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THE FORMATION AND FATE OF CARBONYL SULFIDE (COS) GAS IN ALUMINIUM SMELTING

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ABSTRACT

Carbonyl sulfide (COS) gas is emitted from aluminium smelters at concentrations of 1 – 8 ppmv or 0.2 – 1.6 kg-t Al produced. While COS emissions are relatively small compared to emissions of HF or SO₂, previous measurements suggest that COS is not efficiently captured in the scrubbing systems used by aluminium smelters and it has been suggested that the industry is a significant anthropogenic emitter of COS. COS is a unique sulfur gas in the atmosphere, due to its stability, lifetime of several years and implication in ozone depletion.

The source of COS and other sulfur gases from aluminium smelters, is the 1 – 4 mass% S content of anodes, consumed during aluminium electrolysis. These anodes are primarily made from petroleum coke, a low value and therefore high sulfur product, of crude oil refining. This thesis examines aspects of the formation and fate of COS in aluminium reduction cells.

One thesis objective was to confirm the nature of sulfur species present in petroleum cokes and anodes. A XANES (X-ray Absorption Near Edge Structure) spectroscopy study of cokes from the major suppliers and anode core samples showed that organic sulfur containing ring structures were the dominant sulfur species, before and after anode baking and even after significant desulfurisation at 1500ºC.

Thermodynamic calculations performed using the HSC Chemistry© computer package agreed with previous smelter measurements that COS gas was the dominant sulfur gas to form at the anode face and SO₂ became the dominant sulfur gas after the anode gases left the cell and mixed with an induced air draft in the cell hooding.

Previous smelter measurements showed that some COS (about 5 ppmv) did survive through the cell ducting into the dry scrubber and that there were only negligible reductions in COS concentration after dry scrubbing. The dry scrubber contains smelter-grade alumina, which adsorbs HF and other smelter gases, before the alumina is recycled to the cells.
Another objective of this thesis was to study the effect dry scrubbing had on COS emissions in greater detail in the laboratory to better understand any reactions that may be occurring. A thermodynamic analysis using HSC Chemistry© determined that alumina would reduce the stability of COS at a typical dry scrubbing temperature of 80°C. The dry scrubber was modelled in the laboratory using an alumina containing fluidised bed reactor, with the inlet and outlet gas composition monitored using mass spectrometry. Adsorbed species resulting from COS adsorption on alumina were studied separately using DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy).

Experiments showed that COS was stable in the fluidised bed apparatus in isolation. The presence of smelter-grade alumina led to the adsorption of COS in its molecular form and as adsorbed hydrogen thiocarbonate. The latter species is believed to be an intermediate in the hydrolysis of COS into H₂S on alumina. The effect of conditions which may vary in the dry scrubbing system, such as humidity, SO₂ and HF concentrations, were studied. The presence of optimum humidity levels ensured sustained hydrolysis of COS over several hours, but adsorbed SO₂ and HF interfered with COS conversion. This suggests that COS hydrolysis would be unlikely to occur to a great extent in commercial dry scrubbers used in the aluminium smelter industry.
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<thead>
<tr>
<th>Symbol/Abbreviation</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha'$</td>
<td>eV</td>
<td>Modified Na Auger parameter</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>eV</td>
<td>Resolution</td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>kJmol$^{-1}$</td>
<td>Standard change in Gibbs energy</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pa</td>
<td>Pressure drop across fluidised bed reactor</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Å</td>
<td>Wavelength of x-ray source</td>
</tr>
<tr>
<td>$\Theta$, $\theta$</td>
<td>$^\circ$</td>
<td>XRD angle of diffraction</td>
</tr>
<tr>
<td>$ad$</td>
<td></td>
<td>Adsorbed species</td>
</tr>
<tr>
<td>B, b, $\beta$</td>
<td>rads</td>
<td>XRD peak broadening due to sample and/or instrument</td>
</tr>
<tr>
<td>BE</td>
<td>eV</td>
<td>Binding energy</td>
</tr>
<tr>
<td>$C_a$</td>
<td>ppmv</td>
<td>Concentration of gas $a$</td>
</tr>
<tr>
<td>CSRF</td>
<td></td>
<td>Canadian Synchrotron Radiation Facility</td>
</tr>
<tr>
<td>d</td>
<td>Å</td>
<td>Interplanar spacing</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>Daily mass spectrometer correction factor</td>
</tr>
<tr>
<td>DCM</td>
<td></td>
<td>Double Crystal Monochromator</td>
</tr>
<tr>
<td>DRIFTS</td>
<td></td>
<td>Diffuse Reflectance Infrared Fourier Transform Spectroscopy</td>
</tr>
<tr>
<td>E</td>
<td>eV</td>
<td>Beam energy at edge</td>
</tr>
<tr>
<td>$E^0$</td>
<td>V</td>
<td>Standard electronic potential for redox reaction</td>
</tr>
<tr>
<td>EDS</td>
<td></td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td></td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FTIR</td>
<td></td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td></td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>FLY</td>
<td></td>
<td>Fluorescence Yield</td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>Gaseous species</td>
</tr>
<tr>
<td>GC-MS</td>
<td></td>
<td>Gas Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>HTC</td>
<td></td>
<td>Hydrogen thiocarbonate (adsorbed species)</td>
</tr>
</tbody>
</table>
## Symbol/Abbreviation

<table>
<thead>
<tr>
<th>Symbol/Abbreviation</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>hν</td>
<td>eV</td>
<td>Energy of the x-ray source in XPS</td>
</tr>
<tr>
<td>I</td>
<td>torr/ppmv</td>
<td>Ionisation correction factor</td>
</tr>
<tr>
<td>k</td>
<td></td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>K</td>
<td></td>
<td>Equilibrium constant for reaction</td>
</tr>
<tr>
<td>KE</td>
<td>eV</td>
<td>XPS kinetic energy</td>
</tr>
<tr>
<td>L</td>
<td>mm</td>
<td>Fluidised alumina bed height</td>
</tr>
<tr>
<td>Lc</td>
<td>Å</td>
<td>Crystallite size</td>
</tr>
<tr>
<td>m/z</td>
<td></td>
<td>Mass to charge ratio of ions in mass spectrometer</td>
</tr>
<tr>
<td>pₐ</td>
<td>torr</td>
<td>Partial pressure of gas a</td>
</tr>
<tr>
<td>pₐᵇ</td>
<td>torr</td>
<td>Background partial pressure of gas a</td>
</tr>
<tr>
<td>pₐᶜ</td>
<td>torr</td>
<td>Partial pressure of gas a at time of calibration</td>
</tr>
<tr>
<td>Pₚʳ</td>
<td>torr</td>
<td>Total pressure</td>
</tr>
<tr>
<td>r</td>
<td></td>
<td>Reaction rate</td>
</tr>
<tr>
<td>RH</td>
<td>%</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td></td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SRC</td>
<td></td>
<td>Synchrotron Radiation Center</td>
</tr>
<tr>
<td>TEY</td>
<td></td>
<td>Total Electron Yield</td>
</tr>
<tr>
<td>V₀</td>
<td>ms⁻¹</td>
<td>Superficial gas velocity in fluidised bed</td>
</tr>
<tr>
<td>[x]</td>
<td>ppmv, kmol</td>
<td>Concentration of species x</td>
</tr>
<tr>
<td>XANES</td>
<td></td>
<td>X-ray Absorption Near Edge Structure Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td></td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td></td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td></td>
<td>X-Ray Fluorescence</td>
</tr>
<tr>
<td>yₐ</td>
<td></td>
<td>Mole fraction of gas a</td>
</tr>
</tbody>
</table>
Chapter 1  INTRODUCTION

1.1 COS Emissions

COS forms as a by-product from the use of sulfur containing carbonaceous fossil fuels [1, 2]. In aluminium production, the anode is consumed during smelting, releasing the 1 – 4 mass% sulfur impurity present in the petroleum coke, the dominant component used to make the anode [3]. The resulting sulfur gas that forms under the anode is predominantly COS [4, 5]. The type of sulfur species present in cokes and anodes are not well understood and this prevents a complete mechanism for sulfur gas formation at the anode from being postulated. Therefore, one aim of this thesis was to determine the sulfur species present in petroleum cokes and anodes and to use this information to predict the thermodynamics of sulfur gas formation.

Gases that form at the anode bubble through the electrolyte and are released into the cell hood, where they are mixed with an induced air draft. At this stage, COS is largely oxidised into SO$_2$, although some COS does survive through the ducting to the scrubbing systems [4, 5]. Smelter-grade alumina is used to scrub the duct gases emitted from the reduction cells, particularly HF. Thus another aim of this thesis was to determine, based on further thermodynamic calculations and two major laboratory studies, how effective the dry scrubber is in removing COS.

The aluminium industry has been identified as a significant anthropogenic emitter of COS [6, 7]. COS is undesirable in the environment, because of its long lifetime and stability in the lower atmosphere. It is also one of the few sources of sulfur to the upper atmosphere, where it can decompose to form sulfate aerosols, which are implicated in ozone depletion. Sources of COS are numerous and currently outnumber the known sinks for COS [1, 8, 9]. Thus it is
important to understand the genesis and emission dynamics of COS from aluminium smelters.

1.2 Project Objectives

The main objectives of this project were:

1. To determine the forms of sulfur that exist in the carbonaceous material (petroleum coke) of an anode used in an aluminium smelting cell, since COS is produced from the consumption of the anode. Knowing the sulfur species present in anodes allows some insight into the mechanism for COS formation and the formation of other sulfur gases.

2. To study the thermodynamics of COS formation at the anode and subsequent partial oxidation to SO\(_2\) in cell ducting.

3. To study the activity of COS towards adsorption and reaction on alumina in the dry scrubbing system.

4. To find out how reactive COS is towards adsorption on alumina under conditions typical of a dry scrubber, particularly in the presence of HF, SO\(_2\) and H\(_2\)O, which are typical gases in aluminium smelting exhaust gas.

5. To determine the mechanism of reaction occurring between the alumina surface and COS, so that the stability of any adsorbed COS (or its reaction products) can be determined, with regard to potential recycle on secondary alumina.

1.3 Thesis Layout

The second chapter of the thesis details the present state of knowledge about the path of COS through an aluminium smelter. Then the thesis is split into two main bodies of work, relating to the formation and fate of COS in aluminium smelting:

**Part 1: The Formation of COS in Aluminium Smelting**: details experimental work using XANES (X-ray Absorption Near Edge Spectroscopy) to analyse the sulfur species present in petroleum cokes and anodes. This technique has been applied successfully to similar carbonaceous materials in the past, such as coal, and some of these studies are detailed in
Chapter 3. An explanation of XANES theory and the methods used are in Chapter 4, and results are in Chapter 5. Chapter 5 also includes thermodynamic calculations to predict the formation of sulfur gases at the anode and their stability leaving the cell.

**Part II: The Fate of COS in Aluminium Smelting**; describes two sets of experimental programmes investigating the effect of smelter-grade alumina on COS stability. Fluidised bed reactor studies of COS and smelter grade alumina were designed to simulate dry scrubbing conditions in the laboratory, using mass spectrometry to measure inlet and outlet gas composition of the reactor. DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) allowed unstable adsorbed species to be studied *in-situ* as the alumina surface was exposed to COS gas. Chapter 6 details literature on the interaction between COS and alumina, which has previously focussed on its role in Claus catalysis. Thermodynamic calculations to predict the stability of COS in the dry scrubber at equilibrium are discussed in Chapter 7. Chapter 8 covers the methods (fluidised bed, mass spectrometry and DRIFTS) used to investigate these reactions and Chapter 9 summarises these results to determine the impact of dry scrubbing on COS emissions.

The main conclusions from the studies of both the formation and fate of COS in aluminium smelting are summarised in Chapter 10. This chapter also includes the wider implications of this thesis to aluminium smelting.
Chapter 2  THE ROLE OF SULFUR IN ALUMINIUM SMELTING

The source of COS and other sulfur gases in aluminium smelting is mainly the carbon coke used to make anodes. As the anodes are consumed, sulfur is released as various sulfur gases, predominantly COS. When these gases leave the cell, COS is largely oxidised into SO\(_2\). The sulfur gases then pass through dry scrubbing, and sometimes wet scrubbing systems, before any remaining sulfur gases are released into the environment. The aluminium industry represents a significant proportion of the global anthropogenic COS emissions. COS gas is implicated in ozone depletion reactions in the upper atmosphere. This chapter examines the literature pertaining to each step in this process.

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2.6  SUMMARY ....................................................................................................30
2.1 The Aluminium Smelting Process

Aluminium is produced using the Hall-Héroult Process (see Figure 2.1), which reduces alumina electrolytically at around 960°C according to the following reaction:

\[ 2\text{Al}_2\text{O}_3\text{(soln)} + 3\text{C}\text{(s)} \rightarrow 4\text{Al}\text{(l)} + 3\text{CO}_2\text{(g)} \quad E^\circ = -1.18\text{V} \]  

(2.1)

Carbon anodes are consumed in the process to produce predominantly CO\(_2\) gas (Reaction (2.1)). However some CO can also form, resulting in increased carbon consumption according to the following net reaction:

\[ \text{Al}_2\text{O}_3\text{(soln)} + 3\text{C}\text{(s)} \rightarrow 2\text{Al}\text{(l)} + 3\text{CO}\text{(g)} \quad E^\circ = -1.06\text{V} \]  

(2.2)

Although Reaction (2.2) is thermodynamically preferred, reaction kinetics and polarisation result in anode gas being more than 90% CO\(_2\). CO formation becomes more significant at the anode sides, where the current density is lower [11]. A major source of CO, however, is due
to reaction of $\text{CO}_2$ with available carbon or back reaction with aluminium metal (see Section 2.3.2) [12].

Production occurs in a series of cells, containing a number of carbon anodes and a carbon cathode block. Alumina is added into the top of the cell and dissolves in an electrolytic bath of molten cryolite, which lies between the anodes and cathode block. Aluminium forms in a layer on the carbon cathode, so this molten aluminium layer effectively becomes the cathode, and is tapped off periodically.

### 2.1.1 Anodes

Anodes are of central importance in the current study, since they are the major source (>85%) of sulfur to the cell, resulting in the formation of COS and other sulfur gases. Anode gases form underneath the anode as a layer of bubbles before leaving the cell. Anodes are generally made from coke (petroleum or pitch coke) bound together with pitch (coal tar or petroleum pitch) and the majority of sulfur in the anode originates from the coke.

There are two common cell technologies in use for producing aluminium, which differ according to the type of anode used. Söderberg cells are one cell technology featuring continuous self baked anodes. The high emissions from these anodes (particularly polyaromatic hydrocarbons or PAHs) have lead to this technology being phased out [10], although perhaps 15% of world aluminium production still uses this technology. The dominant technology is the Prebake cell (see Figure 2.1), where the anode is baked outside of the cell before use. Söderberg anodes require about twice as much pitch as prebake. Normally, a prebake anode lasts 2 – 3 weeks and typical carbon consumption is 400 to 480 kgt$^{-1}$ Al [10], compared to a stoichiometric requirement of 334 kgt$^{-1}$ Al (with 100% current efficiency) [13].

In addition to cell anode technology, another important influence on the composition of sulfur emissions from the cell is the occurrence of anode effects. An anode effect occurs when the cell is depleted of alumina and is characterised by a sudden, uncontrolled voltage rise corresponding to electrolysis of the electrolyte itself and the formation of a gas film at the anode surface. Increased anode consumption during an anode effect results in the formation
of reduced gases such as CO, fluorocarbons (CF$_4$, C$_2$F$_6$) and CS$_2$. Measurements of anode gas composition during normal electrolysis and anode effect are detailed in Section 2.4.2.

Anode grade petroleum coke contains a number of impurities (typical values are shown in Table 2.1). The most substantial impurity in coke is sulfur and this is discussed in Section 2.3.

Table 2.1: The typical impurity composition of anode grade petroleum coke (based on [14], the remainder of the coke is carbon).

<table>
<thead>
<tr>
<th>Component</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>1.6 – 1.8</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1 – 0.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.1 – 0.3</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>0.1 – 0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal Content</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>275 – 325</td>
</tr>
<tr>
<td>Vanadium</td>
<td>130 – 200</td>
</tr>
<tr>
<td>Nickel</td>
<td>50 – 100</td>
</tr>
<tr>
<td>Calcium</td>
<td>75 – 125</td>
</tr>
<tr>
<td>Sodium</td>
<td>75 – 125</td>
</tr>
<tr>
<td>Silicon</td>
<td>100 – 150</td>
</tr>
</tbody>
</table>

2.1.2 Smelter Grade Alumina

Alumina is commonly used outside of aluminium smelting to adsorb or catalyse pollutant gases. However, these operations are usually carried out with catalyst grade alumina – the aluminium industry is unique in using its own convenient supply of smelter grade alumina to adsorb HF. Due to the strong activity of alumina towards HF capture, smelter grade alumina is acceptable, however it has a much lower surface area than catalyst alumina and a different composition.
Alumina is produced for aluminium smelting from the Bayer Process using the ore bauxite. It is initially extracted predominantly in the form of gibbsite, Al(OH)₃, then calcined to dehydrate it, resulting in a series of phase transformations (see Figure 2.2). The degree of calcination determines the final phase composition – α-alumina is fully calcined alumina and the least active (lowest surface area) phase – smelter grade is usually a mixture of phases including α-alumina, residual gibbsite and transition phases such as γ-alumina. Catalyst grade alumina is generally γ-alumina, providing it with a high surface area, and thus a greater adsorption or reaction capacity per unit mass of the alumina. The BET surface area of smelter grade alumina is typically 60 – 70 m²g⁻¹ due to it’s α-Al₂O₃ content, while that of catalyst alumina can be greater than 200 m²g⁻¹.

![Graph of Alumina Transformation Sequence](image)

**Figure 2.2:** Alumina transformation sequence Al(OH)₃ gibbsite → α-Al₂O₃ [15].

Loss on Ignition (L.O.I.) is a standard test method used in the aluminium industry and is the mass of moisture lost from alumina in an inert atmosphere under specific heating regimes. Free water mass can be determined by heating the alumina from 25°C to somewhere between 110 to 300°C. The loss of chemisorbed water occurs between 300 and 1000°C. L.O.I. can also be reported as the total mass lost at 1000 to 1200°C. A low value for L.O.I. is preferable in aluminium production because water entering the cell bath may result in increased fluoride emissions. However, higher moisture content in the alumina can increase the adsorption capacity in the dry scrubber [16].
In addition to BET surface area and L.O.I. there are a number of other specifications for smelter grade alumina and these are detailed in Table 2.2, along with typical values [10]. Balancing the requirements of the reduction cell and dry scrubber has lead most smelters to specify a free-flowing, moderately calcined alumina with relatively coarse, strong particles, a narrow size-distribution and low chemical impurity levels [17].

Table 2.2: Physical characteristics of smelter grade alumina [10].

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical Smelter Specifications</th>
<th>Weipa Bauxite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$ (wt%)</td>
<td>&lt;0.03</td>
<td>0.013</td>
</tr>
<tr>
<td>SiO$_2$ (wt%)</td>
<td>&lt;0.03</td>
<td>0.013</td>
</tr>
<tr>
<td>TiO$_2$ (wt%)</td>
<td>&lt;0.006</td>
<td>0.002</td>
</tr>
<tr>
<td>P$_2$O (wt%)</td>
<td>&lt;0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Na$_2$O (wt%)</td>
<td>&lt;0.65</td>
<td>0.55</td>
</tr>
<tr>
<td>CaO (wt%)</td>
<td>&lt;0.06</td>
<td>0.015</td>
</tr>
<tr>
<td>L.O.I. (%)</td>
<td>&lt;1.0</td>
<td>1.00</td>
</tr>
<tr>
<td>BET surface area (m$^2$g$^{-1}$)</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>Bulk density (kgm$^{-3}$)</td>
<td>0.95-1.05</td>
<td>1.07</td>
</tr>
<tr>
<td>Pyconometric density (kgdm$^{-3}$)</td>
<td>-</td>
<td>3.55</td>
</tr>
<tr>
<td>Fine particles (% &lt;45 µm mesh)</td>
<td>&lt;15</td>
<td>8</td>
</tr>
<tr>
<td>Coarse particles (% &gt;150 µm mesh)</td>
<td>&lt;3</td>
<td>3</td>
</tr>
<tr>
<td>$\alpha$-Alumina (wt%)</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>Angle of repose (º)</td>
<td>32</td>
<td>44</td>
</tr>
</tbody>
</table>

### 2.2 Dry Scrubbing

Gases from the aluminium smelting process leave the cell and pass through ducting to an alumina dry scrubbing system. The alumina used in the dry scrubbers is recycled to the cell, along with any impurities and adsorbed gases collected during scrubbing.

