typical Jamaican spent Bayer liquor compositions

#Total caustic concentration is the sum of sodium carbonate and sodium hydroxide concentrations

§A/C is a ratio of the alumina concentration (A) in g/l Al₂O₃ and the total caustic concentration (C) in g/l.

Ni²⁴ reported that the sodium aluminosilicate solubility increases with an increase in alkali concentration when no sodium carbonate is added. Similar equilibrium sodium aluminosilicate solubilities were recorded by Zheng²⁵. Zheng²⁵ also reported that the solubility of two forms of aluminosilicate scale, cancrinite (160 °C) and sodalite (90 °C) decreases as the concentration of sodium carbonate in the synthetic liquor increases. This increase in concentration of sodium carbonate and decrease in scale formation irrespective of temperature is shown in Figure 1.6.

---

Chapter One: Introduction.
Figure 1.6: The Effect of Sodium Carbonate Concentration on Scale Formation.

The causticity of the Bayer liquor can be increased to digest bauxite more rapidly, and this is particularly useful when the bauxite is boehmite rich. However, increasing the causticity of the Bayer liquor also increases the quantity of dissolved silica in solution. Theoretically increasing the silicate concentration will lengthen the desilication process and cause more scale to precipitate, thus increase the scaling problem within the Bayer plant. However, the amount of silicate in solution is only one of the factors involved in scale formation. As previously observed, the solubility of DSP is thought to vary depending on temperature/carbonate and hydroxide concentration. Part of the work described in this thesis attempts to determine the effect of increasing the caustic concentration from 210 g/l to 300 g/l on the yield of scale produced.

1.7 Acid Cleaning Report

The Acid Cleaning Report was commissioned to study the practises used in the acid cleaning of Bayer plants across the world. The aim was to investigate possible cost saving methods and improve existing processes. Problems with safety and with process variation site to site were also highlighted.
1.7.1 Background

An acid clean takes approximately nine hours to complete, the cleaning takes between 3-5 hours, the rest is preparation of the acid and heating of the pipes. On average the acid is passed through the heaters for about 1.5 hours. The acid clean should leave the heater tubes free of scale, however this technique can also dissolve the protective activated metal oxide layer on the pipes. The loss of the protective oxide layer unfortunately allows the mild steel surfaces to be corroded more easily by both the acid cleaning solution and the caustic Bayer liquor.

The processing parameters of the acid clean have a large effect on the corrosion and cleaning observed. Ideally the condition of the clean should be:

- Moderate temperatures (<50 °C): high temperatures degrade additives and accelerate attack on the heater tubes.
- Moderate acid concentration (<10 wt%). Higher acid concentration also increases acid attack on the heater tubes.
- The final rinse with water should neutralise the acid left on the walls of the tubes.
- When possible the heater should be left empty for more than 24 hours before being re-used to help the protective oxides reform on the metal surface.

1.7.2 Amounts of Scale Removed by Cleaning

The low temperature plant heaters have bigger internal volumes and more passes but have the same 1140 tubes as the high temperature heaters. It has been estimated that:27

"At a normal scale thickness of 0.8 mm a high temperature heater will contain some 6190 kg of scale and a low temperature heater 7730 kg. 2 kg of 98 % sulfuric acid are required to dissolve 1 kg of sodalite scale."

Aluminosilicate scale reacts with sulfuric acid according to Equation 1.4

\[
\text{Na}_8[\text{AlSiO}_4]\text{(CO}_3 + 13\text{H}_2\text{SO}_4 \rightarrow 4\text{Na}_2\text{SO}_4 + 3\text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{SiO}_3 + 7\text{H}_2\text{O} + \text{CO}_2}
\]

Equation 1.4
2 kg of 98% sulfuric acid is equivalent to 0.72 litres of acid or 13 moles of sulphuric acid. One mole of scale weighs approximately 1100 g. This gives a molar ratio of 1 [scale] : 13 [H_2SO_4], in agreement with the quantities calculated in Equation 1.4.

These figures suggest that about 832 tonnes of scale are removed each year from an average plant; 372 tonnes of scale from the low temperature heaters and 460 tonnes from the high temperature heaters. This means that the theoretical usage of acid would be 14000 litres of 98% sulphuric acid. During a clean, the concentration falls to 5% implying that only about 7000 litres are consumed during the clean; only half the amount originally added. Suggesting one or a combination of the following:

- The estimate of the amount of scale is too high
- The acid required to dissolve scale is less than expected
- Less scale was on the heater then the average 0.8 mm when a clean was triggered.

If acid concentrations fall below 5%, during the cleaning process, longer times are required to effectively remove the scale from the heat exchangers. Thus operators are tempted to start the acid clean with a higher acid concentration. The starting average acid concentration recorded is 10.6 wt.% and should be 10 wt.%. During the acid clean the concentration is recorded three times at 15-minute intervals. When two consecutive acid concentrations are equal the clean is stopped. The average final acid concentration is 6.3 wt.% compared with the predicted figure of 5 wt.%. As downtime is a major concern in the industrial process, the protocol used for acid cleaning is often not correctly followed and the acid clean is stopped before all the scale has been removed. Incomplete removal of scale can lead to problems in the plant such as:

- Heaters being brought back on line, which are not fully clean.
- Unnecessary heater cleans due to convenience
- Water and acid mixing in heaters due to faulty valves
- Over use of acid and additives.
1.7.4 Temperature of the Acid

To ensure that the temperature of the acid does not exceed 60 °C, alarms are incorporated into the plant regulated by valves. Failure of these safety measures can lead to overheating. Temperatures of 60 °C and above cause additives, such as defoamers, to decompose and react with the pipes. A high temperature also promotes gellation of the acid, this is particularly prevalent when the acid is of a higher strength and contains large quantities of dissolved aluminosilicate scale. Typical acid return temperatures are between 10-30 °C in winter and 30 – 50 °C in the summer.

1.7.5 Variation of Acid Cleaning Between Plants

There are wide variations between plants and their acid cleaning methods. For example an Irish plants use 22% more acid per acid clean, but a Jamaican plant would do 20% more acid cleans. The Irish method reduces acid cleaning to a two-stage process, which seems to use more of the acids capacity to dissolve scale, unlike the Jamaican plant. However the real benefit to prolonging the life of the heat exchangers is unknown; although the heater tubes are exposed to an acid of lower strength, the longer contact time with the pipes may be just as damaging.

The Jamaican plant uses a fresh acid batch mixed to 10 wt.% concentration at the start of every clean, with a 5 % limit to terminate. Every second batch in an Irish plant is prepared from the previous acid batch, by spiking with new acid to 10 wt.%.

This cost effective method is not uniform practice even though there is no evidence of problems with solids or gellation.

Part of this work is to investigate the action of different acids at different temperatures on plant scale to determine the source of the requirement for large acid excess in plant cleaning.

1.7.6 Future of Aluminium Production

There is plenty of research into the problems within the Bayer process.

- Reducing the precipitation of the aluminosilicate scale by using additives
- Reducing the corrosion of the metal pipes by investigating the effects of acids.
- Improving the cleaning method of the aluminosilicate scale in the pipes.
The work reported here investigates ways of reducing, or removing the scales formed within the Bayer process.
Chapter Two

Methodology

2.1 Introduction

In this chapter the methods used to characterise and formulate the scales will be discussed. The theory behind each method, including the reasons for its use will also be reported and discussed.