At its simplest, a dry scrubber is a cross current device as shown in Figure 2.3, where gases are passed through a fluidised bed of alumina before passing through bag filters that separate
the alumina and particulates from the gases, which then exit through a stack to the atmosphere. Modern dry scrubbers are more sophisticated in order to maximise contact between the alumina and the duct gases. In one commercial scrubber design, a “precontact” step is added, where raw duct gases are contacted with enriched alumina from the main scrubber. This initial step reduces the concentration of HF sufficiently to improve the ability of the alumina to adsorb low concentrations of HF in the main scrubber, with a resulting increase in overall efficiency [18].

![Figure 2.3: A simple cross current dry scrubber [19].](image)

### 2.2.1 Gaseous Emissions From Aluminium Smelting

As already mentioned, the primary reason for dry scrubbing is to remove HF, impurities (Fe, Ni, V) and particulate fluorides from the electrolyte bath (NaAlF$_4$, Na$_3$AlF$_6$, Na$_5$AlF$_{14}$) [10]. However, as these emissions are efficiently captured in the dry scrubber, some attention has been focussed on the emissions of lesser gases (see Table 2.3). Capture of these other emissions can have downstream consequences on the alumina from the dry scrubbers recycled into the cell. Inability to capture these emissions could become problematic if tougher emission legislation for the specific gases involved is introduced.

In terms of environmental effects, fluorocarbon emissions, CF$_4$ and C$_2$F$_6$, are the next most concerning after HF. However, these are produced only during anode effect, along with CS$_2$ and CO, so with effective control over anode effects these emissions can be minimised.
### Table 2.3: Species present in the fumes from a smelting cell [20]

<table>
<thead>
<tr>
<th><strong>Fluoride Gases</strong></th>
<th><strong>Sulfurous Gases</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Fluoride (HF)</td>
<td>Sulfur dioxide (SO₂)</td>
</tr>
<tr>
<td>Carbon Tetrafluoride (CF₄)</td>
<td>Carbonyl sulfide (COS)</td>
</tr>
<tr>
<td>Dicarbon hexafluoride (C₂F₆)</td>
<td>Hydrogen sulfide (H₂S)</td>
</tr>
<tr>
<td>Silica tetrafluoride (SiF₄)</td>
<td>Carbon disulfide (CS₂)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Other Gases</strong></th>
<th><strong>Particulates</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide (CO₂)</td>
<td>Carbon soot (C)</td>
</tr>
<tr>
<td>Carbon monoxide (CO)</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td>Water (H₂O)</td>
<td>Alumina (Al₂O₃)</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Cryolite (Na₃AlF₆)</td>
</tr>
<tr>
<td></td>
<td>Chiolite (Na₅AlF₁₄)</td>
</tr>
<tr>
<td></td>
<td>Aluminium fluoride (AlF₃)</td>
</tr>
<tr>
<td></td>
<td>Calcium fluoride (CaF₂)</td>
</tr>
</tbody>
</table>

Following HF emissions, the next most significant emission from a prebake smelter during normal operation is SO₂. Dry scrubbing can sometimes be followed by wet scrubbing, in order to capture SO₂ emissions, which are not efficiently captured in the dry scrubber since HF adsorbs in preference to (and will displace) SO₂ on alumina [21]. However, unlike regulations over HF emissions, regulation of SO₂ emissions exists only in a few countries (Scandinavia and parts of the US), so wet scrubbing is not commonplace [22].

No technology exists for effective capture of the other sulfur gases, COS and H₂S [5]. These are produced in much smaller quantities than SO₂, but the publication of several recent papers suggests that the aluminium industry is a significant source of COS [6, 7].
2.3 Sulfur in Cokes and Anodes

The origin of sulfur gases in aluminium smelting is chiefly from the 1 to 4 wt% sulfur impurity present in anodes. The exact sulfur species in the anode are not well understood. The major source of the sulfur impurity is petroleum coke, the major component of the anodes, which is obtained from crude oil, as summarised in Figure 2.4.

Sulfur is incorporated into crude oil when $\text{H}_2\text{S}$ and polysulfides produced by anaerobic bacteria react with either unstable organic structures [24], or with ferrous ions to form pyrite (or other metal sulfides, particularly in marine environments) early on in crude oil formation [25]. More than 1500 sulfur compounds have been identified in crude oil, with a dominance of organic, sulfur containing ring structures within the carbon structure [24]. The sulfur species present in any one coke will therefore depend on the location and mechanism of formation of the parent crude oil.
To produce coke, crude oil is first distilled for petroleum refining, and then the residuum fraction is the feedstock for the coking process, which is carried out at about 450°C [26]. Coke accounts for about 4 – 6 % of the products by volume from crude oil, but only 2 % by value [23], making it the least valuable product in petroleum refining and so it is where sulfur species tend to be concentrated, to maintain the quality of the other fractions. The sulfur content of cokes is increasing, as supply and cost factors dictate that progressively more sour crude oils are refined. A process can be developed to desulfurise the coker feed, producing light products for further refining and sulfur gases to be processed into sulfur as a by-product, in addition to desulfurised coker feed. Although this hydrodesulfurisation of residual oil is not commonly carried out at the moment, it is the most efficient way of removing sulfur from coke [23].

![Thermogravimetric analysis of emissions during coke calcination. The weight loss above 1500°C was attributed to desulfurisation [27].](image)

**Figure 2.5: Thermogravimetric analysis of emissions during coke calcination. The weight loss above 1500°C was attributed to desulfurisation [27].**

Some sulfur is lost during coke calcination, however a significant sulfur impurity remains. Since it is uncommon to desulphurise coker feed, desulphurisation of coke has been considered. Jones *et al.*’s study of high sulfur cokes [27] determined that sulfur species in coke are largely stable up to about 1500°C, with maximum emission of sulfur species from cokes at around 1600°C, as shown in Figure 2.5. Thus, desulphurising coke is impractical since it would be overcalcined for optimum anode and energy usage. In the absence of any desulphurisation process, green coke is calcined at 1250°C [26] prior to being mixed with pitch (and anode butts) to produce green anodes. After the anodes are baked, they are then ready for smelter
use. The complete process of producing coke from crude oil and then making anodes is illustrated in Figure 2.4 [23].

2.3.1 Desulfurisation During Anode Baking

To make anodes, calcined coke and crushed anode butts are bound with pitch and baked at 1000 – 1250°C over 5 – 8 days [28]. While pitch contains about 0.5%S, it makes up less than 20% of the anode and most is lost on baking. Sørlie et al. [29] tried adding elemental sulfur or dibenzothiophene into the pitch used to make anodes. Neither elemental sulfur or dibenzothiophene survived in significant amounts in the final baked anodes, producing anodes containing ranges of 1.25-1.34 %S and 1.19-1.33 %S respectively.

Thus the majority of sulfur in the final baked anode comes from the coke, which contains 0.7 to 3.7%S. Depending on the process conditions used, sulfur loss can occur during anode baking, however the majority of sulfur loss has already occurred in coke calcination [3]. Desulfurisation on anode baking leads to increased porosity, resulting in reduced performance of the anode.

Desulfurisation has been detected as a function of both soak time and temperature [30], thus allowing a slow rate of sulfur loss at lower temperatures than those used for coke calcination. Sulfur loss due to a long soak time, has been found to result in more porosity than sulfur loss in an anode baked at a higher temperature [30]. An optimum baking temperature and soak time will therefore result in the best physical properties of the anode, due to the competing processes of densification due to graphitisation and porosity resulting from desulfurisation.

2.3.2 The Effect of Sulfur on Anode Performance

When the anode is in the cell, it is consumed to form predominantly CO$_2$ and some CO according to Reactions (2.1) and (2.2). In addition to these reactions, the Boudouard reaction may take place at the anode:
$$\text{C} (s) + \text{CO}_2 (g) \rightarrow 2\text{CO} (g) \quad (2.3)$$

The reactivity of the anode towards $\text{CO}_2$ is thus important to determine the overall carbon consumption during electrolysis. Oxidation by $\text{O}_2$ in the cell hood is another mechanism for excess carbon consumption of the anode. The composition of the anode can alter its sensitivity towards $\text{CO}_2$ and $\text{O}_2$ reactivity. However, it is often difficult to attribute increased reactivity to any one impurity and as a result, there are some conflicting results with respect to the effect of sulfur content.

In addition to sulfur, common anode impurities include V, Al, Fe, Ni, Li and Na. The presence of V was found by Kuang et al. [12] to increase carbon consumption (both as carbon dust and carbon gas ($\text{CO}_2$ and CO)). Fe and Ni contaminants also increase carbon consumption and both are known catalysts in $\text{CO}_2$ and $\text{O}_2$ reactions with anodes [12, 31]. Li impurity leads to increased carbon consumption due to carbon dust formation [12]. Na also increases $\text{CO}_2$ reactivity, but Hume et al. found that the presence of sulfur appears to inhibit the reactivity between Na and $\text{CO}_2$ because Na is bound by the sulfur into an inactive form [32].

Vogt et al. [30] found that air reactivity of the anode during electrolysis, and to a lesser extent $\text{CO}_2$ reactivity, increase with the extent of desulfurisation during baking. This evidence also suggests that the presence of sulfur helps to reduce the reactivity of anodes, by binding with potentially catalysing impurities. The increased porosity that occurs with desulfurisation will also make the anode more susceptible to chemical attack.

There is a loose correlation between increasing sulfur content and increasing impurity content in anodes [3]. Therefore, attempts to determine the extent of airburn that may occur with changing sulfur levels is difficult to distinguish from the effects of other airburn catalysing impurities. Jones et al. [27] found that net carbon consumption of the anode increased 2-3% per %S (between 1%S and 4%S), which was attributed to the inefficiency of COS formation and to increased impurity-catalysed airburn. While Sørlie et al. found that air reactivity of the anode went through a minimum at about 1.3 %S [29]. Jones et al. [27] found that the amount of airburn increased with the sulfur content of the anode, due to the increased porosity they
observed in high sulfur anodes (presumably due to desulfurisation) and increased impurity catalysed airburn.

All in all, it seems likely that any increase in airburn with increasing sulfur content is not due to the presence of sulfur itself, but rather the increased catalysing impurity levels and the greater potential for porosity due to desulfurisation on baking. Anodes treated by adding varying amounts of dibenzothiophene (which contains organic sulfur in 5-membered rings) to the pitch prior to baking, were observed to generally have decreased CO$_2$ and air reactivity with increasing sulfur content within the narrow range studied (1.19-1.33 %S) [29].

![Graph of dusting percentage and carbon consumption vs. sulfur content](image)

**Figure 2.6:** The effect of anode sulfur content on carbon consumption found by [12]. Carbon Gasification + Carbon Dust = Carbon Consumption.

Changes in reactivity towards CO$_2$ oxidation due to sulfur content (according to Reaction (2.3)) seem to be easier to identify. Sørlie *et al.* [12, 29] found that when the sulfur content of anodes were varied (1.19-2.85 %S) by the addition of different cokes, a decrease in CO$_2$ reactivity was observed with increasing sulfur content, as shown in Figure 2.6. But at the same time, the amount of carbon dust produced during electrolysis increased with increasing
sulfur content, so the overall effect was a slight decrease in anode consumption with increasing sulfur content.

Likewise, Gilmore and Bullough [33] found that sulfur inhibited the carbon to CO₂ reaction during electrolysis and proposed that this lead to an increased level of carbon dust in the electrolyte. However, they believed that carbon dust was the main carbon source for the Boudouard Reaction (2.3), contrary to Sørlie et al.’s results.

It was also suggested by Gilmore and Bullough [33] that there was increased sulfide corrosion of steel anode pins in a reduction cell with increasing anode sulfur content, based on previous results [34], although their own results were inconclusive.

In conclusion, sulfur appears to reduce airburn by binding to other anode impurities. There is evidence that the presence of sulfur leads in increased levels of carbon dust in the electrolyte, however when this is combined with reduced CO₂ reactivity, its affect on net carbon consumption becomes negligible. Meanwhile, anode performance is also negatively affected by desulfurisation that may occur during anode baking.

2.3.3 Removing the Sulfur Impurity

Where regulations exist, smelters currently deal with the sulfur impurity in aluminium production by removing the resulting SO₂ in wet scrubbers. With the sulfur content currently increasing in cokes, the alternatives that can be considered for removing sulfur can be summarised as follows (See Figure 2.4 [23]):

- Thermal coke desulfurisation and green coke purification processes, both of which destroy or detrimentally alter the coke properties.
- Selection of low sulfur cokes and blending of cokes, both of which are limited by the quality and price of coke available.
- Desulfurisation of coker feed or coal liquefaction of feed stocks, neither of which has been developed into a viable process, and in the latter case, is dependant on crude prices increasing. Desulfurisation of coker feed is however the most promising opportunity to remove sulfurs from the coke fraction of crude oil.
2.4 COS Emissions in Aluminium Smelting

As mentioned in Section 2.2.1, no measures are currently taken in the aluminium industry to capture COS and H₂S emissions, apart from any incidental capture during dry scrubbing (primarily to remove HF) and wet scrubbing (to remove SO₂). Emissions of COS may be minimised by understanding its source and path through an aluminium smelter. This section details the origin of COS and other sulfur gas emissions from anodes through to the emission of COS from scrubbers.

2.4.1 Thermodynamic Predictions of COS Formation at the Anode

During electrolysis, Reactions (2.1), (2.2) and (2.3) occur as the anode is consumed, forming CO₂ and CO. Measurements of anode gas have shown that COS is the major sulfur gas to form during normal electrolysis. In addition to anode gas measurements, thermodynamic calculations have also been used to predict the likely reactions occurring to form COS [4, 11, 35, 36].

Dorreen et al. [11] showed that COS could form electrochemically at a potential lower than for CO₂ (Reaction (2.1)) or CO (Reaction (2.2)) formation, according to the reaction:

\[
\text{Al}_2\text{O}_3 \text{(soln)} + 3\text{C} \text{(s)} + 3\text{S} \text{(s)} \rightarrow 3\text{COS} \text{(g)} + 2\text{Al} \text{(l)} \quad \text{E}^\circ \text{ (970ºC)} = -1.04\text{V} \quad (2.4)
\]

The formation of COS is also thermodynamically possible by a chemical mechanism according to the reaction [11]:

\[
\text{S} \text{(s)} + \text{CO}_2 \text{(g)} + \text{C} \text{(s)} \rightarrow \text{COS} \text{(g)} + \text{CO} \text{(g)} \quad K = 4.44 \times 10^2 \quad (2.5)
\]

\[
\text{S} \text{(s)} + \text{CO} \text{(g)} \rightarrow \text{COS} \text{(g)} \quad K = 4.57 \times 10^0 \quad (2.6)
\]

Thonstad et al. [36] agreed that COS formation was possible electrochemically, according to Reaction (2.4) with E° (960ºC) = -1.104V. S₂ gas formation was also thermodynamically
possible. Due to the higher atomic mass of S compared to C, and the formation of COS, instead of SO$_2$ or CO$_2$, an increase in anode consumption of 1.9% can be calculated [5]. SO$_2$ formation is thermodynamically less favoured (2.7), although the anode potential is high enough to allow COS and SO$_2$ formation reactions to occur [5].

$$2\text{Al}_2\text{O}_3\text{ (soln)} + 3\text{S (s)} \rightarrow 3\text{SO}_2\text{ (g)} + 4\text{Al (l)} \quad E^\circ (960^\circ\text{C}) = -1.51\text{V} \quad \text{(2.7)}$$

Ødegård et al. used thermodynamic calculations to predict the gas composition at the anode of CO$_2$, CO, H$_2$, H$_2$O, H$_2$S, CS$_2$, COS and SO$_2$ at 750, 1000, 1250K, as a function of the CO$_2$/CO partial pressure ratio. COS was the preferred sulfur gas to form at temperatures up to 1000K. At 1250K, the sulfur gas composition was dependant on the CO$_2$/CO ratio. For 3 wt% S in the anode gas, COS was favoured at low pCO$_2$/pCO ratios, as shown in Figure 2.7. The sulfur gas composition also depended on the percentage of total sulfur present in the gas.

![Figure 2.7](image)

**Figure 2.7:** The thermodynamic equilibrium of sulfur and hydrogen containing gases for a gas containing 3wt%S at 1250K when the ratio of CO$_2$ to CO is changing (From [35]).

Figure 2.8 shows another thermodynamic prediction of the sulfur gas composition at (“unburnt”) and leaving (“burnt”) the anode. These calculations also show that COS will be
the dominant sulfur gas to form at the anode (unburnt gas, either in the lab or industrial cell), based on thermodynamic predictions [11]. However, as the gases leave the cell, they are “burnt” by the induced air draft in the cell hood, and these predictions show that SO₂ is then favoured during normal cell operation. During an anode effect, the reduced gases COS, CS₂, and H₂S are favoured and the gas is not fully oxidised to SO₂ on burning.

Figure 2.8: Composition of sulfur species present in the anode gas, both unburnt and burnt, predicted by Dorreen et al.’s thermodynamic calculations. The Lab Cell calculations differ from the Industrial Cell calculations, because the latter takes moisture from the air into account, enabling H₂S formation [11].

Utne et al. [4, 36] calculated that COS will be oxidised in the presence of air (2.8), but the conversion of COS into SO₂ with CO₂ was not favourable (2.9), indicating that COS would be the favoured anode sulfur gas, but would then be converted to SO₂ on exiting the cell.

\[
\begin{align*}
\text{COS} \,(g) + \frac{3}{2} \text{O}_2 \,(g) & \rightarrow \text{CO}_2 \,(g) + \text{SO}_2 \,(g) & \Delta G^\circ \,(970^\circ C) &= -452.2 \text{kJmol}^{-1} \quad (2.8) \\
\text{COS} \,(g) + 2 \text{CO}_2 \,(g) & \rightarrow \text{SO}_2 \,(g) + 3\text{CO} \,(g) & \Delta G^\circ \,(970^\circ C) &= 71.17 \text{kJmol}^{-1} \\
& & K \,(960^\circ C) &= 7.58 \times 10^{-4} \\
& & K \,(600^\circ C) &= 5.9 \times 10^{-9}
\end{align*}
\]
Reaction (2.9) shows that equilibrium favours COS and CO$_2$ in anode gas, and equilibrium is shifted even further to the left as the gas is cooled (in the absence of air) [36].

Overall, thermodynamic calculations show that COS is the stable sulfur species in anode gas, while SO$_2$ is the stable sulfur species in duct gas. Small amounts of H$_2$S, S$_2$ and CS$_2$ are also possible in the anode gas. However, the form of sulfur in the anode at the point of consumption has never been understood well enough to determine the exact reaction that releases sulfur from the anode into the gas.

### 2.4.2 Measurements of COS in Anode Gas

Thermodynamic predictions tell nothing of the rate at which reactions can occur, therefore smelter measurements are the only way to confirm calculations that COS is the dominant anode sulfur gas. Measurements of COS concentration in anode gas have been performed a number of times in both smelters [4-7, 36-38] and laboratory scale cells [11, 35].

<table>
<thead>
<tr>
<th>Cell</th>
<th>S Gas ppmv</th>
<th>During Normal Operation</th>
<th>During Anode Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anode Gas</td>
<td>Burned Gas</td>
</tr>
<tr>
<td>Prebake</td>
<td>COS</td>
<td>3100</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>SO$_2$</td>
<td>-</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>CS$_2$</td>
<td>-</td>
<td>3900</td>
</tr>
<tr>
<td></td>
<td>H$_2$S</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>Söderberg</td>
<td>COS</td>
<td>1800</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>SO$_2$</td>
<td>500</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>CS$_2$</td>
<td>-</td>
<td>10100</td>
</tr>
<tr>
<td></td>
<td>H$_2$S</td>
<td>500</td>
<td>-</td>
</tr>
</tbody>
</table>

COS was first detected in anode gas by Henry and Holliday [37], who found that COS was the primary sulfur gas to form at the anode during normal electrolysis and CS$_2$ during anode effect for both prebake and Söderberg cell technologies. They observed an increase in H$_2$S
and SO₂ from hydrolysis and oxidation of COS and CS₂ in the “burned” anode gas. Elemental sulfur was detected in particulate matter collected in the absence of air. These results are shown in Table 2.4.

Table 2.5: Ødegård et al.’s measurement of anode gas in a laboratory cell over time [35].

<table>
<thead>
<tr>
<th>S Gases</th>
<th>Anode Gas with Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14</td>
</tr>
<tr>
<td>COS</td>
<td>2.7</td>
</tr>
<tr>
<td>SO₂</td>
<td>2.7</td>
</tr>
<tr>
<td>CS₂</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Ødegård et al. [35] performed a laboratory investigation of sulfur species in anode gas using prebaked anode samples with 1 – 2 wt%S. COS, SO₂ and CS₂ were detected using gas chromatography over time during electrolysis, with the results shown in Table 2.5. The highest emission of sulfur gases occurred at the start of electrolysis with a new anode. COS was the dominant anode sulfur gas in all but the early stages of electrolysis. A further laboratory study was performed by Dorreen et al. [11], who found that COS was the only sulfurous gas detected in the anode gas either during normal electrolysis or anode effect.

Surprisingly, Kimmerle et al. [38] found that SO₂ was the dominant anode sulfur gas (Table 2.6), despite very low reported air concentrations in their anode gas samples. Their measurements were taken using GC-MS (Gas Chromatography – Mass Spectrometry) from prebake cells, with anodes containing 2.4 wt%S.

Table 2.6: Kimmerle et al. measurements of anode and duct sulfur gas concentrations [38].

<table>
<thead>
<tr>
<th>S Gases</th>
<th>Anode Gas</th>
<th>Duct Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppmv</td>
<td>kg/t Al</td>
</tr>
<tr>
<td>COS</td>
<td>380</td>
<td>-</td>
</tr>
<tr>
<td>SO₂</td>
<td>8000</td>
<td>-</td>
</tr>
<tr>
<td>CS₂</td>
<td>364</td>
<td>-</td>
</tr>
</tbody>
</table>

A comprehensive study of COS emissions at various stages in an aluminium smelter using both prebake (1.1 wt%S in anode) and Söderberg cells (0.86 wt%S in anode) was carried out.
by Utne *et al.* [4, 36], and later followed up by Tveito *et al.* (using prebake anodes with 1.4wt%S) [5]. They found COS levels in anode gas to be one order of magnitude higher than Kimmerle *et al.* and found COS to be the dominant sulfur gas under the anode at concentrations of 3000-4000 ppm. Local O\(_2\) concentration, anode effects and CO concentration were all believed to affect final COS emission levels, resulting in large variability from cell to cell. The gas composition changed in the cell hood and COS was largely oxidised to SO\(_2\), so that only 10-15 ppm COS remained.

Table 2.7: Utne *et al.*’s measurement of anode and cell hood sulfur gases [4].

<table>
<thead>
<tr>
<th>Cell</th>
<th>S Gases</th>
<th>Anode Gas</th>
<th>Cell Hood Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ppmv kg/t Al</td>
<td>ppmv kg/t Al</td>
</tr>
<tr>
<td>Prebake</td>
<td>COS</td>
<td>3800 6.9</td>
<td>15.52 -</td>
</tr>
<tr>
<td></td>
<td>SO(_2)</td>
<td>452 0.9</td>
<td>44 -</td>
</tr>
<tr>
<td></td>
<td>CS(_2)</td>
<td>267 0.6</td>
<td>- -</td>
</tr>
<tr>
<td>Söderberg</td>
<td>COS</td>
<td>2654 4.8</td>
<td>10.60 0.06</td>
</tr>
<tr>
<td></td>
<td>SO(_2)</td>
<td>- -</td>
<td>284 3.5</td>
</tr>
<tr>
<td></td>
<td>CS(_2)</td>
<td>- -</td>
<td>- -</td>
</tr>
</tbody>
</table>

Table 2.8: Tveito *et al.*’s measurement of sulfur gas composition under the anode, at the alumina feeder hole, molten aluminium tap hole and under the top crust in a prebake cell [5].

<table>
<thead>
<tr>
<th>S Gas</th>
<th>Anode Gas</th>
<th>Feeder Hole</th>
<th>Tap Hole</th>
<th>Under Crust</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppmv kg/t Al</td>
<td>ppmv</td>
<td>ppmv</td>
<td>ppmv</td>
</tr>
<tr>
<td>COS</td>
<td>3980 3.74</td>
<td>750</td>
<td>180</td>
<td>36</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>398 0.38</td>
<td>2800</td>
<td>250</td>
<td>240</td>
</tr>
<tr>
<td>CS(_2)</td>
<td>140 0.31</td>
<td>50</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>H(_2)S</td>
<td>130 0.13</td>
<td>250</td>
<td>30</td>
<td>14</td>
</tr>
</tbody>
</table>

Tveito *et al.*’s study was the first study since Henry and Holliday’s to measure H\(_2\)S levels (in addition to COS, SO\(_2\) and CS\(_2\)) and H\(_2\)S was present at significant levels in anode gas [5]. The concentration of COS, CS\(_2\) and SO\(_2\) in anode gas were very similar to previous measurements by Utne *et al.* [4]. Other gas sampling sites included the alumina feeder hole, molten aluminium tap hole and under the top crust, all of which were diluted in air to various extents. These results, given in Table 2.8, show that SO\(_2\) is the dominant sulfur species once
the gas has been mixed with air. However, COS, H₂S and CS₂ are all detected at the various sites, showing that these gases are stable to at least a certain extent.

While there are some discrepancies, it seems realistic to conclude from these studies that COS is the dominant anode sulfur gas to form under the anode. On mixing the anode gas with air in the cell hood, it is then largely oxidised to SO₂, but significant amounts of COS, H₂S and CS₂ remain. Table 2.12 in the next section (Section 2.4.3) summarises all the measurements taken.

### 2.4.3 Impact of Scrubbing on COS

Despite COS oxidation by air to SO₂ in the cell hood and ducting there is still appreciable amounts of COS present as the gas enters the dry scrubbing system. The impact of dry scrubbing and wet scrubbing on COS emission levels have also been measured by various groups.

**Table 2.9: Concentration of COS, SO₂ and CS₂ after dry scrubbing in a prebake smelter, measured by Harnisch et al. [6].**

<table>
<thead>
<tr>
<th>S Gases</th>
<th>After Scrubbing ppmv</th>
<th>kg/t Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>COS</td>
<td>6</td>
<td>1.6</td>
</tr>
<tr>
<td>SO₂</td>
<td>35</td>
<td>10</td>
</tr>
<tr>
<td>CS₂</td>
<td>0.1</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Harnisch *et al.* [6] measured the concentration of COS and CS₂ using mass spectrometry after dry scrubbing from a smelter with 1.1wt%S prebake anodes. Data on SO₂ emissions was provided by the smelter. The sulfur gas composition, given in Table 2.9, shows that COS accounts for about 15% of the sulfur emissions measured (H₂S levels were not measured).

Kimmerle *et al.* [38] used GC-MS to continuously measure CO₂, CO, COS and CS₂ emissions and ion chromatography to measure SO₂ emissions from a prebake smelter. Samples at the entrance and exit of the dry scrubber had the same composition, so they assumed that dry scrubbing had no effect on emission levels and carried out subsequent
measurements at the dry scrubber entrance only. COS and SO₂ measurements were confirmed using tuneable diode laser absorption spectroscopy continuously over 2 days for 64 cells. They found that COS emissions could fluctuate by 20% over 24 hours at the dry scrubbing entrance, but daily averages fluctuated by only 2%. They suggested that COS emissions were inversely related to SO₂ emissions, from the results shown in Figure 2.9. COS emissions were measured at 6.4 ppmv before the dry scrubber, which was about 4% of the total sulfur gas emissions (although, once again, H₂S levels were not measured) – this data is included in Table 2.6.

![Figure 2.9: Variation in continuous COS and SO₂ concentrations before dry scrubbing measured by Kimmerle et al. [38].](image)

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>S Gases</th>
<th>Dry Scrubber</th>
<th>Bagfilter</th>
<th>Wet Scrubber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inlet ppmv kg/t Al</td>
<td>House Exit ppmv kg/t Al</td>
<td>Exit ppmv kg/t Al</td>
</tr>
<tr>
<td>Prebake</td>
<td>COS</td>
<td>1.5 0.37</td>
<td>0.9 0.21</td>
<td>1.0 0.24</td>
</tr>
<tr>
<td></td>
<td>SO₂</td>
<td>158 16.1</td>
<td>110 11.2</td>
<td>14.8 2.32</td>
</tr>
<tr>
<td></td>
<td>CS₂</td>
<td>- -</td>
<td>- -</td>
<td>- -</td>
</tr>
<tr>
<td>Söderberg</td>
<td>COS</td>
<td>6.6 0.42</td>
<td>5.1 0.33</td>
<td>3.5 0.23</td>
</tr>
<tr>
<td></td>
<td>SO₂</td>
<td>489 12.7</td>
<td>304 7.92</td>
<td>1.2 0.26</td>
</tr>
<tr>
<td></td>
<td>CS₂</td>
<td>- -</td>
<td>- -</td>
<td>- -</td>
</tr>
</tbody>
</table>

Table 2.10: Utne et al.’s [4, 36] measurements of sulfur gas emissions before and after dry scrubbing and after wet scrubbing.
Utne et al. [4, 36] used gas chromatography to measure sulfur gas concentrations before and after dry scrubbing and after wet scrubbing for both prebake and Söderberg cells. COS emissions were found to be similar for prebake and Söderberg cells in kg/t Al and were lower than emissions levels measured by Kimmerle et al. A small decrease in COS levels was observed across the dry scrubber. The effect of wet scrubbing on COS levels was not clear. Dry and wet scrubber emissions are included in Table 2.10, anode gas emissions are in Table 2.7.

Table 2.11: Sulfur gas composition around the dry and wet scrubbers measured by Tveito et al. [5] from the same cell-line as earlier measurements by Utne et al. [4].

<table>
<thead>
<tr>
<th>S Gas</th>
<th>Dry Scrubber Inlet ppmv</th>
<th>Dry Scrubber Outlet ppmv</th>
<th>Wet Scrubber Outlet ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>COS</td>
<td>2.58</td>
<td>0.70</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>0.63</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>63.1</td>
<td>12.6</td>
<td>5.21</td>
</tr>
<tr>
<td></td>
<td>18.1</td>
<td></td>
<td>1.50</td>
</tr>
<tr>
<td>CS₂</td>
<td>0.69</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂S</td>
<td>1.47</td>
<td>0.22</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>0.21</td>
<td></td>
<td>0.20</td>
</tr>
</tbody>
</table>

Most recently, Tveito et al. [5] measured sulfur gas levels (including H₂S) before and after the dry scrubber and after wet scrubbing. Measurements were taken when no operations such as tapping and anode changing were taking place, since these resulted in large variations in emission levels. However, this may mean that they underestimated overall emission levels. Dry scrubbing was found to decrease COS levels (see Table 2.11), but to a lesser extent than found by Utne et al., while wet scrubbing resulted in a very slight increase in COS levels. It was suggested that this was perhaps due to dissolved COS present in the scrubber seawater. Post-dry scrubber COS emissions in kg/t Al were much higher than Utne et al. found based on measurements on the same cell line two years earlier.
Table 2.12: A summary of previous smelter measurements of sulfur gas composition.

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Anode Type</th>
<th>Anode S Content</th>
<th>[COS] at Anode</th>
<th>[COS] before Dry Scrubber</th>
<th>[COS] after Dry Scrubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry and Holliday</td>
<td>Prebake</td>
<td>-</td>
<td>3100 ppmv</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Söderberg</td>
<td></td>
<td>-</td>
<td>1800 ppmv</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Harnisch et al.</td>
<td>Prebake</td>
<td>1.1 wt%</td>
<td>380 ppmv</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kimmerle et al.</td>
<td>Prebake</td>
<td>2.4 wt%</td>
<td>380 ppmv</td>
<td>6.4 ppmv</td>
<td>1.1 ppmv</td>
</tr>
<tr>
<td>Utne et al.</td>
<td>Prebake</td>
<td>1.1 wt%</td>
<td>3800 ppmv</td>
<td>6.9 ppmv</td>
<td>1.5 ppmv</td>
</tr>
<tr>
<td>Söderberg</td>
<td></td>
<td>0.86 wt%</td>
<td>2654 ppmv</td>
<td>4.8 ppmv</td>
<td>6.6 ppmv</td>
</tr>
<tr>
<td>Tveito et al.</td>
<td>Prebake</td>
<td>1.4 wt%</td>
<td>3980 ppmv</td>
<td>3.74 ppmv</td>
<td>2.58 ppmv</td>
</tr>
</tbody>
</table>

A summary of the COS emission data that has been collected is given in Table 2.12. Generally, the different results agree in that there is little if any decrease in COS levels after dry scrubbing. However, there is some significant variation in emission levels, with measured COS emission levels exiting the anode at 380 to 3980 ppmv or 3.74 to 6.9 kg/t Al, and COS emissions exiting the smelter (after scrubbing) varying from 1 to 6 ppmv or 0.2 to 1.6 kg/t Al.

There are some considerable difficulties accurately measuring gas concentrations at the anode, due to temperature changes and air exposure as the gases exit the cell crust, which may in part explain some of the differences in anode sulfur gas composition. In addition, differences to the operation of the cell (aluminium tapping, anode change, anode effect, alumina addition) and the sulfur content of the anode in different smelters will impact on measurement of sulfur gas composition at the various points from the anode through to the scrubbing system. The variation observed in sulfur gas composition measurements by different groups is a driver for this research on the mechanism of sulfur gas formation at the anode and the behaviour of sulfur gases, particularly COS, through the dry scrubbing system.
2.5 COS in the Atmosphere

Surprisingly, COS is the dominant sulfur gas in the atmosphere. This is largely due to its stability in the lower atmosphere, with a lifetime of several years. Most other sulfur gases last only hours or days in the atmosphere, before being converted. It is unique in another way, since it is one of the few conduits of sulfur into the stratosphere (upper atmosphere), where it has been implicated in ozone depletion reactions.

SO\textsubscript{2} and other sulfur gases are also of concern as pollutants, because although they are very short lived in the troposphere, they exit the atmosphere as sulfate aerosols, contributing to acid rain.

![The atmospheric sulfur cycle, including sources and sinks of sulfur gases to the atmosphere](image)

Figure 2.10: The atmospheric sulfur cycle, including sources and sinks of sulfur gases to the atmosphere [1, 39, 40]. Dotted lines represent sinks.

In 1995, measurements of COS emissions from a prebake aluminium smelter were used by Harnisch et al. [6, 7] to calculate that aluminium production was responsible for about 6% of
all COS emissions and for about 20% of the anthropogenic share. Based on these results, they suggested that aluminium smelting was probably the most important direct industrial source of COS.

The petroleum and steel industries, forest fires, automotive tire wear and petrol usage are also anthropogenic sources of COS [2, 7, 41-46]. There are natural sources of COS discharging into the atmosphere too, such as microbial decomposition, oxidation of CS$_2$, fires and volcanic eruptions [8, 47]. In fact, there are more known sources of COS than there are sinks, two of which have been identified (see Figure 2.10).

One major method of removal for COS from the atmosphere is uptake by vegetation as shown in Figure 2.10. Recent evidence suggests that this may be the most important route for COS removal [9, 48-51]. This may have negative implications if COS is replacing CO$_2$ uptake by vegetation.

However, another more concerning mechanism of COS removal is oxidation in the stratosphere [1, 39, 52]. Most other sulfur gases survive for only hours or days in the atmosphere because they are quickly oxidised by hydroxyl radicals in the troposphere (lower atmosphere). COS is unusual, since it is stable in the troposphere, resulting in it having a lifetime of several years in the atmosphere [1]. Its stability allows it to be transported into the stratosphere (upper atmosphere). The only other sources of sulfur to the stratosphere are SO$_2$ during periods of heavy volcanic activity and emissions from high altitude aircraft [1].

In the stratosphere, COS is oxidised to SO$_2$ and then sulfate aerosols, which collect in a layer at the bottom of the stratosphere. This Junge layer has a cooling effect by reflecting radiation from the sun. Sulfate aerosols also catalyse certain ozone depletion reactions [53]. Sulfate aerosols leave the atmosphere after they have been transported back down to the troposphere by either a dry (adsorption onto land or sea) or wet (rain) deposition and are a major cause of acid rain.

COS is present at 500 pptv in the atmosphere, which is 80% of the total sulfur content of the atmosphere [1, 8]. After more than twenty years of research, the effect of COS emissions is still not well understood. However, since the annual input of COS into the atmosphere has doubled due to anthropogenic emissions (although an increase in the level detected in the
atmosphere has not been observed), the potential consequences of uncontrolled COS emissions make regulation desirable.

### 2.6 Summary

- COS and other sulfur gases form due to the 1 – 4 wt%S impurity present in the coke used to make anodes. It is believed that this sulfur is present in carbon ring structures as part of the structure of the coke, but this is not well understood.

- Most smelter measurements show that COS is the major sulfur gas to form during aluminium electrolysis under the anode during normal operation at levels of around 3000 ppmv. This has been confirmed both experimentally in the laboratory and using thermodynamic predictions.

- On exiting the cell, the majority of COS is oxidised with the induced air draft present in the cell hooding to SO$_2$. Despite this, some COS (several ppmv) survives through the cell ducting to the dry scrubber inlet.

- COS levels are only slightly reduced or not affected by either dry or wet scrubbing, according to smelter measurements. Overall, there is considerable discrepancies in COS emission measurements, which vary are between 1 – 6 ppmv or 0.2 to 1.6 kgt$^{-1}$ Al.

- In the atmosphere, COS is stable enough to be both the dominant sulfur gas and to allow some of it to enter the stratosphere (upper atmosphere). COS is one of the few sources of sulfur to the stratosphere and decomposes there into sulfate aerosols, which are implicated in ozone depletion.
PART I: FORMATION OF COS IN ALUMINIUM SMELTING
Chapter 3  PREVIOUS SULFUR SPECIATION STUDIES IN CARBONACEOUS MATERIALS

The exact form of sulfur in cokes, and hence in anodes, is not understood. However, sulfur speciation must be known in order to determine the specific reactions that occur at the anode/electrolyte interface during anode consumption to form the sulfur gases which are discharged. Experimental studies suggest that initially this is mostly in the form of COS (see Chapter 2). This chapter thus focuses on sulfur speciation studies of petroleum cokes using XPS (X-ray Photoelectron Spectroscopy) and sulfur speciation of materials similar to cokes using XANES (X-Ray Absorption Near Edge Structure) spectroscopy. XANES has been successfully used to determine sulfur speciation in a large variety of carbon based materials and has advantages over other analysis techniques. Work on the application of XANES to anodes carried out during this study is discussed in Chapter 5.