2.2 Hydrothermal synthesis

A small number of zeolites can be prepared by direct reaction of suitable starting materials at low temperature in solution. The range of these reactions can be extended by heating the solutions above their boiling point in a hydrothermal reaction vessel. This type of reaction is particularly useful in the preparation of aluminosilicate zeolites. They are formed from an aluminium and silicon source heated in the presence of a templating agent. The templating agent is typically an anion or cation of particular shape, for example tetramethyl ammonium cations are often used for silicon rich zeolites such as ZSM5. The tetrahedral units in solution use the templating agent to form the framework by linking together around it. Although crystallisation does occur at low temperatures, hydrothermal methods are often used to speed up the rate of reaction by raising the temperature to above the boiling point of water (160-250 °C). Numerous templating agents have been used in the formulation of zeolitic materials. For example, the channel structure of the cancrinite system can use the three-fold symmetry of the carbonate anion to direct the same symmetry in the framework. A cross section of the hydrothermal bomb used in this type of synthesis can be seen in Figure 2.1.
2.3 Powder X-ray Diffraction (XRD)

Powder X-ray diffraction was performed on a Bruker D8 diffractometer operating with monochromatic copper radiation over the 2θ range 10°-60° using a PSD detector. XRD is one of the principal techniques available to analyse solids. Its uses include crystal structure determination, measurement of particle size, detection of crystal defects and disorder and the determination of phase transitions.

2.3.1 Principles of X-ray Diffraction

X-rays interact with the electrons in matter. A beam of electrons striking a metal plate will eject an electron from one of the metal atom core orbitals provided the electrons are sufficiently energetic. In the copper source used in the D8 diffractometer, the core electron vacancies formed by bombardment with electrons, can be filled by decay from various electrons in higher energy orbitals. The wavelength of X-rays used in X-ray diffraction experiments typically lie between 0.6 and 1.9 Å. For the copper target used in these experiments, $\lambda = 1.54$ Å.
2.3.2 X-ray Tube.

The electrons are created by heating a tungsten filament in a vacuum and then accelerated by high voltage towards a metal target. Core electrons are knocked out of the metal target and electrons from higher energy orbitals drop down to fill the vacancy. The energy difference between the two orbitals is emitted as an X-ray of precise energy. The beryllium window in the tube allows the X-rays to escape from the tube because it has a low atomic number and is transparent to X-rays. A spectrum of the output from an X-ray tube is shown in Figure 2.2. The background is known as Bremsstrahlung radiation, which is caused by the energy loss of the X-rays as they enter the metal. On top of the braking radiation are sharp lines generated by the quantized transitions, which are labelled according to which orbital the decaying electron has come from.

![Figure 2.2: Output from an X-ray tube](image)

Quantised transitions superimposed on a background of braking radiation.

The high intensity X-ray lines need to be isolated in order to carry out an X-ray diffraction experiment. The majority of unwanted X-rays can be removed using a metal filter of atomic number one below that of the target (these remove $K_p$ lines and background). A single wavelength can be selected by separating the $K_\alpha$ lines using a single crystal monochromator and Bragg's Law (which relates the distance between the lattice planes, $d_{hkl}$, to the X-ray wavelength); *vide infra*.

Every atom within a crystal lies on crystallographic plane that are described by the Miller indices $h$, $k$ and $l$. Each Miller index can take values that are either positive or negative integers or zero. Each plane is a representative member of a parallel set of equally spaced planes that reflect the full translational symmetry of the structure. The separation of the planes is known as the d-spacing and is given the symbol $d_{hkl}$. For
the data to be useful, X-ray photons must be scattered from these parallel sets of planes in phase. This is only possible when the path difference, equal to the distance between the planes, is an integral number of wavelengths. The equation relating the path difference to the X-ray wavelength was derived by Bragg and is given in Equation 2.1.

\[ n \lambda = 2d_{hkl}\sin \theta \]

Equation 2.1

Where \( n \) is an integer and \( \lambda \) is the X-ray wavelength. The path difference is therefore dependant on both the lattice d-spacing \( d_{hkl} \) and the angle of incidence of the X-ray beam \( \theta \). Hence if the monochromator is a single crystal, with only one \( d_{hkl} \), and is held at a fixed angle to the X-ray beam, a single wavelength must be selected.

In contrast, in a powder X-ray diffraction experiment, scattering from all planes is observed simultaneously since powdered samples contain large amounts of very small crystals, typically \( 10^{-7}-10^{-4} \) m in size, which randomly adopt the whole range of possible orientations at once.

The diffracted X-rays are detected by either a PSD (position sensitive detector) or a scintillation counter. The sample rotates with constant angular velocity changing the angle of incidence, while the detector rotates at double the angular velocity around the sample. A diagram of a powder X-ray diffractometer is shown in Figure 2.3. The X-rays produced by the X-ray tube, are aligned to fall on the sample through a slit and then are scattered in all directions by the sample according to Bragg's Law.

![Diagram of a Powder X-ray Diffractometer.](image)

Figure 2.3: Diagram of a Powder X-ray Diffractometer.
By scanning the detector around the sample along the circumference of a circle, it is made to cut through the diffraction cones at various diffraction maxima. The X-ray diffraction pattern displays intensity as a function of the detector angle \( \theta \).

As all crystalline phases will contribute to an overall powder X-ray diffraction pattern, this technique can also be used to monitor the purity of products. Comparisons cannot be carried out if one sample contains heavier elements, as the more intense pattern will mask the other.

The lattice parameters were calculated using the CELL program which minimises equation 2.2 using an iterative least squares formula where \( \omega_i \) is a weighting factor proportional to \( \tan \theta \).

\[
M = \sum \omega_i (\sin^2 \theta_i^{\text{obs}} - \sin^2 \theta_i^{\text{calc}})^2.
\]

Equation 2.2

Although there is a high degree of overlap between the sodalite and cancrinite XRD patterns, the presence of cancrinite can be confirmed by a reflection at 19°. Three different cancrinite phases are expected depending on the hydroxide/carbonate ratio and the temperature of formation. The major differences in these patterns, is the ratio of the intensities of the 24° and 28° reflections that are indicative of ordering in the occlusion channel. This will be dealt with in greater detail in chapter three.

2.4 Fourier transform Infra-red Spectroscopy (FT-IR)

FT-IR Spectra of the samples were recorded using a Perkin-Elmer system 2000 FTIR spectrometer over the range 4000-220 cm\(^{-1}\) using pressed KBr disks. The vibrational frequency depends on the mass of the two atoms at either end of the bond and the strength of the bond. Therefore heavier atoms held by weak bonds vibrate at lower frequencies than lighter atoms with multiple bonds. Vibrations arise from changes in the bond lengths and angles and in most non-cyclic molecules they can be referred to as bond stretching and bending. Most bonds do not vibrate independently, their motions are coupled, which result in the movement being in phase or out of phase. This results in symmetric stretches (uniform stretching) and asymmetric stretches (uneven stretching). This is shown in Figure 2.4. For a vibration to be infrared active there must be a change in the electric dipole of the molecule.
In contrast to the spectra observed for simple molecules, the IR spectra observed for zeolite systems are complex. Essentially the spectra are comprised of absorptions from both the enclathrated species and the framework. There have been extensive reports on the IR of aluminosilicate zeolites. The frequency range of most interest in FT-IR spectroscopy for zeolite systems is the region between 400–1400 cm$^{-1}$ where vibrations from the framework are observed. Framework stretches occur in the region 600–1400 cm$^{-1}$, while framework deformations occur between 400–600 cm$^{-1}$. Characteristic absorptions are observed in these regions, which are unique to each zeolite phase, allowing the phases to be distinguished. For example, the spectrum of sodalite exhibits a single broad absorption at approximately 1000 cm$^{-1}$. In contrast, cancrinite has several discernable absorptions in this same region (900–1100 cm$^{-1}$) and four characteristic absorptions in the region 500–800 cm$^{-1}$. The intermediate phase has a very similar spectrum to the cancrinite except the band at 770 cm$^{-1}$ is absent. The expected absorptions for sodalite, cancrinite and intermediate phase are summarised in Table 2.1.