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3.1 Introduction

There are a number of analysis techniques that might be useful in determining the type of sulfur species present in anodes – these include XPS (X-ray Photoelectron Spectroscopy), SIMS (Secondary Ion Mass Spectrometry) and XANES (X-ray Absorption Near Edge Spectroscopy).

Petroleum cokes, which make up the bulk of the anode composition, have been studied by several groups using XPS [32, 54, 55]. However, these studies showed that using XPS derived chemical shifts, only a limited amount of information could be obtained on the sulfur species present. The XANES spectrum potentially provides far more detailed chemical information, and has been used to study materials such as crude oil and coal, which could be expected to have similar sulfur containing structures to petroleum cokes and anodes. Some of these studies are detailed in this chapter to show how this technique has the potential to be applied to determining the sulfur speciation in anodes.

3.2 Sulfur Studies with XANES

A similar issue to determining the mechanism of sulfur gas emission in smelters arises in the combustion of sulfur containing fossil fuels. XANES (X-ray Absorption Near Edge Structure) spectroscopy has proven to be very useful in analysing the sulfur in such materials. More conventional techniques (such an XPS) for obtaining chemical structure information either don’t have sufficient sensitivity or have not given sufficient chemical detail to determine the nature of sulfur in a complicated structure such as coke [32]. Combined S K- and L-edge XANES studies have been the most successful method to determine the sulfur speciation in fossil fuel derived materials. Some of the differences between S K- and L-edge measurements will be described shortly.

A detailed explanation of XANES theory is included in Chapter 4. XANES studies at the S K-edge show an energy shift of the edge as a function of oxidation state and speciation, and allow approximate quantification according to peak size (e.g. see Figure 3.4). XANES at the
Sulfur in Carbonaceous Materials

Chapter 3

S L-edge reveals a change in the fine peak structure above the edge (for example, see Figure 3.5) allowing similar organic sulfur species to be distinguished from each other. As discussed in Chapter 4, this chemical state information is significantly more detailed than that available in the XPS spectrum.

Thus a combined approach, collecting XANES spectra at both the S K- and L-edges gives the maximum information – semi-quantification at the K-edge, complemented by the extra fingerprinting detail provided by the L-edge. While this approach has never been used for cokes and anodes before, it has been successfully applied to similar materials, which will be discussed below. In the examples discussed, the process of analysing XANES data is the focus, since this formed the basis of experimental work and analysis for this thesis.

3.2.1 S K-edge XANES Studies

Measurement of the S K-edge using XANES has been commonly employed in the analysis of sulfur species in complex materials. It is usually performed over a 2465 – 2490 eV photon energy range and is a useful technique to simultaneously analyse for organic and inorganic sulfur species non-destructively. A linear correlation exists between energy position ($E_k$) and the white line peak area (area under the major edge peak), which allows quantification of the sulfur species present in the sample [56]. A common technique to determine sulfur speciation semi-quantitatively is to measure the edge spectra for various reference compounds (containing one of the sulfur species of interest). Then the summation of these reference spectra in various proportions comprises a model of the spectrum of an unknown sample, using a least squares minimisation to get the best fit [57, 58].

Vairavamurthy [59] performed S K-edge XANES spectroscopy to compare the actual oxidation state (“oxidation index”) of sulfur compounds with their traditionally assigned values, since there is a linear empirical correlation between oxidation state and XANES fine structure [60]. Sulfate (+6) and elemental sulfur (0) were used as reference compounds and samples were spiked with NaCl so that the Cl-edge could be used as an internal standard. Pre-edge and post-edge data were used to correct for the background signal. Some of the more complicated organic sulfur compounds had an oxidation state that differed from their
conventionally assigned oxidation state. It was believed that oxidation indices could potentially be used to deconvolute XANES S K-edge spectra.

### 3.2.2 S L-edge XANES Studies

Unlike K-edge analysis, quantification of L-edge peaks is not possible due to uncertainties in normalising the spectrum and only one part of the spectrum being measured. Additionally, it is technically more difficult to set up a beamline to measure in the L-edge range – a very soft X-ray beam (160 – 190 eV for the S L-edge) and high vacuum conditions (< 10^{-9} torr) are required [56].

Despite these limitations, L-edge spectra of sulfur are richer in detail than K-edge, with better peak resolution, and so are a more useful “fingerprinting” tool. The improvement in peak resolution is due to the smaller natural L-edge width, better photon resolution and greater probability of electron transitions (p → d) compared to K-edge (s → p). Proximity to the valence shell means L-edge spectra have been found to be more sensitive to geometrical and chemical changes for the particular atom, and this is the more surface sensitive technique due to the lower photon energies [61, 62].

Although some XANES sulfur speciation studies have been carried out at the L-edge only, it is more common to study both the K- and L-edges, making the best use of the different information available at each edge.

### 3.3 Sulfur Speciation in Carbonaceous Materials

#### 3.3.1 Coal

Kasraie et al. [61] performed a detailed XANES study of the S L-edge of coals. The spectra of total electron yield at the S L-edge were measured up to 80 eV above the edge (160 – 240 eV), as shown in Figure 3.1.
Three regions of the spectra in Figure 3.1 were identified. In the first 15 eV (approx. 165 – 180 eV) above the edge (peaks a – g), the peaks were attributed to photoelectron transitions from the 2p level to vacant bound states at and above the ionisation threshold of the sulfur atom. This is the “fingerprinting” region, which is sensitive to the electronic state of the atom.

The interpretation of the second region (15 – 70 eV above edge, 180 – 235 eV) was not clear and so no peak assignments were made, but these peaks were believed to arise from multiple and, at the upper end of the energy range, single scattering processes. In any case, peaks in this region tend to be broader and less sensitive to chemical changes, so of little use for fingerprinting.

The final region, 70 – 80 eV (234 – 245 eV) above the edge (peaks h – j), overlaps with transitions of electrons from the 2s level to unoccupied bound states. While the first region...
(electrons originating from the 2p levels) is most useful for fingerprinting, transitions from the more deeply lying 2s level can provide additional fingerprinting information.

**Table 3.1: Peak positions of sulfur L-edges for reference compounds and coal samples**

(See Figure 3.1 [61]).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( L_{2,3} ) edge</th>
<th>( L_1 ) edge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a )</td>
<td>( b )</td>
</tr>
<tr>
<td>Pyrite (FeS(_2))</td>
<td>164.0</td>
<td>170.7</td>
</tr>
<tr>
<td>Sulfur (S(_8))</td>
<td>164.2</td>
<td>171.0</td>
</tr>
<tr>
<td>Na(_2)S(_2)O(_3)</td>
<td>163.8</td>
<td>166.6</td>
</tr>
<tr>
<td>FeSO(_4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfamic acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thianthrene</td>
<td>166.6</td>
<td></td>
</tr>
<tr>
<td>4-4-Thiodiphenol</td>
<td>166.9</td>
<td></td>
</tr>
<tr>
<td>2-2-Thiodiacetamide</td>
<td>165.9</td>
<td>169.8</td>
</tr>
<tr>
<td>Coal-1 (powder)</td>
<td>163.9</td>
<td>170.2</td>
</tr>
<tr>
<td>Coal-2 (piece)</td>
<td>167.0</td>
<td>172.2</td>
</tr>
<tr>
<td>Coal-2 (powder)</td>
<td>163.9</td>
<td>167.3</td>
</tr>
<tr>
<td>Coal-3 (powder)</td>
<td>167.2</td>
<td>173.6</td>
</tr>
<tr>
<td>Coal-4 (powder)</td>
<td>162.6</td>
<td>168.6</td>
</tr>
</tbody>
</table>

Peak positions were assigned to various sulfur species in the coal samples by drawing up a table to compare the spectra of standards with coal samples (see Table 3.1). Peak a (sometimes a doublet, see Table 3.1, Figure 3.1), the closest peak to the absorption edge, was found to relate to S-S bonds in forms such as S\(_8\), S\(_2\)O\(_3\)\(^{-2}\) and S\(_2\)\(^{-2}\). Highly oxidised species, such as SO\(_4\)\(^{-2}\), S\(_2\)O\(_3\)\(^{-2}\) and H\(_2\)NSO\(_2\)OH (sulfamic acid), always had peaks E and G. In this manner, most samples could be distinguished on the basis of these characteristic peaks.

The resolution of the L-edge spectra allowed pyrite to be resolved from organic sulfur compounds, which was difficult at the S K-edge. Pyrite (FeS\(_2\)), sulfate and organosulfur compounds were identified in most coal samples. Sulfate species were possibly present due to surface oxidation of pyrite. By analysing various samples of the same coal, it was confirmed that pyrite and sulfate were not evenly distributed (which had been previously observed), while organosulfur compounds were an integral part of the coal structure.

Huffman *et al.* [58] were able to quantitatively determine sulfur species in coal (5 organic and 3 inorganic forms were found to be present) with an accuracy of 5 – 10 % using least squares...
analysis of the sulfur K-edge XANES spectra. They determined the effect of various desulfurisation treatments on the sulfur speciation in coals. Desulfurisation treatments are designed to remove organic sulfur, so the pyritic sulfur content was used to compare coals (to account for possible dilution effects) before and after four different desulfurisation treatments. The possible sulfur species considered were pyrite ($S_2^{2-}$), elemental ($S_8$), organic sulfide (C-S-C or C-S-H), thiophene (S in 5-membered C ring), sulfone (R-SO$_2$-R) and sulfate ($SO_4^{2-}$).

Spectra were normalised to the $s \rightarrow p$ transition peak (“white line” or main absorption edge) of elemental sulfur, which was given a value of 0 eV. Spectra were fitted using a series of mixed (50:50) Lorentzian-Gaussian peaks, representing the $s \rightarrow p$ transitions and scattering resonance peaks, and an arc tan step function to represent the transition of the photoelectrons to the continuum (see Figure 3.2). Then the $s \rightarrow p$ peak areas were transformed into sulfur percentages using experimentally determined calibration constants. An example of this modelling is shown in Figure 3.2.

Figure 3.2: An example of a fitted XANES S K-edge spectrum (of Illinois No. 6 Coal) by Huffman et al. [58]. The dotted lines are $s \rightarrow p$ transitions for various species and the dot-dashed line is the arc tan step function.

Kasrai et al. [62] reported further XANES studies of coal at both the S K- and L-edges, measuring both total electron yield and fluorescence yield. In particular, they were interested in determining the nature of organic sulfur species in coal better, since these are harder to remove in desulfurisation processes than inorganic species. Spectra were normalised to the
beam current, $I_0$, using a 90% transmission gold mesh for the L-edge and an ionisation chamber for the K-edge. The energy scale was calibrated for the L-edge using the lowest pre-edge peak for S of 162.7 eV and for the K-edge by setting the strongest absorption peak of S at 2472.0 eV; a linear background was also removed. Total electron spectra were used for quantitative estimation. Peak intensity of model compounds was normalised to the highest peak intensity in coal. A linear combination of model compounds spectra was used to fit coal spectra. Quantification was only done for organic sulfur in the $S^{2-}$ oxidation state, with an estimated error of 10-15%.

Figure 3.3: S L-edge XANES spectra (as labelled on the right hand side) from Kasrai et al. [62] comparing Rasa coal (A) with various model compounds (B-G).

A variety of model sulfur compounds were chosen to compare to the coals studied. Pyrite, elemental sulfur, sodium thiosulfate and sulfate were all considered as possible inorganic species present. Pyrite is the most common mineral sulfide in coal and represented all mineral sulfides in coal for this study, since they were difficult to distinguish from each other in dilute form. Sulfate was not believed to naturally exist in coal, but was present due to weathering.
Organic sulfur species were more difficult to characterise, since they had to be chosen to represent all sulfur-containing functional groups. Various straight-chain compounds (R-C-S-C-R, R-C-S-S-C-R and R-C-SH) were considered, as well as sulfur in various 5- and 6-membered ring structures.

Coals of different ages and from different sites were compared. Some example spectra at the L-edge from this study are shown in Figure 3.3, comparing “Rasa” coal with various organic sulfide model compounds. Peaks a, b and c shown in the figure were used to identify major species. In addition to pyrite and sulfate, a variety of organic sulfur groups were identified in the coals. Most organic sulfur was bound to sp\(^2\) carbon (as aryl sulfides and disulfides and heterocyclic sulfur). Some oxidised organic sulfur in the form of sulfone (R-SO\(_2\)-R) and sulfonic acid (R-SO\(_3\)H) was also identified.

### 3.3.2 Asphaltene Fraction of Crude Oil

![Reference compound spectra for the S K-edge measured by Sarret et al. [56].](image)
Asphaltene was the focus of a S K- and L-edge XANES study performed by Sarret et al. [56]. Asphaltene is a high molecular weight fraction of crude oil that is rich in sulfur. Spectra were collected using total electron yield and the background subtracted linearly by extrapolating from the pre-edge region. Reference spectra for the K- and L-edges are given in Figure 3.4 and Figure 3.5 respectively.

S K-edge spectra were fitted using a linear combination of reference spectra optimised with a least squares fitting programme. The intensity was normalised to the height of the edge jump at the K-edge. S K-edge spectra (Figure 3.4) show an increase in position and amplitude of the white line (main absorption edge peak) with increasing oxidation state. A large number of model compounds were chosen (Figure 3.4), to limit the effect of substituent groups on the spectra (as was observed in reference [63]) of each sulfur species. This effect of substituent groups was found to be more important in reduced sulfur compounds, and so quantification at the K-edge was limited to oxidised sulfur compounds.

![Figure 3.5: Reference compound spectra for the S L-edge measured by Sarret et al. [56].](image)
Identification of sulfur species at the L-edge was limited to the 162 – 170 eV range, which included reduced sulfur species and some sulfoxide and sulfone peaks, but not sulfonate and sulfate peaks. These two latter species had peaks at higher energies, but they were too broad to allow identification in the complex spectra of the samples. The L-edge spectra could not be normalised to the edge jump, as was done for the K-edge spectra, due to broad oscillations in the after peaks region. Instead L-edge spectra were arbitrarily normalised to peak B (Figure 3.5) and the spectra were analysed semi-quantitatively (although quantification to any extent at the L-edge is not strictly possible).

Figure 3.6: Comparison between S L-edge XANES spectra for reference compounds and asphaltene samples.
A detailed analysis at the L-edge of the various sample spectra was completed by Sarret et al. by comparing asphaltene spectra to reference compounds, as shown in Figure 3.6. While the major reduced sulfur species appeared to be similar to dibenzothiophene (S in a 5-membered ring between two benzene rings), other sulfur species identified in the asphaltenes included disulfides, alkyl and aryl sulfides and sulfoxides. As the “alteration” of a sample increased (“alteration” was a measure of factors such as oxidation due to weathering, and depended on where the sample originated) more oxidised sulfur species were found, such as sulfoxides ($R_2SO$), sulfones ($R_2SO_2$), sulfonates ($RSO_3H$) and sulfates.

### 3.3.3 Kerogen from Kashpir Oil Shales

Riboulleau et al. [64] studied the sulfur speciation in sulfur-rich kerogen from Kashpir oil shales at the S K- and L-edges. Reference spectra used in this study were collected by Sarret et al. [56] and are given in Figure 3.4 (K-edge) and in Figure 3.5 (L-edge). K-edge spectra were analysed in a similar manner to the previous studies discussed. Spectra were first normalised to the beam current and normalised to each other using the absorption edge or peak maximum near the edge. The energies of the $s \to p$ transitions were used to identify the sulfur forms present, and then the peak areas were used to quantify the different forms of sulfur. Kerogen spectra (total electron yield) were then simulated using a linear combination of reference spectra in a least squares fitting programme. S L-edge spectra of kerogens were compared with reference L-edge spectra and used to distinguish between sulfur functional groups whose spectra were too similar at the K-edge.

Quantification at the K-edge showed that the major sulfur species present were alkyl (C-S-C) or heterocyclic (e.g. thiophene) sulfides (76%), while the L-edge results confirmed that these species were alkyl sulfides. Lesser amounts of di(poly)sulfides were identified at both the K- (11%) and L-edges. Sulfoxides, sulfonates and sulfates were also identified at the K-edge, while at the L-edge sulfoxides were also identified.
3.3.4 Sediment Extracts and Petroleum

Sulfur K-edge analysis has been applied to the study of sediment extracts and petroleum by Schouten et al. [57]. XANES was found to be a successful way to detect the presence of sulfoxides (R-S(=O)-R) in these materials, which had been difficult to detect using more common techniques (infrared spectroscopy, GC-MS). XANES analysis (using least squares curve fitting) was used to determine the percentage of sulfide, sulfoxide and thiophene in the polar fraction of the samples studied.

3.3.5 Polysulfides and Rubbers

Chauvistré et al. [63] studied various sulfanes (R-S\(_n\)-R, \(n = 2 - 4\), also known as polysulfides), hoping that S K-edge XANES could be a reliable quantitative tool for determining the relative polysulfidic content in vulcanised rubbers. The 1s → 4p Rydberg transition in Ar gas (3203.54 eV) was the primary energy standard used, in addition to ZnSO\(_4\) (2481.44 eV), which is closer to the S K-edge. A Voigt profile (a convolution of Gaussian and Lorenztian profiles, used to mathematically model the shape of a spectrum [65]) was chosen to fit the form of the absorption lines. The integrated Voigt profile was used to model the edge step function (unlike Huffman et al. who used an arc tan function, see Figure 3.2).

A linear correlation was observed between the splitting of the sulfur 1s → \(\sigma^*\) (S-C) and 1s → \(\sigma^*\) (S-S) transitions and the S-C bond length, despite the sulfanes studied being very similar in structure. These results implied that the substituent R groups were important in determining peak shape (and hence, peak area) at the K-edge, since the energy of transition depended on the nature of the second and higher order coordination shells around the sulfur atom. While this study reported that attached organic side chains to a sulfur functional group did affect the resulting spectra, Vairavamurthy et al. reported contrary results in this matter (described in detail in Section 3.2.1, [59]).
3.3.6 Soils and Sediments

In order to better understand the sulfur biogeochemistry in soils and sediments, Morra et al. [66] carried out a XANES S K-edge study of purified humic and fulvic acids. The white line peak maximum for elemental S was used as a reference (2472.5 eV) and this was used for recalibration between each scan. White line position and intensity were determined using a derivative curve, allowing semi-quantitative estimation of specific S species. To determine the inflection point in a derivative curve (for white line position), a series of Gaussian-Lorenzian lines were fitted to the derivative curve allowing oxidation states of S to be determined. The sulfur species found to be present depended on where the sample originated, but sulfonates (R-SO$_3$H), ester-bonded sulfates and reduced sulfur species (organic, formal oxidation state $-1$) were commonly present.

3.3.7 Proteins

S L-edge XANES was used to determine the sulfur bonding in metallothionein structures [67]. Metallothioneins are low molecular weight, cysteine-rich proteins containing 20 SH groups per molecule that bind to a wide range of metal ions. It was found that sulfur bonding with some metal ions was distinguishable from XANES K-edge spectra (e.g. Hg), while for others it was not (e.g. Zn and Cd).

3.4 Sulfur in Petroleum Coke

There have been several studies of the sulfur species present in petroleum coke, but none using XANES. Hume et al. [32] detected sulfate (2s BE = 236.8 eV) and carbon sulfide (2s BE = 228.3 eV) type species in cokes using XPS. The sulfate species was believed to be associated with sodium at the surface of the anode.

In another XPS study of petroleum fuel cokes, the speciation of sulfur and nitrogen were studied using the S 2p and N 1s narrow scan spectra [54]. Although several components were
identified, both spectra were described as rather complex. Sulfur was found to be distributed evenly on the surface and in the bulk of the cokes studied and the major species was a low $E_b$ component, which was assigned to thiophenic sulfur and had previously been found the most stable sulfur species against calcination [55]. There were two other significant high $E_b$ sulfur species that were not identified, but were observed to increase with increasing calcination temperature. They corresponded with the binding energies for sulfoxides, sulfones and sulfonates, but the authors believed that these species were unlikely to increase with temperature, since they would not be stable against calcination. The authors believed instead that some of the sulfur was replacing carbon in the graphene layers of the coke [54].

### 3.5 Applying XANES Analysis to Petroleum Cokes and Anodes

Several examples have been described to show how XANES has been used to study the types of sulfur present in a number of different complex carbonaceous materials. For example, in coal it appears that speciation is location specific and that heterocyclic S, organic sulfides/disulfides, sulfones and sulfonic acid are the sulfur species commonly present. However, it was expected that while materials such as coal would be similar in structure to petroleum coke and anodes, the heat treatments to prepare cokes and anodes would result in differences in the sulfur speciation. XPS studies of sulfur in petroleum cokes have been described and these have detected a C-S bonded species, and another more oxidised S species. It was anticipated that a XANES study of cokes and anodes should provide more detailed information on sulfur speciation in cokes and anodes, providing some insight into the subsequent generation of sulfur containing gases at the anode surface during electrolysis.
Chapter 4  XANES: THEORY AND EXPERIMENTAL METHOD

This chapter explains the theory behind the technique XANES (X-ray Absorption Near Edge Structure). The synchrotron radiation ring required and specific beamlines used for these experiments are described. The analysis method for the S K- and L-edge spectra is also detailed.

4.1 INTRODUCTION TO XANES .................................................................48
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4.1 Introduction to XANES

The techniques XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) Spectroscopy became popular in the 1970’s with the advent of synchrotron radiation (see Figure 4.1). This type of radiation is produced by acceleration of electrons at high energies and is unique because it provides a continuous spectrum of energy at a flux that is many orders of magnitude more intense than conventional X-ray sources [68, 69].

![Image of electron storage ring](image)

Figure 4.1: Principal components of the electron storage ring used as a synchrotron radiation source [68].

The first K-edge spectrum of sulfur using X-ray Absorption was produced by Frick in 1920 [69, 70] using an X-ray tube source. When X-rays hit a sample surface with enough energy, they can excite an electron within an atom sufficiently for it to be ejected from the sample. By choosing the correct wavelength and energy of the X-rays, a specific core electron level of an element in the sample can be targeted, resulting in the emission of a photoelectron from a specific electron shell. The spectrum is obtained by measuring the electron yield or X-ray
fluorescence resulting from electron transitions subsequent to photoabsorption. The photoelectron emission process leads to a jump (or edge) in the absorption spectrum over the selected energy range, followed by a series of peaks near the edge. Measuring the spectrum in this region for XANES spectroscopy, gives information on the chemical and physical state of that element within a sample.

XANES is sometimes known as NEXAFS (Near Edge X-ray Absorption Fine Structure) and is similar to EXAFS, the two of which are generally distinguished in the following arbitrary way:

1. XANES: The 0 – 50 eV range directly above the ionisation threshold energy (absorption edge). The threshold is the minimum energy required for excitation of an electron from a core energy level (e.g. K, L shell) within an atom into the continuum.

2. EXAFS: Oscillations in the several hundred eV beyond the XANES region.

However, the difference between XANES and EXAFS also has a structural significance that will be described later.

4.2 XANES Theory

Figure 4.2: The process of X-ray absorption (left), the interaction between the photoelectron wave and backscattered wave (middle) and the spectrum produced (right) (adapted from [71]).
The general principal of XANES (and X-ray absorption) is that absorption of a photon from the X-ray source leads to emission of a photoelectron, as shown in Figure 4.2. The energy required to eject an electron is specific to the type of atom and the core level, so the photon energy range is chosen to target a specific electron core level resulting in an absorption edge in the electron yield system. The resulting photoelectron, propagating as a wave, may be scattered from neighbouring atoms. The backscattered wave interferes constructively or destructively with the outgoing wave (see Figure 4.2), depending on its wavelength and the distance to neighbouring atoms, leading to peaks in the measured absorption spectrum following the absorption edge [71].

Unlike XRD, no long-range order is required in the sample since, in the EXAFS region at least, electrons are only affected by scattering from their nearest neighbour atoms [72]. On the other hand, the XANES energy region (the first 50 eV after the edge) contains high amplitude peaks generally attributed to multiple scattering. Since this makes understanding XANES spectra more complicated, the theory of EXAFS will be described first (see Figure 4.2 for the XANES and EXAFS regions).

Moving further away from the edge are weak amplitude oscillations superimposed on a smooth background, that are in the range considered for EXAFS analysis. The amplitude of EXAFS oscillations depends on the number of neighbours, strength of their scattering and the static and dynamic disorder in their position. The frequency depends on the wavevector, \( k \), of the photoelectrons (related to their kinetic energy) and the distance to neighbouring atoms and is defined by [71]:

\[
k = \sqrt{\frac{2m_e(E-E_0)}{h^2}}
\]  

(4.1)

\( k = \) Wavevector (inverse photoelectron wavelength) \\
\( m_e = \) Electron mass \\
\( E = \) Photon energy \\
\( E_0 = \) Threshold or binding energy \\
\( h = \) Planck’s constant
The fractional modulation of the X-ray absorption coefficient, $\chi(k)$, is used to define the EXAFS oscillations [71]:

$$
\chi(k) = \sum_i N_i A_s(k) S_0^2 \exp\left(-\frac{2R_{as}}{\lambda(k)}\right) \exp\left(-2k^2\sigma_{as}^2\right) \sin(2kR_{as} + \phi_{as}(k)) \tag{4.2}
$$

$\chi(k) = $ Fractional modulation of the X-ray absorption coefficient  
$N_i = $ Number of scattering atoms  
$R_{as} = $ Absorber-scatterer distance  
$A_s(k) = $ Represents the energy dependence of the photoelectron scattering (amplitude)  
$\phi_{as}(k) = $ Phase shift that the photoelectron wave undergoes when passing through the potential of the absorbing and scattering atoms  
$\sigma_{as} = $ Root mean square deviation in absorber-scatterer distance (Debye-Waller factor)  
$\lambda(k) = $ Mean free path of the photoelectron  
$S_0^2 = $ A term to allow for inelastic loss processes

$A_s(k)$ and $\phi_{as}(k)$ depend weakly on scatterer identity, so can be used to identify certain elements, but usually the elements present are known. However, the amplitude, $A_s(k)$, does depend largely on the mass of the scattering partner. $N_i$ can be approximated to EXAFS amplitude, while frequency can be approximated to $R_{as}$ (nearest neighbour separation). There are four damping factors in the equation:

1. EXAFS amplitude falls off by $1/R_{as}^2$
2. $S_0^2$ allows for inelastic loss processes
3. The first exponential term, representing mean free path
4. $\sigma_{as}$ accounts for more than one absorber-scatterer distance

Since all absorber-scatterer pairs contribute to the observed oscillations, the equation requires a summation, although in practice this can be simplified into groups of shells [71].

The absorption edge position identifies the absorbing atom and the period of oscillation gives the bond length or distance to the nearest neighbour. To calculate the distance of atoms other than nearest neighbours from the different constituent frequencies in a frequency-space signal, Fourier transformation can be used. Curve-fitting the model to experimental data can
be done in k or R (Fourier transform) space [72]. Newer EXAFS models take multiscattering into account, but single scattering (where the electrons from the absorber atom interact with only one backscatterer) can be assumed, due to the short path length of the electron [71]. EXAFS can be used, for example, to compare the oscillations produced when X-rays hit a sample from different angles.

Since the factors that produce EXAFS spectra can be modelled relatively easily, its potential was realised sooner than that of XANES. XANES peaks are closer to the absorption edge, and are therefore due to lower kinetic energy electrons with longer pathlengths, so cannot be modelled in the same way as EXAFS. The Debye-Waller factor in (4.2) becomes negligible, while the effect of multiscattering, where the electron path is influenced significantly by more than three surrounding atoms (other than the absorbing atom), is important in determining XANES peaks. Correspondingly, the XANES region becomes sensitive to a wider range of absorber-scatterer distances than EXAFS [71, 72].

Previously, it was mentioned that XANES spectroscopy is usually defined as transitions in the first 50 eV above the absorption edge. Figure 4.3 summarises some of the important features of a typical XANES spectrum. The XANES energy range can be more specifically defined, with three different regions of the absorption edge [73]:

1. Absorption threshold: the minimum energy required to remove an electron from a specific inner shell.
2. Absorption jump edge (rising edge): the energy where the absorption coefficient, $\alpha_A$, (see Figure 4.3) is at half-height of the threshold.
3. Continuum threshold (ionisation threshold): the energy where an electron is ejected into the continuum. This energy depends on the type of material – a vacuum for atoms and molecules, the Fermi level (see Figure 4.4) in metals and the bottom of the conduction band (see Figure 4.4) in insulators.
Figure 4.3: An example of a K-edge absorption spectrum, showing the XANES and EXAFS regions [73]. The spectrum has been normalised to the high energy atomic absorption ($\alpha_A$). $\alpha$ is the measured absorption coefficient after pre-edge subtraction.

- **Absorption Coefficient** ($\alpha/\alpha_A$)
- **Continuum Threshold**
- **XANES**
- **EXAFS**

Photon Energy (eV)

Figure 4.4: Electron energy level diagram in an atom (adapted from [74]).
The muffin tin approximation is a theory that relates XANES electronic processes to the potential energy, and is commonly used to explain the XANES spectra arising from more symmetrical structures. This approximation divides a solid up into continuous spheres – each sphere centred around an atom. The potential energy within each sphere is spherically averaged and the volume outside of the spheres is also averaged [75]. Then the one electron Schrödinger equation can be applied (see definitions in Appendix A), having simplified all possible electron paths and multiscattering effects. Recent developments in XANES theory with respect to modelling are described in reference [76].

4.3 XANES in Practice

The position of the absorption edge is shifted by the chemical environment, as core level binding energies respond to changes in electron density in the valence shell. In one system, complex modelling determined more than 30 atoms were involved in scattering more than 5 Å from the absorbing atom. In addition, measuring the intensity of XANES peaks is complicated by the removal of experimental artefacts and the subtraction of the atomic absorption background [71]. As a result, the use of XANES is generally limited to fingerprinting, where spectra from samples are compared with standard compounds.

However, the advantages of XANES over EXAFS are that the effect of multiscattering allows for multi-atom correlations and bond angles to be obtained using XANES and there is a potential to study chemical structure in 3D in the future. XANES is the only analysis option in situations where two edges overlap within a window of around 300 eV [75].

High resolution spectra are required for XANES analysis, because the splitting or small energy shift (0.2 eV) of an absorption peak can give extra structural information [73].

The physical origin of the absorption features in the 10 eV range above the absorption threshold depend on the material: Rhyberg states in atoms, bound valence states or bound multiple-scattering resonances in molecules, core excitations in ionic crystals, multiplet splitting, many-body singularities and multielectron configuration interactions [73].
4.4 XANES Experimental Method

XANES Experiments were performed to determine the sulfur speciation of anodes and cokes by measuring the S K- and L-edges. These were performed at the Synchrotron Radiation Center (SRC) in Stoughton, Wisconsin, USA, which is home to the 1 GeV Aladdin electron storage ring.

![Monochromator Optics](image)

**Figure 4.5: The monochromator optics for a) the Grasshopper and b) the DCM (Double Crystal Monochromator). Each one tunes to a different part of the synchrotron continuum, 40 – 200 eV for the Grasshopper (B K-edge, Al, Si, P and S L-edges) and 1500 – 4000 eV for the DCM (4d, 5d, Si, P, S, Al K-edges).**

The Canadian Synchrotron Research Facility (CSRF) is housed within the SRC. Two beamlines operated by the CSRF were used for experimental work: the DCM (double crystal monochromator) [78] and Grasshopper [79], the layout of each beamline is shown in Figure 4.5. Beamlines usually contain a grating or crystal monochromator to reduce the spectral range of the radiation to one or several wavelengths and produce the required spectral...
resolution. One or more mirrors in the beamline guide and focus the beam onto the sample. The beamlines use soft to medium X-rays for analysis, which have a wavelength similar to the dimensions of atoms and molecules and an energy up to several thousand eV (hard X-rays are at higher energies) [68]. There is only a small range of energies that a single beamline can scan and thus the DCM beamline is used to measure the S K-edge, while the Grasshopper measures the S L-edge.

![Diagram of a typical endstation at the grasshopper and DCM beamlines.](image)

**Figure 4.6: Schematic of a typical endstation at the grasshopper and DCM beamlines.**

XANES measurements at the S K-edge and S L-edge could be collected in TEY (total electron yield) mode or FLY (fluorescence yield) mode. Figure 4.6 shows how measurements were collected at the endstation of each beamline. The sample (coke, anode, etc.) was transferred into a prechamber to be pumped down to a vacuum of ultimately around $10^{-9}$ torr (once in analysis chamber), before being transferred into the main chamber and rotated so that it was normal to the beam current for measurement. For measurement, a number of valves positioned along the beamline were opened to allow the beam to hit the sample. Total electron yield (TEY) was measured by sample current, while fluorescence yield (FLY) was measured with a fluorescence detector at 45º to the sample in the plane of the beam. With regard to analysis depth, at the S K-edge in TEY mode analysis depth is around 100 Å and in FLY mode analysis depth is 500 – 700 Å. At the S L-edge, analysis depth in TEY mode is 300 – 700 Å, and 1500 Å in FLY mode. If desired, the different measurement modes (TEY, FLY) can therefore become a useful depth analysis tool.
Table 4.1: Anodes and cokes studied using XANES.

<table>
<thead>
<tr>
<th>Name</th>
<th>%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cokes</td>
<td></td>
</tr>
<tr>
<td>C6575</td>
<td>1.75</td>
</tr>
<tr>
<td>C6618</td>
<td>3.67</td>
</tr>
<tr>
<td>C6440</td>
<td>2.60</td>
</tr>
<tr>
<td>C6438</td>
<td>1.03</td>
</tr>
<tr>
<td>C4130</td>
<td>2.73</td>
</tr>
<tr>
<td>C6448</td>
<td>2.29</td>
</tr>
<tr>
<td>C6435</td>
<td>0.81</td>
</tr>
<tr>
<td>C6445</td>
<td>1.32</td>
</tr>
<tr>
<td>Anode Coke</td>
<td>1.37</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anodes</th>
<th>Equivalent Temp (Baking) ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>401118</td>
<td>1.19 944</td>
</tr>
<tr>
<td>425102</td>
<td>1.14 1117</td>
</tr>
<tr>
<td>425703</td>
<td>1.11 1124</td>
</tr>
<tr>
<td>101405</td>
<td>1.14 1280</td>
</tr>
<tr>
<td>401118</td>
<td>1.09 1400</td>
</tr>
<tr>
<td>401118</td>
<td>0.65 1500</td>
</tr>
<tr>
<td>Butt</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 4.1 shows the samples analysed, including coke samples from all the major suppliers to the aluminium industry and anode samples with different thermal histories. Coke and anode samples were ground to a powder and mounted on the sample holder using double-sided carbon tape for XANES analysis (a list of the samples studied (including sulfur contents) is shown in Table 4.1). The coke samples were provided with their respective sulfur contents. A ground sample (2g, mixed with 3g boric acid powder and pressed into a pellet) of each anode was sent for XRF analysis to determine the sulfur content summarised in Table 4.1.

 Portions of the anode baked at 944ºC were rebaked in the laboratory to see the effect of desulfurisation at higher temperatures. Samples were covered with graphite powder and heated in a graphite crucible with Ar flowing (3 Lmin⁻¹) at 1400ºC and 1500ºC respectively for 150 minutes (heat up rate was 20ºCmin⁻¹). Despite significant oxidation of the crucible, the samples were relatively intact after heat treatment. Both baking temperature and soak time affect the final properties in the anode and laboratory prepared anodes typically have shorter soak times. The temperature of a laboratory heat treatment can be related to the equivalent temperature of an anode baked commercially by calculating the \( L_e \) value (crystallite size) and using a correlation (such as in Chapter 5). In addition to comparing
anodes prepared commercially and in the laboratory, $L_c$ values are a more convenient way of determining baking temperature in commercial anodes, rather than measuring temperature directly during baking.

A detailed method for $L_c$ determination is in [80]. $L_c$ can be determined by measuring the graphite hkl (002) peak using XRD (X-Ray Diffraction), then measuring the FWHM (Full Width and Half Maximum). The Scherrer equation [81] can then be used to determine $L_c$:

$$L_c = \frac{K\lambda}{\beta \cos \Theta}$$  \hspace{1cm} (4.3)

$L_c$ = Crystallite size (Å)

$K$ = A factor that depends on crystallite shape = 0.89 (for $L_c$)

$\lambda$ = Wavelength of x-ray source = 1.5406 Å (Cu)

$\Theta$ = Scattering angle of hkl (002) peak $\approx 25.5^\circ$ (for anodes)

$\beta$ = Sample broadening (related to FWHM)

$\beta^2 = B^2 - b^2$

$B$ = Observed broadening (measured FWHM, in rads)

$b$ = Instrument broadening (FWHM of a highly crystalline reference sample, e.g. NaCl, in rads)

Reference sulfur compounds were analysed using XANES at the S K-edge and S L-edge to compare to the anodes and cokes studies. Inorganic sulfur reference compounds were chosen to represent all the oxidation states of sulfur. Organic sulfur reference compounds were chosen to represent the major sulfur functional groups identified in analyses of coke precursors (see Chapter 3). For analysis, inorganic salt standards were ground, pressed into wafers and attached using carbon tape to the sample holder. Organic standards were usually provided in the form of powders and also attached using carbon tape. For sulfide standards, the cleaved surface of a chunk of pyrite and sphalerite were analysed – the pyrite was etched using hydrofluoric acid to remove the surface oxide layer. Polymers and rubbers were analysed as cut chunks. A complete list of the standard sulfur compounds analysed is shown in Table 4.2.
Table 4.2: Standard sulfur compounds used for XANES analysis.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition/Structure</th>
<th>Ox. State</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental sulfur/Graphite</td>
<td>10%S</td>
<td>0</td>
<td>Lab Supply Pierce</td>
</tr>
<tr>
<td></td>
<td>25%S</td>
<td>0</td>
<td>Lab Supply Pierce</td>
</tr>
<tr>
<td></td>
<td>50%S</td>
<td>0</td>
<td>Lab Supply Pierce</td>
</tr>
<tr>
<td>Inorganic S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>Na₂SO₄</td>
<td>+6</td>
<td>Biolab</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>Na₂SO₃</td>
<td>+4</td>
<td>Scientific Supplies</td>
</tr>
<tr>
<td>Sodium metabisulfite</td>
<td>Na₂S₂O₅</td>
<td>+4</td>
<td>Biolab</td>
</tr>
<tr>
<td>Potassium thiosulfate</td>
<td>K₂S₂O₃</td>
<td>+2</td>
<td>Selby Wilton Scientific</td>
</tr>
<tr>
<td>Pyrite</td>
<td>FeS₂</td>
<td>-1</td>
<td>Ward's Natural Science</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>ZnS</td>
<td>-2</td>
<td>Ward's Natural Science</td>
</tr>
<tr>
<td>Organic S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L-methionine</td>
<td></td>
<td>280</td>
<td>0 Alfa Aesar</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td></td>
<td>97-99</td>
<td>0 Alfa Aesar</td>
</tr>
<tr>
<td>Thianaphene-2-carboxylic acid</td>
<td></td>
<td>238-240</td>
<td>0 Alfa Aesar</td>
</tr>
<tr>
<td>Phenothiazine</td>
<td></td>
<td>182-185</td>
<td>0 Alfa Aesar</td>
</tr>
<tr>
<td>DL-Methionine sulfoxide</td>
<td></td>
<td>231-233</td>
<td>+2 Alfa Aesar</td>
</tr>
<tr>
<td>5-Sulfosalicylic acid</td>
<td></td>
<td>108-110</td>
<td>+6 Alfa Aesar</td>
</tr>
<tr>
<td>Vulcanised rubber</td>
<td></td>
<td>0</td>
<td>Gulf Rubber</td>
</tr>
<tr>
<td>Polyphenylene sulfide</td>
<td>[n]</td>
<td>0</td>
<td>Ludowici Plastics</td>
</tr>
<tr>
<td>Polysulfone</td>
<td>[n]</td>
<td>4</td>
<td>Ludowici Plastics</td>
</tr>
</tbody>
</table>

XANES measurements were carried out over three weeks in January 2001, September 2001 and April 2002 on the Aladdin ring at the SRC, which is an 800 MeV to 1 GeV electron storage ring. Some S K-edge measurements on the DCM beamline were made using a 1 GeV beam, however most were done at 800 MeV. This beamline had a photon resolution of about 0.9 eV [62].
Grasshopper measurements in the first and second weeks were carried out on the CSRF Grasshopper Mark IV and in the third week on the same end station, but attached to a different beamline (called the Grasshopper Mark V). The main difference between the two grasshopper beamlines is the grating – the CSRF beamline has a grating of 1800 line/mm, while the Mark V has one of 900 line/mm. The former is more suitable for high energy work (>120 eV), with better intensity and resolution (likewise a grating of 600 line/mm would be better for low energy work). Resolution depends on the slit size and dispersion of the grating, according to the equation:

\[
\Delta E = \frac{E^2 \Delta \lambda}{12359} \tag{4.4}
\]

\(\Delta E\) = Resolution (eV)
\(E\) = Beam energy (eV) = 162.7 eV for the elemental S L-edge
\(\Delta \lambda\) = f(lines) \times \text{Slit size (} \mu\text{m)}

f(lines) = Dispersion of the grating (Å\(\mu\text{m}^{-1}\)) = 0.0027 Å\(\mu\text{m}^{-1}\) for 1800 line/mm grating
\[= 0.0056 \text{ Å} \mu\text{m}^{-1}\] for 900 line/mm grating
\[= 0.008 \text{ Å} \mu\text{m}^{-1}\] for 600 line/mm grating

12359 = Conversion factor between Å and eV (1 eV = 12359 Å)

The CSRF beamline had the entrance and exit slits set to 30 \(\times\) 30 \(\mu\text{m}\), giving it a theoretical photon resolution of <0.2 eV at the S L-edge. The same resolution could be achieved in the Mark V with the slits at 16 \(\mu\text{m}\), however there is a trade-off with better resolution of less beam intensity. Therefore after some testing, Mark V measurements were carried out with the slits also set to 30 \(\times\) 30 \(\mu\text{m}\), making the resolution at the S L-edge <0.4 eV.