Figure 2.4: Diagram showing Some Different Stretching Modes for an Angular Triatomic Molecule.
Table 2.1: IR Data for Aluminosilicate Scales / cm$^{-1}$.\textsuperscript{19,28,}

<table>
<thead>
<tr>
<th>Scale type</th>
<th>Asym. Stretch</th>
<th>Symmetric stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>1100, 1035, 1000, 970</td>
<td>575, 620, 690, 770</td>
</tr>
<tr>
<td>Intermediate Phase</td>
<td>1100, 1035, 1000, 970</td>
<td>575, 620, 690</td>
</tr>
<tr>
<td>Sodalite</td>
<td>1100, 1000, 980</td>
<td>660, 710, 730</td>
</tr>
</tbody>
</table>

2.5 \textit{Scanning Electron Microscopy} (SEM)
SEM can yield information on the morphology, surface structure and elemental composition (using EDAX) of new or known phases. This technique uses electrons to image structures by analysing the electrons scattered from the structure. The very short wavelengths allow much higher resolution than that of a standard optical microscope. SEM uses the electrons reflected from the surface of a material to form the image. The probe produces a high intensity beam that back scatters from the surface and continuously measures as the microscope moves from point to point on the surface. In non-conducting samples the surface is coated with gold to prevent the build up of surface charge. SEM can be used to image over a very large magnification range from 1 \(\mu\)m (100 Å) to 100 \(\mu\)m allowing the study of particle morphology and size, surface texture, detail and defects such as faults and cavities. The three zeolitic phases produce crystals of distinctly different morphologies and can be easily distinguished using SEM. Sodalite forms cube-octahedral crystals, while cancrite crystals are observed as long thin rods and intermediate phase has a plate-like appearance.

2.6 \textit{Conclusions}
This chapter discussed the methods used to characterise and formulate the aluminosilicate scales. The techniques discussed were FT-IR, SEM and XRD. A combination of IR and XRD can be used to differentiate between sodalite, cancrite and intermediate phase. Morphological differences between sodalite, cancrite and intermediate phase can also provide a way to distinguish between the phases using SEM.
Chapter Three

Synthesis and Characterisation of Model Scale Compounds.

3.1 Introduction
This chapter will describe the methods used to produce and characterise the three-aluminosilicate scales precipitated during the Bayer process. A large sample of scale that had precipitated in the pipes during the Bayer process had previously been analysed and found to be non uniform. Obtaining newly precipitated samples of the scale is also a problem, as the scale is precipitated within sealed vessels on the plant. The age of the samples of the scales is uncertain, as it is unrealistic to know exactly how long the scale has been forming in the pipes. Therefore batches of the synthetic scale were made to achieve consistency within a particular scale morphology. These model scales will be used to accurately compare reactivity towards acids.

3.2 Experimental
The three different types of aluminosilicate scales were formed using a non-agitated 23 ml Parr, Teflon-lined, hydrothermal bomb, previously described in chapter 2.2.2. Depending on which aluminosilicate scale was to be produced a different reaction temperature was used. 220 °C for cancrinite, 145 °C for intermediate phase and 90 °C for sodalite. At each of the three temperatures the following method was carried out. Kaolin (1.5 x 10\(^{-3}\) mols) and sodium bicarbonate (1.24 x 10\(^{-2}\) mols) were added to an aqueous solution of sodium hydroxide (4M, 14ml) in a Teflon lined steel autoclave and heated for 48 hours. The above procedure was adapted to replace the NaOH with spent Bayer liquor of different causticities.

3.3 Results and Discussion
There are three phases of the aluminosilicate scale. As previously discussed these phases depend upon the temperature at which the reaction takes place. Cancrinite forms at 220 °C, the intermediate phase forms at 145 °C and sodalite forms at 90 °C. The reaction scheme for the synthesis of cancrinite is shown in Equation 3.1
Cancrinite is the only product formed at 220 °C after 48 h, there are no minor products.

The reaction scheme for the synthesis of the intermediate phase is shown in Equation 3.2.

$$3[Al_2O_3.2SiO_2.2H_2O] + Na_2CO_3 + 6NaOH \rightarrow Na_4[AlSiO_4]_6( CO_3)nH_2O + 9-nH_2O$$

*Equation 3.1*

The intermediate phase is the major product formed at 145 °C after 48 h. There are also small amounts sodalite and cancrinite present at this temperature.

The reaction scheme for the synthesis of sodalite is shown in Equation 3.3

$$3[Al_2O_3.2SiO_2.2H_2O] + 8NaOH \rightarrow Na_8[AlSiO_4]_6(OH)_{2-x}H_2O + 1+xH_2O$$

*Equation 3.2*

*Equation 3.3*

Sodalite is the only product formed at 90°C after 24 h.

A list of the aluminosilicate scales and their IR data are shown in Table 3.1

**Table 3.1: IR data for Aluminosilicate Scales / cm⁻¹.**

<table>
<thead>
<tr>
<th>Scale type</th>
<th>Asym. Stretch</th>
<th>Symmetric stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>1110, 1033, 1002, 961</td>
<td>760, 688, 621, 570</td>
</tr>
<tr>
<td>Intermediate</td>
<td>997</td>
<td>688, 626, 570</td>
</tr>
<tr>
<td>Sodalite</td>
<td>979</td>
<td>735, 708, 664</td>
</tr>
<tr>
<td>Cancrinite*</td>
<td>1107, 1038, 1010, 960</td>
<td>679, 619, 573</td>
</tr>
<tr>
<td>Intermediate*</td>
<td>991</td>
<td>688, 616, 565</td>
</tr>
<tr>
<td>Sodalite*</td>
<td>979</td>
<td>735, 708, 664</td>
</tr>
</tbody>
</table>

* with spent Bayer liquor.
FT-IR’s of the three synthetic aluminosilicate scales are shown in Figure 3.1.

Figure 3.1: FT-IR spectra of the Three Aluminosilicate Phases formed at Different Temperatures using NaOH Solution.

The solid state IR spectra of the aluminosilicate scales are in good agreement with the literature values. The frequency range of most interest in FT-IR spectroscopy for zeolite systems is the region between 400–1400 cm\(^{-1}\) where vibrations from the framework are observed. Framework stretches occur in the region 600 - 1400 cm\(^{-1}\), while framework deformations occur between 400 - 600 cm\(^{-1}\). Characteristic absorptions are observed in these regions, which are unique to each zeolite phase, allowing the phases to be distinguished. The IR spectrum of sodalite exhibits the
characteristic single broad absorption at approximately 1000 cm\(^{-1}\). (Figure 3.1). In contrast, cancrinite exhibits several discernable absorptions in this same region (900-1100 cm\(^{-1}\)) and four characteristic absorptions in the region 500 - 800 cm\(^{-1}\). The intermediate phase produces a very similar spectrum to the cancrinite except the band at 762 cm\(^{-1}\) is absent.

Powder X-ray diffraction studies were carried out on the three-aluminosilicate scales and these are shown in Figure 3.2 and the data are presented in Table 3.2.

![Sodalite XRD Pattern](image)

![Intermediate Phase XRD Pattern](image)

![Cancrinite XRD Pattern](image)

**Figure 3.2**: Powder XRD Patterns of the Aluminosilicate Scales formed at Different temperatures using NaOH Solution.

Although there is a high degree of overlap between the sodalite, cancrinite and intermediate XRD patterns, the presence of cancrinite can be confirmed by a reflection at \(2\theta = 19^\circ\).\(^{25}\) Cancrinite has different phases depending on the hydroxide to carbonate ratio and the temperature of formation. Order or disorder of the structure, results from ordering of carbonate and water in the channels. The major differences in the patterns, is the ratio of the intensities of the \(2\theta = 24^\circ\) and \(2\theta = 28^\circ\) reflections which are indicative of this ordering. When comparing the three phases made with NaOH and those made with Bayer liquor it can be seen in Figure 3.3 that the scales formed with the Bayer liquor have impurities within the scale due to the impurities within the liquor. Due to the large number of weak overlapping reflections, attempts to identify the impurities by XRD were unsuccessful.
Table 3.2: Reflections Observed for the Aluminosilicate Scales.