S K-edge spectra from the DCM beamline were collected from two scans between 2450 – 2530 eV, with a dwell time of 2s and a step size of 0.2 eV. Grasshopper measurements were also taken from two scans between 155 – 190 eV, with a step size of 0.08 eV and 6 averages (in the third week) or from 3 scans with a step size of 0.04 eV (in the first and second weeks).
The spectra collected were normalised as follows:

1. Spectra were normalised to the beam current, $I_0$, to account for fluctuations and decay in the beam current.
2. To the beam energy by setting the elemental S K-edge white line position to 2472.5 eV (at the K-edge) and 162.7 eV (at the L-edge) and normalising to the pyrite and sulfate edges over each of the three weeks. The edge position was determined using derivative curves.
3. By performing a linear background subtraction extrapolated from the pre-edge region.
4. Spectra were also normalised to the height of the maximum for L-edge and to the height of the edge jump for the K-edge.

### 4.5 HSC Calculations

The HSC Chemistry© computer package [82] was used to determine equilibrium for sulfur gas formation at the anode. Equilibrium is determined by a Gibbs energy minimisation using initial conditions specified by the user. The anode gas at equilibrium was calculated with different starting sulfur species present in the anode in an increasing oxidising atmosphere and for changing $CO_2/CO$ ratios. The change in the stable sulfur species at equilibrium was then determined as the anode gases were cooled and exposed to air when they leave the anode and enter the cell hood and ducting. More specific details of the calculations are included in the results in Chapter 5.
Chapter 5  RESULTS: XANES STUDY OF SULFUR SPECIATION IN COKES AND ANODES

Sulfur speciation in cokes and anodes was determined using XANES at both the S K- and L-edge. The spectra show that sulfur was present in predominantly organic ring structures in both cokes and anodes. The results are followed by some thermodynamic predictions of the nature of sulfur gas formation at the anode and the change in gas composition as the gases leave the cell.

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5.1 Sulfur Reference Compounds

The X-ray Absorption Near Edge Structure (XANES) Spectrum typically consists of a complex peak envelope representing a variety of transitions to bound states at the ionisation threshold. Therefore in the absence of knowledge of the relevant density of states at this threshold, the method is most effectively used in fingerprinting mode (See Chapter 4 [61, 62]). Therefore, a series of reference compounds were chosen to represent all the major organic and inorganic forms of sulfur that may be present in cokes and anodes. Spectra from each of these compounds were collected to compare to coke and anode spectra with unknown sulfur speciation. Measurements were taken at both the K- and L-edges in both TEY (total electron yield) and FLY (fluorescence yield) modes. In some cases, the extra sampling depth of FLY mode was required to obtain useful spectra (e.g. when collecting spectra from polymers). The K-edge spectra are discussed here first, since K-edge spectra are of lower resolution than L-edge, and therefore are simpler spectra to analyse.

5.1.1 Inorganic Reference Compounds

XANES spectra for the inorganic reference compounds studied are given in Figure 5.1 (at the K-edge) and Figure 5.2 (at the L-edge). Spectra shown in these Figures are a measure of the total electron yield (TEY). In fluorescence yield (FLY) mode peak intensity was observed to differ slightly from that in TEY, but the peak positions were generally identical, so FLY results have not been included. The results have been plotted in order of oxidation state of the sulfur atom, since this is an important factor in determining the energy position of the edge.

The lowest oxidation state (-2) for sulfur (S^{2-}) is found in sphalerite, ZnS, where the spectrum was significantly different from any of the other inorganic reference compounds at both the K- and L-edges. Vairavamurthy observed a linear increase in the main edge peak at the K-edge with oxidation state [59]. Contrary to previous XANES studies of FeS with the same oxidation state [59], the main edge peak for sphalerite is at a higher energy than would be expected, given its oxidation state. The one previous XANES spectra of sphalerite at the L-edge found is published only as a derivative curve on a large energy scale, but peak positions
do appear very similar [67]. The most likely reason for the higher than expected energy of the main edge peak is that sphalerite lacks the S-S bonding of pyrite and elemental sulfur.

At the K-edge, the sphalerite spectrum was characterised by a strong initial peak at 2473.6 eV followed by a series of increasingly weaker peaks. The main peak observed at the L-edge was at 164.4 eV, followed by a triplet of peaks centred around 168.1 eV. Beyond this, the peak shape and position was similar to sulfate, and since the L-edge is more surface sensitive than the K-edge [61, 62], this perhaps reflects surface oxidation of the sphalerite sample.

Pyrite, FeS$_2$ ($S_2^{2-}$, oxidation state -1) and elemental S (S$_8$, oxidation state 0) gave very similar spectra at the K- and L-edges. The presence of S-S bonding resulted in the position of the K-edge being 2471.8 eV for pyrite and 2472.4 eV for elemental S. This shift of 0.6 eV between the two species is similar to previous work [59]. In both cases, this was followed by a broader and much smaller peak at around 2480 eV. At the L-edge, S-S bonding also resulted in a very characteristic low energy doublet at 162.6/163.8 eV for pyrite and 162.8/164.1 eV for elemental S, which was followed by the dominant peak at 168.3 eV and 168.6 eV respectively. Peak positions in pyrite and elemental S spectra matched previous measurements at the K-edge [58, 66] and L-edge [61].

Next in order of oxidation state are thiosulfate (S$_2$O$_3^{2-}$) and metabisulfite (S$_2$O$_5^{2-}$). Although these species have different S oxidation states (+2 and +4 respectively), they produced similar-shaped spectra because the types of bonding are the same (S-S, S-O, S=O). At the K-edge, the low energy S-S peak occurred at 2471.4 eV for thiosulfate and 2471.8 eV for metabisulfite, with the main edge peaks at 2480.4 eV and 2480.6 eV respectively. The K-edge thiosulfate spectrum was identical to a previously measured one by Morra et al. [66] Complicated L-edge spectra were observed, starting with an S-S doublet at around 163 eV, with a dominant peak at 171.7 eV for thiosulfate and 171.8 eV for metabisulfite, which agreed reasonably well with the observations of Kasrai et al. [61].

Sulfite (SO$_3^{2-}$) has the same sulfur oxidation state as metabisulfite (+4), but a very different spectrum at the K-edge due to the lack of S-S bonding. It was characterised by two main peaks at 2477.8 and 2481.8 eV. The L-edge spectrum was disappointingly noisy, but the peak shape was similar to metabisulfite and thiosulfate, apart from the absence of low energy S-S peaks.
Figure 5.1: XANES S K-edge spectra of the inorganic reference compounds studied.
Figure 5.2: XANES S L-edge spectra of the inorganic reference compounds studied.
Finally, sulfate (SO$_4^{2-}$), with an S oxidation state of +6, showed a single main peak at the K-edge at 2482.2 eV. At the L-edge, the main edge peaks are centred around 172-173 eV, with a higher energy doublet at 180.3/181.2 eV. The K- and L-edge sulfate spectra agreed well with previous measurements [56, 62, 66].

Overall, there were several distinctive features observed from XANES spectra of inorganic sulfur. The first of which was the low energy single peak (about 2472 eV at the K-edge) and doublet (162.5-164 eV at the L-edge). The second was the presence of oxidised sulfur, which resulted in a shift to higher energy peaks; 2482 eV at the K-edge and 172-173 and 180-181 eV at the L-edge. Thus the K-edge resolves complex chemical shifts of the edge in response to oxidation state changes and the nature of S bonding, while the L-edge provides a more detailed fingerprint of the specific species.

5.1.2 Organic Reference Compounds

TEY spectra at the K- and L-edges for the organic reference compounds studied are given in Figure 5.3 and Figure 5.4 respectively. There are several main groups of organic sulfur that have been identified including alkyl and aryl sulfides, 6-membered heterocyclic ring sulfur, thiophenic sulfur and mercaptanic sulfur (thiols, -SH) [62].

Two oxidised forms of organic sulfur were considered (S bonded to one or three O atoms) and four forms of sulfur bonded to carbon in different configurations. Generally, organic reference spectra obtained were in agreement with previous measurements [56, 62, 66] and there is a reasonable correlation between the main edge peak and oxidation state, especially at the K-edge, but also to a certain extent at the L-edge.

L-methionine is an example of an alkyl sulfide (C-S-C), with an oxidation state of 0. The K-edge was at a slightly higher energy than elemental S, with the main edge peak at 2473.4 eV. The L-edge was significantly different from any inorganic reference compounds studied, with the major feature at this edge being a triplet centred around 164.7 eV.

Three compounds were studied where S is present in a ring structure. In phenothiazine, S is present in an organic 6-membered heterocyclic ring with four C’s and one N (see Figure 5.3).
Dibenzothiophene and Thianaphene-2-carboxylic acid are examples of thiophenic sulfur, which contain S in a 5-membered ring. The main K-edge peak for all three compounds is at 2473.6 or 2473.8 eV, which is similar to alkyl sulfide. This edge peak is followed by two smaller peaks, which are common to all the cyclic S structures studied.

Alkyl sulfide and sulfur present in ring structures can be distinguished at the L-edge, with a 0.6 eV shift in the largest edge peak from L-methionine (straight chain S) to phenothiazine (S in 6-membered heterocyclic ring), whose edge is centred around a peak at 165.3 eV. There is nearly a further 1 eV shift from phenothiazine to thianaphene-2-carboxylic acid (thiophenic sulfur), which has its main edge peak at 166.2 eV. There are differences here in peak shape too – the L-edge of L-methionine is characterised by a triplet, while four peaks can be distinguished at the edge for phenothiazine and thianaphene-2-carboxylic acid. Unfortunately, the low melting point of dibenzothiophene made it too unstable to measure its L-edge accurately.

Sulfur is double bonded to a single O in DL-methionine sulfoxide, resulting in a shift of the K-edge peak up to 2475.9 eV. At the L-edge, a distinctive triplet peak shape (closer in shape to L-methionine) was observed for this compound centred at 167.7 eV. In 5-sulfosalicylic acid, S is bonded to three O’s (one singly bonded, two doubly bonded), and has a broad K-edge peak at 2481.3 eV, with a shoulder at about 2479.3 eV. At the L-edge, 5-sulfosalicylic acid also had a broad peak centred at 171.4 eV.

Generally, organic sulfur structures were easier to distinguish at the L-edge than the K-edge, due to better peak resolution and the more complex and distinctive peak envelope. This reflects the proximity of the L shell to the Fermi level, relative to the more deeply buried K shell. All organic compounds had significantly different K- and L-edge spectra to any of the inorganic compounds.
Chapter 5

Results: XANES Study of S in Cokes and Anodes

Organic Reference Compounds - K Edge

**5-Sulfosalicylic acid**

- Formel S

**Dibenzothiophene**

- Oxidation State: 0

**Phenothiazine**

- Oxidation State: 0

**L-methionine sulfoxide**

- Oxidation State: 0

**DL-methionine sulfoxide**

- Oxidation State: +2

**Thianaphene-2-carboxylic acid**

- Oxidation State: 0

**5-Sulfosalicylic acid**

- Oxidation State: +6

Figure 5.3: XANES S K-edge spectra of the organic reference compounds studied.
Figure 5.4: XANES S L-edge spectra of the organic reference compounds studied.
5.1.3 Polymer Reference Compounds

The sulfur in petroleum cokes and anodes is likely to be contained in large organic structures, rather than in small molecules, so it seemed appropriate to study polymers as additional model compounds, whose sulfur speciation was known. Polymer spectra were harder to measure because they were more susceptible to surface beam damage and so some spectra in this section were measured only in FLY mode, since it is less surface sensitive (see Section 4.3). Spectra at the K-edge are shown in Figure 5.5 and at the L-edge in Figure 5.6.

At the K-edge, the rubbers (vulcanised and EDPM rubber) were characterised by two major peaks at 2473.6/2473.4 eV and 2482.0/2481.6 eV (see Figure 5.5). In the vulcanised rubber sample the latter peak was the largest in the TEY spectra, but was significantly smaller in FLY mode. This suggests that this peak is due to an oxidised sulfur species, which dominates the surface, but is less significant further into the material. The former peak (at around 2473.5 eV) is at the same beam energy as the edge observed in other C-S-C organic structures given in Figure 5.3, reflecting the common oxidation state (0) of rubbers and these other reference compounds.

Slightly more information was found in TEY mode than in FLY mode at the L-edge for these rubber samples – probably because the fluorescence yield is generally smaller than the electron yield for atoms with relatively low mass like S. A small L-edge peak was detected at 164.5 eV for EDPM rubber and at 166.0 eV for vulcanised rubber – these are also comparable to the other organic structures studied.

In polyphenylene sulfide, S is straight-chain bonded between benzene rings, with a formal oxidation state of 0. The K-edge peak of this material was at 2474.2 eV, with a much smaller peak at 2481.4 eV. The edge peak is at a slightly higher beam energy than the K-edge for the other C-S-C structures studied (0 oxidation state), but significantly lower than any oxidised sulfur species. The FLY spectrum for this sample at the L-edge shows a triplet structure centred around 165.5 eV (similar to previous measurement [62]), which is closer to S contained in a ring (thianaphene-2-carboxylic acid, phenothiazine) than it is to straight chain S (L-methionine).
Figure 5.5: XANES S K-edge spectra of the polymeric reference compounds studied.
Figure 5.6: XANES S L-edge spectra of the polymeric reference compounds studied. The vulcanised and EDPM rubber spectra were measured in TEY mode, polyphenylene sulfide and polysulfone in FLY mode.
The higher energy shift in the K-edge for polysulfone reflects its degree of oxidation (the S is doubly bonded to two O’s, with a formal oxidation state of +4). With a main K-edge peak at 2480.4 eV, the polysulfone edge fits in between the DL-methionine sulfoxide (+2) and 5-sulfosalicylic acid (+6) organic reference spectra in Figure 5.3. At the L-edge in FLY mode, the polysulfone spectrum consists of a series of peaks around 169 – 172 eV, with a pre-edge peak at 167.7 eV. The peak shape here is similar to 5-sulfosalicylic acid, although there was a 1 eV shift downwards in energy.

The spectra obtained from the polymeric materials studied fit in well with the observations made with respect to peak shape and position in the organic materials of the previous section. So, as might be anticipated, the fact that the molecules in these samples have much larger structures does not affect the position of the K- and L-edges.

Comparing all the reference compounds studied, the materials with a negative oxidation state (pyrite and sphalerite) seem to be affected mostly by the atoms sulfur is bonded to in the structure. A number of compounds with zero oxidation state were studied. Inorganic S(0) has a K-edge about 1 eV lower than organic S(0), reflecting S-S bonding in elemental sulfur. The K-edge for all organic S(0) is about 2473.5 eV (± 0.3 eV). Beyond this, the K-edge for organic oxidised S is approximately linear, but once again, S-S bonding affects the K-edge for inorganic reference compounds. Similar trends are observed at the L-edge, in addition to the extra detail resolved for each reference material.

5.2 Sulfur Speciation in Cokes

Eight petroleum coke samples were chosen for XANES analysis, representing all significant coke suppliers to the aluminium smelting industry. All were from distinct origins and had sulfur contents ranging from 0.81%S to 3.67%S (see Chapter 4). The K- and L-edge were measured for each coke in both TEY and FLY mode. At the K-edge, peak position and shape were similar in TEY and FLY modes, however, some of the spectra were less noisy in FLY mode than in TEY mode. Although analysis depth is larger in FLY mode (see Section 4.3), no differences in spectra can be attributed to surface and bulk material differences, since all coke (and anode) samples were ground just before analysis. Since all the K-edge spectra for
reference compounds have been given in TEY mode, these are included, but FLY spectra are also included for comparison.

The first obvious observation from K-edge results (see TEY spectra in Figure 5.7 and Figure 5.9) is that despite the cokes being from different suppliers, the edge is always at 2473.6 – 2473.8 eV, which is consistent with organic sulfur in the zero oxidation state. This is a little surprising, given the potentially large differences in the origin of different parent crude oils used to make the petroleum cokes studied.

Figure 5.7 shows the K-edge TEY spectra and Figure 5.8 the FLY spectra for the low sulfur petroleum cokes. Likewise, Figure 5.9 and Figure 5.10 show the K-edge spectra for high sulfur cokes in TEY and FLY modes respectively. In terms of sensitivity, the method is clearly viable in producing a detailed spectrum from these materials. To summarise the major peaks observed at the K-edge, the first and largest K-edge peak was consistently at 2473.8 eV, representing organic S(0), as already mentioned. In FLY mode, the edge was followed by two smaller, broader, overlapping peaks at about 2480 and 2483 eV. In TEY mode, often only the former of these two peaks was observed. A shoulder after the main edge peak at about 2476 eV was present in some of the cokes in both TEY and FLY modes. In FLY mode, a pre-edge shoulder at approximately 2472 eV was also observed in two of the high sulfur cokes (similar to elemental S). None of the variations observed in XANES spectra appeared to be a function of the sulfur content of the coke.