<table>
<thead>
<tr>
<th>Cancrinite / $2\theta^\circ$</th>
<th>Intermediate Phase / $2\theta^\circ$</th>
<th>Sodalite / $2\theta^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.96</td>
<td>13.98</td>
<td>14.07</td>
</tr>
<tr>
<td>18.96</td>
<td>18.96*</td>
<td>/</td>
</tr>
<tr>
<td>22.19</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>24.31</td>
<td>24.34</td>
<td>24.50</td>
</tr>
<tr>
<td>28.19</td>
<td>28.19*</td>
<td>/</td>
</tr>
<tr>
<td>34.70</td>
<td>34.67</td>
<td>34.92</td>
</tr>
<tr>
<td>42.79</td>
<td>42.79</td>
<td>43.11</td>
</tr>
</tbody>
</table>

* Weak reflections indicating a small amount of cancrinite in the intermediate phase.

Figure 3.3 XRD Patterns of the Aluminosilicate Scales formed from Bayer Liquor.

To assess the morphology of the phases the SEM micrographs were obtained. The SEMs of cancrinite, sodalite and intermediate phase are given in Figures 3.4, 3.5 and 3.6 respectively.
Cancrinite crystals are imaged in the SEM with a rod-shaped morphology. This can be clearly seen in Figure 3.4.

Intermediate phase is the intergrowth between sodalite and cancrinite. It has plate-like crystals imaged in the SEM. Also present is rod-shape morphology typifying cancrinite and cube octahedral morphology typifying sodalite. Sodalite crystals exhibit a cube octahedral morphology.
The SEMs clearly show the differing morphologies of the phases. The high temperature phase is identified as cancrinite as it crystallises with a rod-like morphology. In contrast the low temperature phase is identified as sodalite because the characteristic crystals with cube octahedral morphology dominated the photograph. The intermediate phase has characteristic plate like crystals, as the phase is not entirely pure the SEM picture also shows sodalite and cancrinite present.

3.4 Conclusions
Several techniques were employed to characterise sodalite, cancrinite and the intermediate phase. The techniques used were FT-IR, SEM and XRD. Using these methods the characterisation of the three types of scale was afforded. XRD was the quickest and most efficient method of analysis. Due to its accessibility and speed it was used as the main method of characterising the rest of the scales formed. The synthetic scales formed from NaOH solutions produced more crystalline products compared with the scales formed from the spent Bayer liquor. Impurities present in the Bayer liquor cocrystallise with the aluminosilicate scales and are observed in the powder XRD pattern. Since it was apparent that impurities were present in the aluminosilicate scale formed using Bayer liquor, it was decided to proceed with the acid dissolution experiments using aluminosilicate scale produced from the NaOH solutions as the impurities could not be identified or quantified and hence their interaction with the acids could not be predicted.
Chapter Four

Acid Dissolution

4.1 Introduction
Acid cleaning is an integral part of the successful function of the Bayer plant, since aluminosilicate scaling results in poor thermal conductivity in the heat exchangers and impurities in the products. This chapter investigates the effect that different mineral acids have upon the rate of dissolution of scale as a function of temperature and the amount of scale dissolved. The aim of this work was to find the optimum process conditions for acid cleaning to transfer knowledge to the industrial process. To achieve this, a common methodology was devised so the ability of each acid to dissolve scale could be determined.

4.2 Experimental
The common methodology followed in each experiment is detailed below.

10 ml of test acid of known molarity was measured into a beaker. The beaker was placed in a water bath of known temperature (30 °C or 60 °C). Once the acid had reached the required temperature, synthetic scale (0.200g) was added to the acid. The beaker remained in the water bath for a set time period (30 min). The resulting mixture was filtered and washed in distilled water into a beaker. A known excess of sodium hydroxide (20ml, 2M) was added to the filtrate along with 4 drops of phenolphthalein as an indicator. The solution was then back titrated against HCl (2M). All titrations were carried out five times; the mean was calculated and is given in the results section below.

4.3 Results and Discussion

4.3.1 The Effect of temperature on acid dissolution
Two temperatures at the maximum (60°C) and minimum (30°C) of the temperature range used for the acid cleaning process in the Bayer plants were chosen in order to find the limits of the effect of temperature. Unfortunately the exact contact time the acid has with the aluminosilicate scales in the heat exchangers is unknown, so an
appropriate time period of 30 min was chosen. The amount of acid used to dissolve the scale was proportional to the amount used during acid cleaning on the plant. The titre values are assumed to be directly proportional to the amount of scale dissolved as shown in Equation 1.4 for sulfuric acid. Since hydrochloric and nitric acids are monoprotic, twice as many moles of these acids are required to dissolve the scale as shown in Equation 4.1

\[
\text{Na}_8[\text{AlSiO}_4]_6\text{CO}_3 + 26\text{HCl} \rightarrow 8\text{NaCl} + 6\text{AlCl}_3 + 6\text{H}_2\text{SiO}_3 + 7\text{H}_2\text{O} + \text{CO}_2
\]

Equation 4.1

This gives a molar ratio of 1[scale]:26 [HCl/HNO\textsubscript{3}]. The quantity of scale is calculated, assuming that all the acid reacted with the aluminosilicate scale and no impurities.

The results of this work are compared at the end of the chapter with previous studies of Riley\textsuperscript{30} to draw conclusions in respect of this work.

4.3.1.1 Sulfuric Acid

The first scale sample was dissolved in 10\% (1.8M) sulfuric acid at both 30 and 60 °C. The results are shown in Table 4.1 and Figure 4.1.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>30 °C / x 10\textsuperscript{-4} mols.</th>
<th>60 °C / x 10\textsuperscript{-4} mols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>1.34(3)</td>
<td>2.30(3)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>2.32(3)</td>
<td>0.92(3)</td>
</tr>
<tr>
<td>Sodalite</td>
<td>2.06(3)</td>
<td>1.53(3)</td>
</tr>
</tbody>
</table>

Table 4.1. Moles of Aluminosilicate Scales Dissolved in 10\% (1.8 M) sulfuric acid; e.s.d.'s are given in parentheses.
Figure 4.1: Moles of Scale Dissolved in 10 % (1.8M) Sulfuric Acid at Different Temperatures.

The results show that at the higher temperature, more cancrinite dissolves in sulfuric acid; this is expected with respect to the laws of reaction kinetics. However both intermediate and sodalite scale shows a decrease in the amount dissolved with an increase in temperature. The decrease in solubility at the higher temperatures for the intermediate phase and sodalite scale is not expected as solubility should increase with temperature. The difference in solubility between the different structures could be due to the differences in morphology of the scales. Channels in the cancrinite structure could allow quicker access to the acid, whereas the cube-octahedral crystals of sodalite and the plate-like crystals of the intermediate phase have a lower surface area for the acid to attack, resulting in less scale dissolving. This observation of solubility decreasing with temperature could also be attributed to the gelation of the solution. Total gelation was observed when the acid and scale solutions were heated for over 5 hours. This will be explained in more detail in Chapter 4.3.1. This gelation phenomenon is observed in the aluminium refining plants and could be attributed to decreasing solubility of scale as the temperature increases. The formation of the gel does not allow the acid to come into contact with unreacted particles and hence the scale solubility falls as the temperature increases and the probability of gel formation increases.
The scale was dissolved in 10 % (1.1 M) nitric acid again at 30 and 60 °C. The results are shown in Tables 4.2 and Figure 4.2.

Table 4.2: Moles of Aluminosilicate Scales dissolved in 10% (1.1M) Nitric acid; e.s.d.'s are given in parentheses.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>$30 ^\circ C \times 10^{-4}$ mols.</th>
<th>$60 , ^\circ C \times 10^{-4}$ mols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>0.64(3)</td>
<td>0.30(3)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>0.53(3)</td>
<td>0.59(3)</td>
</tr>
<tr>
<td>Sodalite</td>
<td>0.54(3)</td>
<td>0.52(3)</td>
</tr>
</tbody>
</table>

Figure 4.2: Moles of Scale Dissolved in 10 % (1.1M) Nitric Acid at Different Temperatures.

The results show a decrease in scale solubility with temperature for both cancrrinite and sodalite. However the solubility of the intermediate phase slightly increases in with the increase in temperature. The overall lower solubility of the scales in nitric acid compared to sulfuric acid is most likely to be due to the acid concentration, where concentrated sulfuric acid is roughly 18 M in comparison to concentrated nitric acid at 11 M. However, the relative solubilities of the different types of scale is different for nitric in comparison to sulfuric acid. The solubility of sodalite and cancrrinite decrease with increasing temperature in nitric acid. This phenomenon can again be attributed to the partial gelation of the solution for these phases at higher temperature in nitric acid.

Chapter Four: Acid Dissolution
The scale was dissolved in 10% (1.2M) hydrochloric acid again at 30 and 60 °C. The results are shown in Table 4.3 and Figure 4.3.

Table 4.3. Moles of Aluminosilicate Scales Dissolved in 10% (1.2 M) Hydrochloric Acid; c.s.d.'s are given in parentheses.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>30°C / x 10⁻⁴ mols.</th>
<th>60°C / x 10⁻⁴ mols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>1.13(3)</td>
<td>1.41(3)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>1.36(3)</td>
<td>1.02(3)</td>
</tr>
<tr>
<td>Sodalite</td>
<td>1.23(3)</td>
<td>1.10(3)</td>
</tr>
</tbody>
</table>

![Figure 4.3: Moles of Scale Dissolved in 10% (1.2 M) Hydrochloric acid at Different Temperatures.](image)

The results show that cancrite solubility increases with temperature for hydrochloric acid. In a similar way to the nitric acid experiments, the overall lower solubility of the scales in hydrochloric acid compared to sulfuric acid is most likely to be due to the acid concentration, where concentrated sulfuric acid is roughly 18 M in comparison to concentrated hydrochloric acid at 12 M. In this case, the intermediate phase and sodalite solubility both decrease with the increase in temperature. The phenomenon of the scales decreasing in solubility as the temperature increases could be explained by partial gelation of the solution. The phenomenon could also be due to the different morphologies of the three scales. This trend is similar to that seen for
the other two mineral acids, although no particular scale shows a greater tendency to form a gel with respect to the others.

4.3.2 Other reported work
Due to the anomalous behaviour observed, these data were compared with previous studies. A summer student briefly investigated the result of temperature on the acid dissolution and these results are summarised below.

Table 4.4. Moles of Aluminosilicate Scales Dissolved in 10% (1.8 M) Sulfuric Acid reported by Riley; e.s.d.'s are given in parentheses.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>30°C / $10^{-4}$ mols.</th>
<th>60°C / $10^{-4}$ mols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>1.58(2)</td>
<td>1.58(2)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>1.84(2)</td>
<td>1.82(2)</td>
</tr>
<tr>
<td>Sodalite</td>
<td>1.74(2)</td>
<td>1.53(2)</td>
</tr>
</tbody>
</table>

The comparisons between the two sets of results are shown in figure 4.4. Where result set A are from this study and result set B were recorded by E. Riley.

Figure 4.4: Comparison of Scale Dissolved at Different Temperatures using 1.8M Sulfuric Acid by Chester (SET A) and Riley (SET B).
It can be noted that set B values show no significant change in solubility between the temperatures for any of the scales, in contrast to those in Set A. The difference in results between the two methods could be due to the difference in particle size between the scales analysed. In addition, two different experimenters could result in differences in technique and hence systematic error.

The results from Riley's experiments using 10% (1.1M) nitric acid are summarised below in Table 4.5.

Table 4.5: Moles of Aluminosilicate Scales Dissolved in 10% (1.1 M) Nitric Acid reported by Riley; e.s.d.'s are given in parentheses.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>30°C / x 10^-4 mols.</th>
<th>60°C / x 10^-4 mols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>1.00(2)</td>
<td>0.98(2)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>1.32(2)</td>
<td>1.06(2)</td>
</tr>
<tr>
<td>Sodalite</td>
<td>0.76(2)</td>
<td>0.92(2)</td>
</tr>
</tbody>
</table>

The comparisons between the two sets of results are shown in figure 4.5. Where result set A are from this study and result set B were recorded by E. Riley.

Figure 4.5: Comparison of Scale Dissolved at Different temperatures using 10% (1.1M) Nitric Acid by Chester (SET A) and Riley (SET B).
It can be noted that set B values show no significant change in solubility between the temperatures for any of the scales, in contrast to those in set A. The difference in results between the two methods could be due to the difference in particle size between the scales analysed. Titres in these experiments were in the range 0 – 5 ml and hence the percentage error caused by human errors in the titrated volume were potentially large.

4.3.3 A new method for acid dissolution

Since the results of the two previous studies performed using the same experimental parameters by independent scientists were in poor agreement, a new method was devised to attempt to reduce experimental errors. Firstly larger quantities of scale would be use to increase the titres and hence reduce the errors of human errors in the titrated volume. Secondly, the scale would be made in large batches and sampled using the cone and quarter method to produce a representative sample of the scale for dissolution. The latter factor should reduce the errors caused by variable particle sizes within batches of the scale. Whilst the method was being changed, the acid cleaning report was released and stated that the actual amount of acid used during the acid clean was half as much as the theoretical amount. An adaptation of the previous method in section 4.2 was therefore carried out.

20 ml of test acid of known molarity was measured into a beaker. The beaker was placed in a water bath of known temperature. Once the acid had reached the required (30 °C, or 60 °C, synthetic scale (0.200g) was added. The beaker remained in the water bath for 30 min. The resulting mixture was filtered and washed in distilled water into a beaker. A know excess of sodium hydroxide (40ml, 2M) was added to the filtrate along with 4 drops of phenolphthalein as an indicator. The solution was then back titrated against HCl (2M). All titrations were carried out five times; the mean was calculated and is given in the results section below.

Results for the cone and quarter method using 10% (1.8M) sulfuric acid are shown in Table 4.6
Table 4.6. Moles of Aluminosilicate Scales Dissolved in 10% (1.8 M) Sulfuric Acid Using the Cone and Quarter Method; e.s.d.'s are given in parentheses.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>30 °C / x10^{-4} mols.</th>
<th>60 °C / x10^{-4} mols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>0.24(8)</td>
<td>0.58(8)</td>
</tr>
<tr>
<td>Intermediate</td>
<td>0.12(8)</td>
<td>0.12(8)</td>
</tr>
<tr>
<td>Sodalite</td>
<td>0.22(8)</td>
<td>0.30(8)</td>
</tr>
</tbody>
</table>

A comparison of the acid dissolution experiments using the old and new methods is shown in Figure 4.6.

![Bar graph showing scale dissolution at different temperatures and methods.](image)

**Types of aluminosilicate scale**

Figure 4.6: Moles of Scale dissolved at Different Temperatures in Sulfuric Acid using the Batch Scale (method 1) and Cone and Quarter (method 2) Methods.

The results acquired using the two methods are markedly different. The results from the cone and quarter method infer that there is no significant increase of scale dissolution with increasing temperature. The titre values for the new method for a single scale vary significantly more than the old method (four times the standard deviation). Increasing the volume of acid to dissolve the scale has notably increased the errors of the system resulting in another method which is not reproducible. Similar results for the nitric acid dissolution are shown in Table 4.7 and Figure 4.7.
Table 4.7. Moles of Aluminosilicate Scales Dissolved in 10% (1.1M) Nitric Acid Using the Cone and Quarter Method; e.s.d.’s are given in parentheses.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>30 °C / x10⁻³ mols.</th>
<th>60 °C / x10⁻³ mols.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>0.91</td>
<td>0.87</td>
</tr>
<tr>
<td>Intermediate</td>
<td>0.62</td>
<td>0.49</td>
</tr>
<tr>
<td>Sodalite</td>
<td>0.84</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Figure 4.7: Moles of Scale Dissolved at Different Temperatures in Nitric Acid using the Batch Scale (method 1) and Cone and Quarter (method 2) Methods.