Assignment of the main edge peak for the cokes was closest in energy to organic S(0) compounds, phenothiazine, dibenzothiophene and thianaphene-2-carboxylic acid, where S is present as part of an organic ring structure with 5 or 6 members (Figure 5.3). In the XANES spectra for all three of these reference compounds, a small peak after the edge at 2475.7 – 2475.9 eV was observed, which could explain the shoulder at around 2476 eV seen in some of the cokes. The reference compounds also have a higher energy peak at around 2479 eV, with an additional peak at 2480.9 eV for thianaphene-2-carboxylic acid. A combination of these peaks could result in the broad peak at 2480 eV always present in the coke spectra.
Figure 5.7: XANES S K-edge TEY spectra for the low sulfur petroleum cokes studied.
Figure 5.8: XANES S K-edge FLY spectra for the low sulfur petroleum cokes studied.
Figure 5.9: XANES S K-edge TEY spectra for the high sulfur petroleum cokes studied.
Figure 5.10: XANES S K-edge FLY spectra for the high sulfur petroleum cokes studied.
The high energy coke peak at 2483 eV is closest to sulfate (2482.2 eV). Interestingly, this peak is often observed more clearly in FLY mode, which is less surface sensitive than TEY mode, arguing against surface oxidation. However, since the cokes were crushed and ground before analysis, no conclusions can be drawn on whether this was a bulk feature of the cokes, or a surface feature due to atmospheric oxidation.

The final feature observed in two cokes (2.29% S and 3.67% S) is the pre-edge peak at around 2472.2 eV. This is a similar energy to the main edge peak for elemental sulfur (2472.4 eV) and pyrite (2471.8 eV), indicating S-S bonding.

FLY data collected at the L-edge was generally poor in terms of signal to noise, therefore only the TEY results are included here. Figure 5.11 shows the L-edge spectra for low sulfur cokes and Figure 5.12 the L-edge spectra for high sulfur cokes. More detail can be seen at the L-edge than the K-edge, but the spectra are also more affected by noise, particularly the two lowest sulfur cokes.

The largest edge peak was between 165.6 and 165.9 eV, and is usually one of three or four peaks at the edge. A pre-edge peak at 162.8 – 163.0 eV is often observed, as well as peaks at 169.7 – 170.8 eV, 172.1 – 173.1 eV and 180.7 – 182.0 eV.

The position of the main edge peak is closest to phenothiazine (165.3 eV, S in a 6-membered ring) and thianaphene-2-carboxylic acid (166.2 eV, S in a 5-membered ring). The spectral features in the coke containing 1.32 %S clearly resemble thianaphene-2-carboxylic acid, with a central doublet (165.8 and 166.3 eV) surrounded by one peak on either side (164.4 and 167.5 eV) and some weaker, broader peaks at higher energies.

On the other hand, the spectra for the 1.75% S coke is closer to phenothiazine, with a main peak at 165.8 eV, surrounded by two partially unresolved peaks at 164.7 and 167.2 eV. The pre-edge peak at 162.8 eV can also be clearly distinguished. The spectra for the 2.29 %S and 2.73 %S cokes also resemble phenothiazine. The spectra for cokes containing 2.60 %S and 3.67 %S both have pre-edge peaks at 163.0 eV, indicating phenothiazine, with additional peaks at 167.4 – 167.8 eV, indicating thianaphene-2-carboxylic acid. These last two cokes are probably a mixture of S in 5- and 6-membered ring structures.
Figure 5.11: XANES S L-edge TEY spectra for the low sulfur petroleum cokes studied.
Figure 5.12: XANES S L-edge TEY spectra for the high sulfur petroleum cokes studied.
S-S bonding was observed at the K-edge, but it is harder to distinguish at the L-edge, since the phenothiazine-type cokes have a pre-edge peak that is at a similar energy to the first peak in elemental sulfur or pyrite spectra. However, the broad peaks at 172 – 173 eV and 180 – 182 eV are more pronounced in the coke spectra than the organic reference compounds, suggesting once again that some sulfate is present in the cokes.

In conclusion, the major sulfur species in petroleum cokes is an organic ring structure like that found in phenothiazine (S in an organic 6-membered heterocyclic ring) or thianaphene-2-carboxylic acid (thiophenic S), regardless of the supplier of the coke. More detailed analysis at the L-edge, showed that thiophenic S was the dominant species in one coke, while 6-membered heterocyclic ring S dominated in several other cokes, and the remainder of the cokes studied contained a mixture of the two types. S-S bonding, such as in elemental S (S$_8$) or pyrite (S$_2^{2-}$), was observed in small amounts at the K-edge. Evidence of some sulfate (SO$_4^{2-}$) was found at both the K- and L-edges.

Previous XANES studies of fossil fuel materials support the conclusion that cyclic S structures such as thiophene are the dominant S species in petroleum cokes. In a previous study of coals (see Chapter 3 [62]), the major S species in coal was usually thiophenic. Smaller amounts of organic alkyl sulfides, disulfides and 6-membered heterocyclic ring S were also commonly detected from XANES studies, exact amounts depending on the source of the coal. A previous XANES study of asphaltenes (a high molecular weight, high sulfur fraction of crude oil) also found thiophenic S to be the dominant form of sulfur [56]. Asphaltenene samples that had been less exposed to atmospheric oxidation tended to have small amounts of organic sulfides, disulfides and sulfoxides, while more exposed samples had more sulfoxides, sulfones, sulfonates and sulfates. The S species in Kerogens, sulfur-rich organic matter from oil shales, were determined by XANES and were predominantly aliphatic sulfides and disulfides [64].

### 5.2.1 Quantification of Sulfur Composition in Cokes

An attempt was made at quantifying the sulfur composition in the various cokes studied using K-edge spectra (modelling is not possible at the L-edge, due to its complexity). This was
done by a peak deconvolution method with the addition of the various reference spectra to produce a model spectrum as close as possible to the coke spectrum. The minimisation of the square of the difference between the model and actual spectra was used to find the best fit. This method assumes that there is a linear correlation between the percentage of the spectrum relating to a percentage of a particular type of sulfur species. The results of this analysis are shown in Table 5.1.

These quantitative results differ slightly to the qualitative conclusions just discussed. The major species is still an organic ring structure, generally thiophenic S is favoured over a 6-membered heterocyclic ring as the dominant sulfur species present in the cokes. The proportion of 5-membered (thiophenic) to 6-membered ring S changes depending on whether the TEY or FLY spectra are used for modelling. However, this reflects the difficulty in distinguishing these species at the K-edge (which the model is based on) and are better distinguished by peak shape at the L-edge. FLY models generally predict more dibenzothiophene than TEY models, which is probably because FLY spectra have a greater sampling depth than TEY, and dibenzothiophene was susceptible to beam damage during spectra measurement which affected the surface more than the bulk.

None of the petroleum cokes contained significant amounts of alkyl sulfide or sulfone (-SO$_3$) species. Surprisingly large quantities of elemental sulfur were predicted from modelling, particularly using FLY spectra. TEY spectra indicated the presence of inorganic disulfide, but given the lack of evidence in the FLY spectra and the absence of metals in petroleum cokes (see Table 2.1), this is more likely to be elemental sulfur, since the reference spectra were similar for these two compounds. Modelling of the TEY spectra also determined the presence of sulfoxides (R-(S=O)-R). Although some sulfate was present according to the modelling, it is in smaller quantities than was expected from a qualitative analysis of the XANES results. Selected peak models are included in Appendix C.

Despite minor differences in qualitative and modelled results, the XANES spectra clearly show that all the petroleum cokes studied have very similar sulfur speciation, despite their differing origins. Organic ring structures, such as thiophenic and 6-membered heterocyclic ring S dominate in petroleum coke.
Table 5.1: The sulfur composition in cokes calculated using reference spectra to model coke spectra at the K-edge. The proportion of each type of thiophenic S (dibenzothiophene and thianaphene-2-carboxylic acid) are included as well as the total proportion of these two species. Values given in the table are fractional.

| Coke  | %S | 5member ring | 5member ring | 5member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member ring | 6member r
5.3 Sulfur Speciation in Anodes

K- and L-edge spectra collected in TEY and FLY modes were similar for the anodes XANES study, so only TEY results are included here. Several different aspects of anode preparation and life were considered in this study to determine how they affected sulfur speciation. Firstly, the differences in sulfur speciation in a coke, an anode made from this coke and a resulting anode butt after recovery from a smelting cell were studied. These results are included in Figure 5.13 for K-edge spectra and Figure 5.14 for L-edge spectra. The effect of anode baking temperature (944 – 1280°C) on sulfur speciation was studied in Figure 5.16 for the K-edge and Figure 5.17 for the L-edge. The effect of desulfurisation on one anode was studied by rebaking portions of it at 1400°C and 1500°C and these results are in Figure 5.20 for the K-edge and Figure 5.21 for the L-edge. All spectra have been plotted on the appropriate scale to allow direct comparison between figures.

5.3.1 The Effect of Anode Baking and Usage

Differences in sulfur speciation between a coke, baked anode and anode butt could be expected due to desulfurisation. A previous study of desulfurised coals indicated that selective removal of a chosen sulfur species was possible in coal, depending on the desulfurisation method used [58]. Additionally, both baking and anode use involve long soak times and temperatures around 1000°C leading to desulfurisation, which was confirmed using XRF (%S results shown in Chapter 4). The source coke used for this XANES study contained 1.37 %S, successive desulfurisation due to baking and anode use [29, 30] resulted in the anode baked at 944°C contained 1.19 %S and the anode butt 1.05 %S. However, despite this evidence of desulfurisation, the results at the K-edge (Figure 5.13) show that the spectra of the source coke, baked anode (baked at 944°C) and anode butt are very similar to each other and to cokes analysed earlier (see Figure 5.7 and Figure 5.9).
Figure 5.13: XANES S K-edge TEY spectra for anode coke, a baked anode and an anode butt.
Figure 5.14: XANES S L-edge TEY spectra for anode coke, a baked anode and an anode butt.
Summarising the major peaks at the K-edge, the main edge peak is at 2473.9 eV and allowing for slight calibration differences from one experimental session to another, this makes the edge the same as the cokes studied in Section 5.2, indicating organic S(0). A post edge shoulder was identified at 2475.5 – 2475.7 eV, followed by two broad peaks at 2480.3 – 2480.5 eV and 2482.3 – 2482.9 eV. Unlike the cokes studied previously, the second of these two broad peaks dominates, which may be a characteristic of this particular coke.

The energy position of the edge still agrees most closely with the organic ring structures phenothiazine, dibenzothiophene and thianaphene-2-carboxylic acid. This also explains the post-edge shoulder and the first of the two broad peaks. As observed with the cokes in the previous section, the energy position of the final broad peak is most consistent with sulfate, and there may be more of this species than in previous cokes. This sulfate peak may be slightly larger in the anode butt than the other two samples, indicating that the amount of sulfate has increased due to bath reactions, or a change in anode sulfur composition due to the long soak time at around 1000ºC.

The intensity of peaks at the L-edge (see Figure 5.14) does not indicate the total amount of sulfur present – the signal to noise ratio for this data was typically small and peak intensity also depends on the selection of a linear background to subtract. The major L-edge peak (shown in Figure 5.14) is at 165.4 – 165.5 eV in the coke, anode and butt. This is slightly lower than the other cokes studied, which may or may not be significant. A low energy peak at 162.6 eV is observed in the baked anode and butt, but not in the coke. This was probably a feature of S bonding in a ring structure (see reference species in Figure 5.4), rather than an indication of S-S sulfide bonding (such as in S₈ or FeS₂, in Figure 5.2). The peak shape and absence of a peak around 167.6 eV, suggests that these three samples are most similar to phenothiazine, which has S bonding in an organic 6-membered heterocyclic ring. Although there are differences in spectral intensity, peak shape and position is very similar for each sample, suggesting that while some desulfurisation may take place after baking and use, the sulfur speciation does not change significantly.
5.3.2 The Effect of Baking Temperature

The effect of the anode baking process was studied in more detail by considering differences in sulfur speciation between anodes baked at different temperatures between 944°C and 1280°C. As described in Chapter 4, the baking temperature was provided for each of the anode supplied. Baking temperature had been determined by measuring $L_c$, the crystallite size, which gives an indication of the degree of baking in anodes [80, 83]. $L_c$ was re-measured to check the baking temperatures given were accurate, by performing X-Ray Diffraction (XRD) in the manner described in Chapter 4 [80]. The results in Figure 5.15 show that anodes subjected to higher baking temperatures have a narrower hkl (002) graphite plane, which results in a smaller FWHM (Full Width of peak at Half Maximum), due to a higher degree of graphitisation occurring at these higher baking temperatures. As well as the degree of graphitisation increasing with temperature, the amount of desulfurisation also increases [83]. However, the XRF results (given in Chapter 4) show that there is little difference in the amount of sulfur present in these anodes, ranging from 1.11 – 1.19 wt%S.

![XRD of Anodes](image_url)

**Figure 5.15:** Comparison of the hkl (002) graphite plane in anodes baked at various temperatures. The smaller the FWHM (full width at half maximum), the higher the degree of graphitisation.
Figure 5.16: XANES S K-edge TEY spectra for anodes baked at four different temperatures from the same source coke.
Figure 5.17: XANES S L-edge TEY spectra for anodes baked at four different temperatures from the same source coke.
K-edge XANES results, comparing the sulfur speciation in the four anodes (the 944°C results from Section 5.3.1 are repeated for comparison), are shown in Figure 5.16. The main edge peak was at 2473.9 eV, followed by a shoulder at 2475.5 – 2475.9 eV and two broad peaks at 2480.1 – 2480.3 and 2482.3 – 2482.7 eV. The four spectra are very similar to each other (and to the source coke and anode butt in Figure 5.13), although it appears the intensity of the latter peak may be increasing with baking temperature, implying perhaps that a sulfate species is forming. Despite this, the bulk of the sulfur present in the anodes remains organic S in ring structures.

The L-edge results appear to confirm that the rate of sulfate formation is increasing with baking temperature, due to the increase in peak intensity of the 180.4 – 181.0 eV peak in Figure 5.17. Generally, the peak shape at the L-edge shows that the major sulfur species remains unchanged with baking temperature and is most similar to heterocyclic 6-membered ring S, such as the reference compound phenothiazine.

5.3.3 The Effect of Rebaking Anodes at 1400 – 1500°C

Portions of the anode baked at 944°C were rebaked at either 1400°C or 1500°C. It was expected that around this temperature range, significant desulfurisation would occur [27], and this might impact on the sulfur speciation of the anode. In commercially prepared anodes, the soak time is much longer than for this study [83, 84], where the anodes were heat treated for 2 ½ hours. However, the temperatures used to prepare these rebaked anodes can be compared to commercially prepared anodes by estimating a lower temperature that would produce a similar product [83, 84].
Chapter 5

Results: XANES Study of S in Cokes and Anodes

Figure 5.18: XRD results showing the hkl (002) graphite peak for anodes baked at 944°C and then rebaked at either 1400°C or 1500°C.

Figure 5.19: The relationship between $L_c$ (crystallite size) and equivalent baking temperature for an anode [83].
Figure 5.18 shows the XRD results for the three different anodes. The anode rebaked at 1400°C has a sharper, narrower peak and therefore a smaller FWHM, indicating a higher degree of graphitisation. Some desulfurisation has also occurred, since the sulfur content in this anode is 1.09 %S, compared to 1.11 – 1.19 %S in the anodes baked between 944°C and 1280°C (see Chapter 4). The anode rebaked at 1500°C showed a further increase in graphitisation from the XRD results, with an additional graphite peak present at about 26.5°. Further desulfurisation had occurred at 1500°C and XRF results showed that the sulfur content was reduced substantially to 0.65 %S. The anode sample rebaked at 1400°C had a calculated $L_c$ value of 38.3 Å. According to Figure 5.19, the equivalent baking temperature for this anode was therefore 1325°C. The $L_c$ value for the anode sample rebaked at 1500°C was calculated as 65.1 Å. This is well out of range in the correlation in Figure 5.19, so the equivalent temperature cannot be determined. In any case, 1500°C is much higher than any temperature usually used to bake anodes commercially [26].

The K-edge XANES results, shown in Figure 5.20 are similar to those described for the other anodes, but a clear difference is observed between the 944°C anode and those that were rebaked in the last peak at 2482.3 – 2482.5 eV. This was observed to a lesser extent in the anodes baked between 944 and 1280°C and it was proposed that this change was due to the formation of sulfate increasing with increasing temperature. The stability of the majority of the sulfur, present in some type of ring structure has not changed at these higher temperatures however.

At the L-edge, shown in Figure 5.21, there appears to be a dramatic change in peak intensity in the spectrum of the anode rebaked at 1400°C, which cannot be explained, except that it could have been a result of the peak processing method used (selection of a linear background to subtract from the spectrum is dependant on the pre-edge region). The L-edge peak positions have not changed significantly though, with the spectra still closely resembling phenothiazine (6-membered heterocyclic ring S).
Figure 5.20: XANES S K-edge TEY spectra for an anode baked at 944°C, then rebaked at 1400°C or 1500°C.
Figure 5.21: XANES S L-edge TEY spectra for an anode baked at 944°C, then rebaked at 1400°C or 1500°C.
To conclude, the major sulfur species in the anodes appears to be quite stable with increasing temperature, despite the onset of desulfurisation. This species is most similar at the L-edge to organic sulfur containing ring structures. The exact nature of this species will be dependant on the nature of the source coke – it was seen in Section 5.2 that there was some variation here between different cokes. In the case of the anode coke studied, 6 membered organic heterocyclic ring sulfur dominated. There may be a small increase in the amount of sulfate forming as the baking temperature (or soak time in the case of anode butts) increases.

5.3.4 Quantification of Sulfur Composition in Anodes

Table 5.2 shows the calculations to determine the quantities of different sulfur species present in the anodes and source coke obtained by modelling the anode spectra using reference compound spectra. While these results attempt to quantify the sulfur species present, it is difficult to accurately quantify the spectra (see the comments in Section 5.2.1).

In a similar way to quantification of sulfur in the cokes (Table 5.1), this method favoured thiophenic S over 6-membered heterocyclic ring S as the major sulfur species. Once again, these models were only based on the K-edge results, which tend to be less sensitive to differences such as these.

There was no evidence of alkyl sulfides or sulfones, although the TEY models suggested that like the cokes, some sulfoxide was present in the anode samples. High concentrations of elemental sulfur were calculated in the FLY models, with TEY spectra favouring the presence of inorganic disulfide. As with the cokes, elemental sulfur seems more likely to be present than inorganic disulfide. A sample spectrum, of the anode baked at 944°C and its reference compound model, is included in Appendix C. It showed that this sulfide S-S bonding accounts for a shoulder before the main edge peak, which was not observed in the qualitative analysis. The model suggests that some sulfate is present in the anode samples, but there is no specific trends in sulfate concentration with baking temperature of the anode.
Table 5.2: The sulfur composition in source coke, anodes and an anode butt calculated using reference spectra to model sample spectra at the K-edge. The proportion of each type of thiophenic S (dibenzo thiophene and thianaphene-2-carboxylic acid) are included as well as the total proportion of these two species. Values given in the table are fractional.

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<th>5member ring</th>
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<th>R-(S=O)-R</th>
<th>R-(SO_3)-H</th>
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Anode XANES studies showed that sulfur speciation did not change after baking compared to the parent petroleum cokes. The major species, a sulfur containing ring structure, was stable over a range of baking temperatures, even after significant desulfurisation and graphitisation had occurred. Despite predictions that anode use could potentially result in a change in anode speciation, XANES studies of an anode butt showed that once again, the composition of sulfur species present were stable after being exposed to the cell environment.

5.4 Thermodynamic Predictions of Sulfur Gas Formation

Thermodynamic calculations were performed using the computer package HSC Chemistry©, in the manner described in the previous chapter. Based on the XANES results, various sulfur species that might be present in anodes were considered, to predict the formation of sulfur gases at the anode face in the cell, in the presence of varying amounts of O₂ gas. Then the change in sulfur gas equilibrium composition was calculated when air was added, from the induced air draft in the cell hood and as the gases cooled on leaving the cell.