Figure 4.7 also highlights similar differences between results for the two methods using nitric acid instead of sulfuric acid. It can be concluded that neither method is reproducible, with respect to random experimental errors. Due to the time constraints on this project this method cannot be fully investigated. Planned methodological improvements include:

- Repeating the first method as the second method increased the experimental error resulting in anomalous results.
• The number of temperatures studied should be increased to incorporate temperatures in between the two extremes e.g. 35, 40, 45, 50 and 55.
• Using an auto-titrator could reduce the human experimental error.
• The use of a multi-reaction vessel similar to those used for catalytic studies would enable the heating of several acid samples simultaneously. Temperature would be better controlled as the water bath is thermostatically regulated.
• The method needs to incorporate the flow rate of the acid observed within the plant. The plant flow rate is a major part of the acid cleaning. Utilizing the rig system that simulates the Bayer process on a smaller scale, could give further insight into the acid cleaning process.
• Therefore continuous flow reactor required.

4.3.1 Investigating gelation
A gel was formed when carrying out the acid dissolution experiments. It has been reported\textsuperscript{26} that gelation can be a problem within the acid clean in the Bayer process. It was investigated to see if a gel could be systematically produced and under what conditions. The following method was used.

4.3.1.1 Gel Forming Methology
0.2 g of scale was placed in 10 ml of 10\% (1.84 M) sulfuric acid at 30 or 60 °C and was left for 0.5, 1, 2, 3, 4, 5 hours and overnight. The solution was then removed from the water bath and checked for any gellation. The results are given in tables 4.8, 4.9 and 4.10.
Table 4.8: Formation of a Gel from a Cancrinite and Acid Solution.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>Time (hours)</th>
<th>30 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancrinite</td>
<td>0.5</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>1</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>2</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>3</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>4</td>
<td>None</td>
<td>Slight gellation</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>5</td>
<td>None</td>
<td>Gellation</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>Overnight</td>
<td>Slight gellation</td>
<td>Gellation</td>
</tr>
</tbody>
</table>

At the low temperature the cancrinite acid solution started to produce a gel when the solution was left overnight. At the higher temperatures the solution started to form a gel after 4 hours.

Table 4.9: Formation of a Gel from the Intermediate Phase and Acid Solution.

<table>
<thead>
<tr>
<th>Scale type</th>
<th>Time (hours)</th>
<th>30 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermediate phase</td>
<td>0.5</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Intermediate phase</td>
<td>1</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Intermediate phase</td>
<td>2</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Intermediate phase</td>
<td>3</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Intermediate phase</td>
<td>4</td>
<td>None</td>
<td>Slight gellation</td>
</tr>
<tr>
<td>Intermediate phase</td>
<td>5</td>
<td>None</td>
<td>Gellation</td>
</tr>
<tr>
<td>Intermediate phase</td>
<td>Overnight</td>
<td>Slight gellation</td>
<td>Gellation</td>
</tr>
</tbody>
</table>

The sodalite and acid solution produce the gel at the same time as the cancrinite.
The intermediate also produces the gel at the same time duration as the cancrinite and sodalite. The likely source of the gels observed is the formation of hydrated siliceous acids that prevent the scale from further dissolution by providing a viscous protective layer between the acid and the undissolved scale. Since gel formation is more prevalent at high temperature, this suggests that gel formation is more likely to occur when there is a higher concentration of silicon-based species in solution.

4.4 Conclusions
Reproducible results within methods for acid dissolution were not obtainable within the time available. Different acids have different dissolution effects upon the scale. Sulfuric acid was more effective for the dissolution of scale than nitric and hydrochloric acid due to the higher molar concentration at the same percentage by weight. The initial method had the least experimental error, and would be the best methodology to repeat.

Gellation starts to occur after four hours when the scale is dissolved in acid at 60 °C. But at 30 °C gellation occurs after 24 hours. This is the same for each phase of the aluminosilicate scale. Gellation occurs preferentially at higher temperatures and could be a greater problem in the high temperature plants.
Chapter Five

The Effect of Liquor Causticity on Scale Formation

5.1 Introduction
The composition of Bayer liquor varies greatly depending on the country of origin of the bauxite ore. Liquors vary dramatically in both the levels of digested organic species, the supersaturation of the SiO₂ and the causticity. The aim of this work was to investigate the effect that causticity has upon the yield of the aluminosilicate scale precipitated. The spent Bayer liquor used was from a Jamaican plant and three causticities were tested. Low (210 g/l), medium (250 g/l) and high (300 g/l) caustic liquors were used to investigate the effect of causticity upon yield of aluminosilicate scale. The synthesis was performed using an adaptation of the method reported in chapter three. Experiments by N. Kenyon on yield analysis from pure Bayer liquor show very small yields associated with these experiments, 0.01-0.03 g. In order to achieve greater reproducibility and higher yields, Bayer liquor spiked with kaolinite was used to investigate the effect of different caustic concentrations upon the yield of aluminosilicate scale. These experiments also gave an opportunity to investigate the solubility of kaolinite in caustic solutions at different temperatures.

5.2 Experimental
The common methodology followed in each experiment is detailed below.

Kaolin (1.5 x 10⁻³ mols) was added to 14 ml Bayer liquor solution (300, 250 or 210 g/l) in a non-agitated 23 ml Parr, Teflon-lined, hydrothermal bomb and heated to 90, 145 or 220 °C, for 1, 2, 4, 8, 24 or 48 hours. The products were then filtered washed with water and dried to constant weight at 110°C. Each experiment was repeated 8 times, and the average yield of scale was calculated over the 8 experiments and is given in the results section below.
5.3 Results and Discussion

5.3.1 The Effect of temperature on the causticity experiments

Each phase was analysed using XRD to ascertain the purity of the product, the type of phase formed and to ensure that the kaolinite starting material had been consumed. It can be seen in Figure 5.1 that the yields at low temperature (90 °C) are masked by undissolved kaolinite at the shortest reaction times. At higher temperatures, no un-reacted kaolinite is visible in the XRD pattern, even at the shortest reaction times (1 hour) this is shown in Figure 5.2. Undissolved kaolinite has therefore been shown to mask the yield of aluminosilicate scale at low temperatures (90°C) and short reaction times.

![Figure 5.1: Powder XRD Patterns showing the Loss of Kaolinite from the Reaction Product with Time.](image)

Chapter Five: The Effect of Liquor Causticity on Scale Formation
Table 5.1: The Yield of Precipitate at 220 °C.

<table>
<thead>
<tr>
<th>Time / hrs</th>
<th>Causticity 300 g/l</th>
<th>Causticity 250 g/l</th>
<th>Causticity 210 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.800 g</td>
<td>0.797 g</td>
<td>0.710 g</td>
</tr>
<tr>
<td>2</td>
<td>0.811 g</td>
<td>0.806 g</td>
<td>0.772 g</td>
</tr>
<tr>
<td>4</td>
<td>0.830 g</td>
<td>0.830 g</td>
<td>0.779 g</td>
</tr>
<tr>
<td>8</td>
<td>0.885 g</td>
<td>0.849 g</td>
<td>0.789 g</td>
</tr>
<tr>
<td>24</td>
<td>0.915 g</td>
<td>0.856 g</td>
<td>0.827 g</td>
</tr>
<tr>
<td>48</td>
<td>1.041 g</td>
<td>0.943 g</td>
<td>0.928 g</td>
</tr>
</tbody>
</table>

Each result had a standard deviation of ±0.02 g, which equates to approximately ±2 %.

Table 5.2: The Yield of Precipitate at 145 °C

<table>
<thead>
<tr>
<th>Time / hrs</th>
<th>Causticity 300 g/l</th>
<th>Causticity 250 g/l</th>
<th>Causticity 210 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.728 g</td>
<td>0.721 g</td>
<td>0.702 g</td>
</tr>
<tr>
<td>2</td>
<td>0.760 g</td>
<td>0.738 g</td>
<td>0.721 g</td>
</tr>
<tr>
<td>4</td>
<td>0.824 g</td>
<td>0.761 g</td>
<td>0.752 g</td>
</tr>
<tr>
<td>8</td>
<td>0.839 g</td>
<td>0.783 g</td>
<td>0.771 g</td>
</tr>
<tr>
<td>24</td>
<td>0.843 g</td>
<td>0.810 g</td>
<td>0.800 g</td>
</tr>
<tr>
<td>48</td>
<td>0.979 g</td>
<td>0.880 g</td>
<td>0.836 g</td>
</tr>
</tbody>
</table>

Each result had a standard deviation of ±0.02 g, which equates to approximately ±2 %.

Table 5.3: The Yield of Precipitate at 90 °C

<table>
<thead>
<tr>
<th>Time / hrs</th>
<th>Causticity 300 g/l</th>
<th>Causticity 250 g/l</th>
<th>Causticity 210 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.727 g</td>
<td>0.690 g</td>
<td>0.551 g</td>
</tr>
<tr>
<td>2</td>
<td>0.743 g</td>
<td>0.702 g</td>
<td>0.632 g</td>
</tr>
<tr>
<td>4</td>
<td>0.786 g</td>
<td>0.703 g</td>
<td>0.698 g</td>
</tr>
<tr>
<td>8</td>
<td>0.817 g</td>
<td>0.732 g</td>
<td>0.703 g</td>
</tr>
<tr>
<td>24</td>
<td>0.827 g</td>
<td>0.779 g</td>
<td>0.751 g</td>
</tr>
<tr>
<td>48</td>
<td>0.861 g</td>
<td>0.787 g</td>
<td>0.775 g</td>
</tr>
</tbody>
</table>

Each result had a standard deviation of ±0.02 g, which equates to approximately ±2 %.
The comparisons of the yields with time and causticity can be seen for each of the temperatures 220, 145 and 90 °C in the Figures 5.2, 5.3 and 5.4 respectively.

Figure 5.2: Graph to show the Yield of Scale at 220 °C as a Function of Time

Figure 5.2 shows that at 220 °C, approximately 12 % more scale forms with 300 g/l Bayer liquor compared with 210 g/l causticity. At 220 °C, approximately 2 % more scale forms with 250 g/l caustic Bayer liquor than the 210 g/l causticity. The yield of aluminosilicate scale increases with both the causticity of the Bayer liquor and the time. This behaviour is expected since increasing the causticity increases the concentration of silicon-based impurities as more of the silica and silicon-rich impurities dissolve into solution and hence availability of the scale to form aluminosilicate scale. The length of time also has an effect on the yield, as the solution has more time to precipitate the aluminosilicate scale from solution.
Figure 5.3 shows that at 145 °C, approximately 17 % more scale forms with 300 g/l Bayer liquor compared with liquor of only 210 g/l causticity. At 220 °C, approximately 5 % more scale forms with 250 g/l caustic Bayer liquor than the Bayer liquor with 210 g/l causticity. As expected the lowest caustic liquor produces the least amount of scale, and there is a trend of the scale yield increasing with time for all Bayer liquor causticities. The scale yield also increases with the causticity of the Bayer liquor.

Figure 5.4 shows that at 90 °C, approximately 11 % more scale forms with 300 g/l Bayer liquor compared with Bayer liquor with 210 g/l causticity. At 220 °C, approximately 2 % more scale forms with 250 g/l caustic Bayer liquor compared with Bayer liquor of 210 g/l causticity. As expected the scale yield increases with time. The scale yield also increases with the causticity of the Bayer liquor. At 90 °C the difference between the amounts of scale produced by varying the caustic concentration is lower than at higher temperatures. This suggests that temperature has a larger effect on the formation of scale than the causticity of the Bayer liquor. However, the higher the causticity, the larger the amount of scale produced.
Figure 5.4: Graph to show the Yield of Scale at 90 °C as a Function of Time.

Figure 5.5 indicates that a lower quantity of aluminosilicate scale is produced at lower temperatures. The 300 g/l caustic spent Bayer liquor reacting at 220 °C produced approximately 6 % more scale than at 145 °C. The 300 g/l caustic spent Bayer liquor reacting at 145°C produced approximately 12 % more scale than at 90 °C. This can be explained by simple reaction kinetics; reactions occur faster at higher temperatures and more silicon-rich species dissolve into solution at higher temperatures producing more of the aluminosilicate scale. At 300 g/l causticity there is a greater difference in the amount of scale produced between 90 °C and 145 °C than that between 145°C and 220 °C. This suggests that the yield of aluminosilicate scale would continue to increase with temperature. The greater difference in the amount of scale produced at the lower temperature could be explained by the XRD analysis which indicates that at 90 °C the products from the reactions contained un-reacted kaolinite which contributed to the observed yield.

Figure 5.6 shows that the 250 g/l caustic spent Bayer liquor reacting at 220 °C produced approximately 7 % more scale than at 145 °C. The 300 g/l caustic spent Bayer liquor reacting at 145°C produced approximately 12 % more scale than at 90 °C. Simple reaction kinetics can again explain this; reactions occur faster at higher temperatures and more silicon-rich species dissolve into solution at higher temperatures producing more of the aluminosilicate scale. Once again there is a
greater difference in the amount of scale produced between 90 °C and 145 °C than that produced between 145 °C and 220 °C using the medium (250 g/l) caustic Bayer liquor.

Figure 5.5: Yield of Scale at High Caustic Concentration as a Function of Time

Figure 5.6: Yield of Scale at Medium Caustic Concentration as a Function of Time
Figure 5.7 shows that 210 g/l caustic Bayer liquor reacting at 220 °C produces approximately 17% more scale than that at 90 °C. The reactions carried out at 145°C produced approximately 12% more scale than produced at 90 °C. Simple kinetics can again explain this behaviour as reactions occur faster at higher temperatures and more silicon-rich species dissolve into solution at higher temperatures, more aluminosilicate scale is produced. At 210 g/l there is a larger amount of scale produced between the temperatures of 220 °C and 145°C compared with that produced between 145 °C and 90 °C. This would suggest that with a lower (210 g/l) causticity it takes a higher temperature to produce the scale.

Figure 5.7: Yield of Scale at Low Caustic Concentration as a Function of Time.

5.4 Conclusions
Kaolin dissolves after one hour of reacting for the medium (145 °C) and high (220 °C) temperatures whereas it takes twenty-four hours for it to react at the lower (90 °C) temperatures. This process is consistently observed for every Bayer liquor tested, regardless of causticity. Generally, the reactions occur faster at higher temperatures and more silicon-rich species dissolve into solution at higher temperatures producing more of the aluminosilicate scale. The higher the causticity of Bayer liquor the greater the amount of scale formed as the silicon-rich impurities in bauxite such as kaolinite, dissolve more easily as the caustic concentration is increased. The yield of scale increases as the reaction time increases. The 300 g/l caustic Bayer liquor
produces more (12 % compared with 210 g/l and 5 % compared with 250 g/l) scale but only has an 11 % difference in the amount of scale produced between the highest and lowest temperatures. The 250 g/l caustic Bayer liquor produces 10 % more intermediate phase than 210 g/l caustic Bayer liquor but has a 16 % difference in the amount of scale produced between the highest and lowest temperatures. The 210 g/l caustic Bayer liquor produces the least amount of scale but has a 17 % difference of scale production between the highest and lowest temperatures. This suggests that at low temperatures and low causticity a reduced amount of scale is produced. This work has given an insight into the effect of causticity upon scale formation for the Jamaican liquor. As liquor is not uniform between plants, other liquors might have varying results.
Chapter Six
Variable Temperature XRD Study

6.1 Introduction
The behaviour of the three type of aluminosilicate scale differs under dry conditions due to their varying water content and differences in particle size. The removal of the water from plant scale resulted in the sample faulting along well-defined planes within the scale. The incomplete removal of scale and build-up of acid dissolution product on the undissolved scale explains this phenomenon. The thermal behaviour of the scales has been investigated by mimicking drying conditions using the HK1200 furnace attached to the Bruker D8 diffractometer and thermogravimetric analysis.

6.2 Experimental
The common methodology followed in each experiment is detailed below.

The scale sample was loaded into the flat plate sample holder of the HTK furnace and placed in the furnace of the XRD machine. An XRD pattern was initially recorded at room temperature and then at 27, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 °C in air using a ramp rate of 10°C/min and a collection time of 2 h at each temperature. These patterns can be seen in the figures 6.1 to 6.5

6.3 Results and discussion
The thermal behaviour of the scales was investigated by mimicking drying conditions of the scale. The first step observed during the decomposition of the scale is the removal of water, which occurs at low temperature, and is completed removed by 400 °C. Although the loss of water is not directly observed in the diffraction pattern, the water loss can be monitored by an initial decrease in the lattice parameters as the water molecules are lost. As the temperature increases, the zeolite then thermally expands and the lattice parameters increase.

Figure 6.1 shows the thermal decomposition of cancrinite. The synthetic cancrinite scale shows no significant change in phase until 800 °C. At this temperature, additional reflections begin to appear in the XRD pattern with the first reflection of
significant intensity at \(2\theta = 21^\circ\). This reflection increases in intensity as the temperature increases to 1000 °C. Simultaneously, the intensity of the reflections for corresponding to cancrinite gradually decrease and then disappear. This suggests that at high temperatures the structure of the cancrinite is breaking down and reforming into another phase. The database function on the XRD machine suggests that this phase is the cubic form of nepheline, \(\text{NaAlSiO}_4\) shown in figure 6.9. This is formed at \(\sim 750 \text{ °C}\) and is stable up to \(1250 \text{ °C}\). Buhl\(^{18}\) observed the abrupt transition to the nepheline phase that is observed here at \(\sim 800^\circ\text{C}\). Borchert\(^{32}\) first observed the formation of hexagonal \(\text{NaAlSiO}_4\) (also known as ‘stuffed \(\alpha\)-carnegieite’) during thermal destruction of aluminosilicates in presence of a certain amount of sodium oxide.

Figure 6.2 shows the thermal decomposition of the intermediate phase. The synthetic intermediate phase scale also shows no significant change in phase until 800 °C is attained. The XRD pattern again shows the appearance of a reflection at \(2\theta = 21^\circ\), which suggested that intermediate phase also decomposes into the cubic form of nepheline, \(\text{NaAlSiO}_4\). This peak increases with intensity as the temperature increases to 1000 °C. The intensities of the characteristic reflections of intermediate phase reduced in intensity and then disappeared, suggesting that the \((\text{AlSiO}_4)\)-layers of the intermediate phase are rearranging to form the nepheline. The database function on the XRD machine confirmed that this new phase was the cubic form of nepheline implying that this sodium aluminium silicate is the most stable form of scale at these high temperatures.

Figure 6.3 shows the thermal decomposition of sodalite. This synthetic sodalite scale shows the peaks shift to the left at 300 °C. This shift could be due to the loss of the water altering the unit cell size. Once again extra peaks present from 800 °C suggest a new phase is forming. The XRD pattern shows a peaks at \(2\theta = 21^\circ, 23^\circ, 27^\circ, 29^\circ\) and 39° which have no match in the XRD pattern of sodalite. These peaks increase with intensity as the temperature increases to 1000 °C. The reflections synonymous with the sodalite phase simultaneously decrease in intensity as the nepheline reflections increase in intensity. Sodalite decomposes into a different nepheline end product to both the intermediate phase and the cancrinite. This is shown in Figure

---

*Chapter 6. Variable Temperature XRD Study.*
6.10. This nepheline is hexagonal not cubic and is identical to that observed by Borchert. The absence of the carbonate in the sodalite must enable a different motion and rotation during the phase transition to form nepheline with a different structure.

Figure 6.4 shows the thermal decomposition of a high temperature heater scale. This heater scale is has been identified as disordered cancrinite scale. The XRD patterns for this scale should mimic that of the synthetic disordered cancrinite scale. This does not happen, the Na.Al.Si.O₄ product is formed at 900 °C instead of 800 °C. This cannot be explained by the difference in the structure between cancrinite and disordered cancrinite because Buhl has previously reported this difference to be 21 °C not 100 °C. The decomposition temperature for the production of nepheline could be effected by the impurities found in plant scale explaining the 100 °C difference in formation. This is shown in Figure 6.8.

Figure 6.5 shows the thermal decomposition of a 39C Kirkvine works heater scale. This heater scale is has been identified as an ordered cancrinite scale. The XRD patterns for this scale should mimic the synthetic cancrinite scale. This also is not the case and it behaves in a similar way to disordered cancrinite scale in the previous experiment. The NaAlSiO₄ product is formed at 900 °C instead of 800 °C. The decomposition appears to be effected by the impurities found in plant scale, which are absent in the synthetic scale. This is shown in figure 6.8.

Figure 6.6 shows the thermal decomposition of the AAL 9c scale. This scale is a mixture of sodium aluminium silicate hydrate [(Na₂O)(Al₂O₃).1.68(SiO₂).1.8(H₂O)] and silicon oxide (SiO₂) and is not zeolitic in nature. These phases were thermally stable over the chosen temperature range, showing limited decomposition only (loss of water). The reflections at 2θ = 14°, 19°, 24°, 27°, 33°, 35° and 43° are indicative of sodium aluminium silicate hydrate, and reflections lying at 2θ = 22° and 36° are indicative of silicon oxide.

Figure 6.7 compares XRD patterns of synthetic cancrinite and two plant scales at room temperature. It shows that the Kirkvine works scale is a cancrinite scale and the high temperature scale is predominately an intermediate scale.
Figure 6.8 compares XRD patterns of synthetic scale at 600 °C and the two plant scales at 1000°C, showing that the plant scales are decomposing to the nepheline but a much slower rate.

Figure 6.9 compares XRD pattern of synthetic cancrinite at 1000°C with a library XRD pattern of cubic nepheline.

Figure 6.10 compares XRD pattern of synthetic sodalite at 1000°C with a library pattern of hexagonal nepheline.
Figure 6.1: XRD Patterns of Cancrinite with Increasing Temperature.
Figure 6.2: XRD Patterns of Intermediate Phase with Increasing Temperature.
Figure 6.3: XRD Patterns of Sodalite with Increasing Temperature.
Figure 6.4: XRD Patterns of High Temperature Scale with Increasing Temperature

Chapter 6. Variable Temperature XRD Study.

62.
Figure 6.5: XRD Patterns of 39c Kirkvine Works Heater Scale with Increasing Temperature
Figure 6.6: XRD Patterns of AAL 9c scale with Increasing Temperature
Figure 6.7: XRD Comparison of Synthetic and Plant Scales at 27°C
Figure 6.8: XRD Comparison of Cancrinite and Plant Scales (High Temperature).
Figure 6.9: Identification of the Decomposed Product from the Thermal Treatment of Cancrinite at 1000 °C
Figure 6.10: Identification of Decomposition Product from the Thermal Treatment of Sodalite at 1000 °C
6.4 Conclusions

The three synthetic scales decompose over the temperature range 27 – 1000 °C. Synthetic cancrinite and the intermediate phase both decomposed at 800 °C to the cubic form of NaAlSiO₄ (nepheline). This suggests that NaAlSiO₄ is more stable than the zeolites at these high temperatures. In contrast decomposes to the hexagonal form of nepheline. The kirkvine works heater scale is a cancrinite based scale and the high temperature scale is predominately an intermediate scale. These both decompose to form cubic NaAlSiO₄ at 900 °C. This elevated temperature is due to the impurities within the plant scale. The mixed phase AAL 9c scale does not decompose within the temperature range analysed. The scale composition is a mixture of sodium aluminium silicate hydrate, and silicon oxide. The scale is also visibly different to the other scales analysed as it is red and brittle, unlike the cancrinite/intermediate scales which are white and chalky.
References


3. Raw Materials, booklet produced by Alcan Aluminium Ltd.


7. K. J. Bayer, (DE-PS 43977), 1887.


29. Parr Instrument Company, Illinois, USA.