5.4.1 Sulfur Gas Composition at the Anode

A variety of sulfur species were considered to model the formation of sulfur gases from the anode including:

- Elemental sulfur (S₈)
- Aliphatic sulfide, Dimethyl sulfide ((CH₃)₂S)
- Aliphatic sulfide, Tert-butyl ethyl sulfide (C₄H₉SC₂H₅)
- Aliphatic sulfide, Heptadecyl-propyl sulfide (C₁₇H₃₅SC₃H₇)
- Aliphatic disulfide, Dimethyl disulfide ((CH₃)₂S₂)
- Aliphatic disulfide, Didecyl disulfide (C₁₀H₂₁S₂C₁₀H₂₁)
- Aromatic sulfide, Benzenethiol (C₆H₅S)
- S in 5-membered ring, Thiophene (C₄H₄S)
- Sulfoxide, Dimethyl sulfoxide ((CH₃)₂SO)
- Sulfone, Dimethyl sulfone ((CH₃)₂SO₂)
Elemental carbon was also present to provide the balance of the 2 wt% S in the anode. There are a few limitations to thermodynamic calculations of this nature. Firstly, sulfur in anodes is most likely present in very large structures, but the species available for modelling are much smaller molecules. Secondly, only chemical equilibrium could be calculated, not electrochemical equilibrium. Despite these issues, the equilibrium compositions calculated modelled the anode gases observed experimentally in the cell quite successfully (see Chapter 2).

In addition to the sulfur species and elemental carbon present to model the anode (totalling 0.082 kmol), a varying amount of O$_2$ (g) ranging from 0 – 0.2 kmol was added to the system. 0.002 kmol of F$_2$(g) was present to account for the formation of HF(g) in competition with H$_2$S(g). H$_2$(g) was added as a source of H (always present in the anode [14]) for elemental sulfur calculations, for all other sulfur species H was incorporated into the sulfur species.

![Figure 5.22: Thermodynamic equilibrium compositions for sulfur species at 970°C for the starting composition: 0.001 kmol C$_4$H$_4$S (thiophene), 0.082 kmol C, 0.001 kmol F$_2$(g), 0.002 – 0.2 kmol O$_2$ (g).]
The equilibrium result at 970°C for thiophenic sulfur as the anode sulfur species is shown in
Figure 5.22. The formation of COS (g) was favoured at equilibrium between 0.01 and 0.08
kmol O$_2$ (g). At higher O$_2$ concentrations, the formation of SO$_2$ (g) was favoured, and at very
low O$_2$ concentrations elemental S was the favoured species at equilibrium. Small amounts of
CS$_2$ (g) and H$_2$S (g) also formed at low O$_2$ concentrations. H$_2$S (g) formation was generally
not favoured at equilibrium over HF (g) formation. Equilibrium was calculated for all the
sulfur species mentioned earlier in this section, however there were only very minor changes
in the equilibrium composition when the source sulfur species in the anode was changed.

Given the known dominance of COS in the anode gas (See Chapter 2 [4, 5]), the gas
composition from Figure 5.22 at O$_2$ (g) = 0.076 kmol, was chosen to represent anode gas
most closely, and used in further thermodynamic calculations to determine the effect of a
changing CO$_2$/CO ratio. The starting sulfur composition for these calculations was therefore
90.74 % COS, 8.24 % SO$_2$, 0.84 % H$_2$S and 0.18 % CS$_2$. In Figure 5.23, the equilibrium with
changing CO$_2$/CO ratios shows that COS (g) is the favoured sulfur species at all CO$_2$/CO
ratios below 90:1. At typical CO$_2$/CO ratios therefore, COS (g) could be expected to be the
dominant sulfur species in anode gas.

![Figure 5.23: Sulfur species thermodynamic equilibrium at 970°C for the starting
composition at O$_2$ (g) = 0.076 kmol from Figure 5.22 (anode gas composition from
thiophenic S), where the CO$_2$/CO ratio is changing (CO$_2$ (g) + CO (g) = 20 kmol).]
5.4.2 **Sulfur Gas Composition Leaving the Cell**

There are two important factors that could influence stable sulfur species as the anode gases leave the cell and are mixed with the air draft in the cell hood – a significant drop in temperature (970°C down to about 100°C in the ducting) and dilution with air (i.e. increased O$_2$ (g) and humidity levels). Therefore, both of these factors were investigated separately with respect to anode gas.

Equilibrium results for cooling the anode gas calculated in Figure 5.22 from 1000°C down to room temperature are shown in Figure 5.24. Down to about 300°C, COS was favoured as the dominant stable sulfur gas at equilibrium, below this elemental S was the favoured sulfur species. In comparison, the equilibrium produced as the anode gas was mixed with air (up to 99% air, 2 mol % H$_2$O, remainder 21% O$_2$/79% N$_2$) is shown in Figure 5.25. When air was added, SO$_2$ gas was the dominant sulfur species at all air concentrations.

![Graph showing sulfur species distribution](image-url)

**Figure 5.24:** Thermodynamic equilibrium for sulfur species as anode gas from Figure 5.22 (anode gas composition from thiophenic S and O$_2$ (g) = 0.076 kmol) is cooled from 1000°C down to 0°C.
Figure 5.25: Thermodynamic equilibrium at 970°C for sulfur species as air is mixed with anode gas from Figure 5.22 (anode gas composition from thiophenic S and O₂ (g) = 0.076 kmol). “Air” consisted of 2mol% H₂O, with the remainder 21% O₂/79% N₂.

Figure 5.26: Equilibrium composition of anode gas (from Figure 5.22 calculations) as it is cooled from 1000°C down to 0°C in excess (99 mol%) air (2 mol% H₂O, remainder 79% N₂/21% O₂).
Of the two factors (temperature drop and air dilution), addition of air seems to be the more important factor in determining equilibrium, as shown in Figure 5.26. In this case, the anode gas was mixed with 99 mol% air and cooled down from 1000°C. Below around 450°C, $H_2SO_4$ becomes the major sulfur species, although this has not been reported in actual smelter measurements. However, thermodynamics correctly predict that addition of air favours oxidation of COS into $SO_2$, which is observed in smelter studies [4, 5]. Kinetics must also be important since 100% conversion of COS is not achieved in smelters [4, 5].

### 5.5 Summary

XANES was used analyse the sulfur speciation of petroleum cokes and anodes. Measurement of XANES spectra for a number of reference sulfur compounds was performed. Inorganic sulfur species XANES spectra could be distinguished by a shift in the energy position of the K-edge. Different organic sulfur species with a formal oxidation state of (0) tended to have similar K-edges, but they could be characterised by changes in fine structure at the L-edge.

Comparison between reference spectra and petroleum coke spectra determined that sulfur exists in this material mostly in ring structures, such as thiophenic (5-membered) and 6-membered organic rings. Some variation in the exact nature of these ring structures was observed between cokes from different sources. Small amounts of sulfides and sulfates were also present in petroleum cokes.

Very little change in sulfur speciation was observed in anodes after baking compared to the parent petroleum coke, despite evidence of graphitisation and desulfurisation. XANES measurement of an anode butt showed that the dominant ring structures were also stable after the anode had been used in the cell. Likewise, sulfur in organic ring structures was stable even after significant desulfurisation was achieved by rebaking an anode at 1500°C.

Modelling the formation of COS at the anode at equilibrium was performed using thermodynamic calculations. COS was the stable sulfur species at the anode in a range of oxidising atmospheres. On contact with excess air on leaving the cell, $SO_2$ became the stable sulfur species. Thermodynamic calculations generally agreed well with smelter measurements [5].
PART II: FATE OF COS IN ALUMINIUM SMELTING
Chapter 6 COS HYDROLYSIS IN CLAUS CATALYSIS

The aluminium industry is not the only industry to have a COS emission problem, since COS is produced in varying quantities from any combustion process consuming fossil fuels. Claus catalysis is a process that has been developed to convert sulfur gases into elemental sulfur using an alumina catalyst. To increase the overall efficiency of the process, research has been carried out to determine how to maximise the hydrolysis of COS into H$_2$S using this catalyst. Infrared spectroscopy has commonly been employed to study COS hydrolysis, and the adsorption or conversion of other sulfur gases on catalyst alumina.

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6.1 Introduction

A variety of techniques have been developed for gas desulfurisation. The choice of technique usually depends on the concentration of H₂S particularly, and hydrocarbons in the gas. Claus catalysis is a method for desulfurisation of gases by converting H₂S and SO₂ into elemental sulfur using an alumina catalyst:

\[
2\text{H}_2\text{S}_{(g)} + \text{SO}_2_{(g)} \xrightleftharpoons[\text{Al}_2\text{O}_3]{\gamma}\text{Al}_2\text{O}_3 \rightarrow 3\text{S}_{(s)} + 2\text{H}_2\text{O}_{(g)}
\]  

(6.1)

In order to improve the efficiency of this conversion, relevant side reactions such as the hydrolysis of COS have been considered:

\[
\text{COS}_{(g)} + \text{H}_2\text{O}_{(g)} \xrightleftharpoons[\text{Al}_2\text{O}_3]{\gamma}\text{Al}_2\text{O}_3 \rightarrow \text{H}_2\text{S}_{(g)} + \text{CO}_2_{(g)}
\]  

(6.2)

As a heterogeneous catalytic process, the effects of changes to the alumina surface have been studied in some detail. While the aim of Claus catalysis is different to dry scrubbing with respect to COS emissions, research alludes to information that has relevance to the adsorption or reaction of COS using smelter grade alumina, such as the type of sites on which COS and SO₂ will adsorb.

6.2 The Chemistry of the Alumina Surface

Some general information about alumina and its chemistry is useful in understanding COS hydrolysis using alumina. The alumina surface is usually hydrated to a certain extent. On γ-alumina, most of the water is converted to hydroxyl groups chemisorbed on the surface, but some strongly adsorbed water remains in molecular form. Hydroxyl ions can be coordinated in various ways with aluminium cations, depending on whether the cations occupy tetrahedral or octahedral sites at the alumina surface [85]. In addition, hydroxyl ions can be bonded to one, two or three aluminium cations [85]; those coordinated to more cations are more acidic because of the strong polarisation induced by the aluminium ions on the oxygen atom [86]. The various configurations proposed by Tsyganenko and Mardilovich are summarised in
Figure 6.1 [85]. Different hydroxyl groups have different properties and can be distinguished from each other by their IR absorption spectra [86]. Smelter-grade alumina might be expected to have more basic (such as $\text{OH}^6$ and $\text{OH}^4$ in Figure 6.1) than acidic sites, since acidic sites are generated by thermal dehydroxylation or “activation”.

![Diagram of hydroxyl groups on alumina surface](image)

**Figure 6.1:** Six kinds of OH group on the alumina surface, bound to octahedral (Al$^{VI}$) and tetrahedral (Al$^{IV}$) aluminium sites (from reference [85]).

The surface hydroxyl groups and their varying co-ordination are largely responsible for the amphoteric behaviour (capable of acidic and basic behaviour) of alumina immersed in water. The electrical double layer is the term used to describe the complete alumina-water interface including the surface and accumulated counterions that comprise this interface. The catalytic properties of $\gamma$-alumina are believed to be related to the density and type of acidic surface sites. IR spectroscopy is one method that has been employed to determine the relative acidity of the various hydroxyl species on alumina surfaces [86].

The adsorption of metal ions onto alumina from dilute solutions has been found to be dependent on pH and probably involves an ion exchange process with protons on the surface. Anions can also adsorb on alumina – firstly by ion pair formation with positively charged surface sites (e.g. $\text{AlO}H_2^+$, $\text{Al}^{3+}$). Secondly, adsorption can occur by ligand exchange with
surface hydroxyls (bound to one or more Al$^{3+}$ ions), in which case adsorption of anions usually increases with decreasing pH [86].

Generally, Al ions are referred to as Lewis acids, while O ions are referred to as basic or reduction sites. OH groups can be Lewis bases (according to Eng et al. [87]) or Brønsted acids and bases.

During the Bayer processing of alumina, a small amount of sodium is typically incorporated into the alumina. This allows a site for the adsorption of water and CO$_2$ in the form of hydrogen carbonate species [88]. During subsequent calcining or reaction of the alumina with species like SO$_2$, these hydrogen carbonate species are removed. Likewise these species reappear after calcining. These hydrogen carbonate structures can form Dawsonite (NaAl(OH)$_2$CO$_3$) structures and have been reported with bands at 3305, 1520-1580 and 1390 cm$^{-1}$ on catalyst alumina [88].

In one detailed study of CO$_2$ adsorption on $\eta$-alumina (220 m$^2\text{g}^{-1}$) [89], the adsorbed CO$_2$ species were more specifically identified. A bicarbonate was identified with bands at 1650, 1440 and 1230 cm$^{-1}$, while a second bicarbonate displayed a band at 1480 cm$^{-1}$. A further species, bidentate carbonate, was tentatively assigned to bands at 1710 and 1315 cm$^{-1}$. Bands at 1630 – 1600 and 1515 – 1470 cm$^{-1}$ were assigned to monodentates. These latter two species were believed to be only minor species. “Linear CO$_2$” species (an adsorbed species that retains the linear shape of the gas; similar to adsorbed COS at around 2100 cm$^{-1}$, see results in Chapter 9) were detected with bands at 2370 and 2407 cm$^{-1}$ respectively. These have been assigned variously to a plain physical adsorption, a specific physical adsorption or the interaction with a special acid-base site. The authors [89] favoured interaction with Al$_{cus}$ ions (Lewis acidic sites), based on the dehydration characteristics of these species and CO adsorption experiments (where, incidentally, CO was suspected to displace CO$_2$ on the alumina surface [90]).

### 6.3 Claus Catalysis

Claus catalysis can be used for desulfurisation when the feedstock contains more than 200 ppm sulfur, greater than 20 v% H$_2$S and less than 5% hydrocarbons. The process uses
activated alumina (usually γ-alumina based) or alumina supported catalysts of medium purity (0.1 mass% Na), with a surface area of about 300 m²g⁻¹ at 300°C. Alumina is a suitable catalyst because it has a weak affinity for the products of hydrolysis, thus avoiding poisoning of the surface. An alternative is titania, which research suggests may be more effective, but alumina is still preferred industrially because it is proven and less expensive [91].

The two basic steps of Claus catalysis are:

(i) Thermal oxidation using a burner of one third of the existing H₂S at 100°C:

\[
2\text{H}_2\text{S}_{(g)} + 3\text{O}_2_{(g)} \xrightleftharpoons{\text{Al}_2\text{O}_3} \rightarrow 2\text{SO}_2_{(g)} + 2\text{H}_2\text{O}_{(g)} \quad (6.3)
\]

(ii) The SO₂ produced reacts with H₂S to form sulfur and water in the Claus reaction, Reaction (6.1).

One of the problems with this process is that it is only 90 – 93% effective and this needs to be improved to meet even current legislation. The sulfur not removed is mainly in the form of COS and CS₂, so research into improving conversion has been focussed on COS and CS₂ removal [91]. The following sections outline research into the activity of alumina towards adsorption and/or reaction of different sulfur gases, focussing on mechanistic studies (particularly using infrared spectroscopy). As well as COS, the behaviour of SO₂, H₂S and CS₂ have been considered, since these sulfur species are or may also be present in smelter gases.

### 6.4 COS Hydrolysis with Alumina

A number of COS hydrolysis studies have been performed in relation to improving the efficiency of Claus catalysis. Hydrolysis of COS is thermodynamically favoured under Claus conditions (about 250°C), but complete conversion is not achieved and potentially greater conversions can be achieved at lower temperatures [91]. Most studies have been performed at temperatures between 230 – 300°C [92-98], although several studies have been performed at much lower temperatures [96, 99, 100]. The COS concentration considered has often been quite high (several %) [92-98, 101], but concentrations down to 150 ppm have also been examined [99, 100]. Catalyst-grade alumina (typically 150 – 300 m²g⁻¹ BET surface area),
usually γ-alumina, is the only type of alumina that has been considered. Experiments are typically performed in a fixed bed reactor, using GC to measure the gas composition and IR to determine adsorbed species.

The kinetics [92-95, 97-100] of COS hydrolysis have been studied, focusing on the effect of water [93, 95, 98, 99], the effect of doping [91, 100, 102], changes to the surface acidity/basicity [93-95] and the effect of O₂, H₂S, SO₂ addition [91, 103]. The effect of sulfidation and sulfation have also been considered [91, 103-106], where sulfidation is the formation of sulfides due to H₂S addition and sulfation is the formation of sulfates on the alumina surface. The mechanism of COS hydrolysis [93-97, 101] has usually been studied using IR spectroscopy. Particularly relevant to dry scrubbing of COS emissions using smelter-grade alumina are the studies by Williams et al. [99] and West et al. [100], due to the low temperatures and low COS concentrations they considered.

### 6.5 COS Hydrolysis Mechanism

Infrared (IR) studies have often been employed to determine the mechanism of COS adsorption and subsequent hydrolysis to H₂S on alumina (and adsorption of other sulfur gases, described in the following sections). IR studies have identified two main types of COS adsorption on alumina, adsorbed molecular COS and hydrogen thiocarbonate (see summary in Table 6.1). Generally γ-alumina has been considered, with activation temperatures ranging from room temperature (under vacuum) up to 850°C and BET surface areas between 50 and 380 m²g⁻¹ [93-95, 97, 101, 107]. Catalyst activation temperature is an important factor in determining the nature of adsorbed species because this temperature determines the nature and quantity of free hydroxyl groups, and therefore changes the active sites on the alumina surface [108].
Table 6.1: Summary of adsorbed COS bands and their assignments.

<table>
<thead>
<tr>
<th>Bands (cm(^{-1}))</th>
<th>Species</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2070 – 1960</td>
<td>Adsorbed Molecular COS</td>
<td>[95, 101, 107]</td>
</tr>
<tr>
<td>1570 – 1470</td>
<td>Carboxylate</td>
<td>[95]</td>
</tr>
<tr>
<td>1646, 1438, 1230</td>
<td>Hydrogen Carbonate (HCO(_3^-))</td>
<td>[101]</td>
</tr>
<tr>
<td>1572-60, 1350-27</td>
<td>Hydrogen Thiocarbonate (HCO(_2)S(^-))</td>
<td>[101]</td>
</tr>
</tbody>
</table>

6.5.1 Adsorbed Molecular COS

IR spectroscopy has established that two types of adsorbed species arise from contact between COS and alumina; molecular COS and hydrogen thiocarbonates. Molecular or “linear” COS (slightly perturbed COS) appears at a similar wavenumber to COS gas, but has a different peak shape (there is an equivalent “linear” CO\(_2\) species at around 2350 cm\(^{-1}\)). This species has been reported at various wavenumbers between 1900 and 2100 cm\(^{-1}\). It was reported at 2070 cm\(^{-1}\) on a 91 m\(^2\)g\(^{-1}\) alumina activated at 600ºC [95] and at 2000 cm\(^{-1}\) on a 380 m\(^2\)g\(^{-1}\) alumina activated at 450ºC in an O\(_2\) atmosphere [107].

In another case, molecular COS was identified at 1900 – 2000 cm\(^{-1}\) for a 207 m\(^2\)g\(^{-1}\) alumina activated at 500ºC and 1990 and 1960 cm\(^{-1}\) for the same type of alumina activated at 850ºC [101]. The 1990 cm\(^{-1}\) band was the only form observed on sulfated alumina [96] or on very dehydroxylated alumina [101]. Adsorbed molecular COS species appeared more strongly on alumina activated at higher temperatures [101].

Figure 6.2 shows possible adsorption sites for molecular COS (evidence suggests that hydroxyl groups are not involved in this type of species) postulated in reference [101]. The 1990 cm\(^{-1}\) band was associated with very weakly acidic or basic sites (species A), while the 1960 cm\(^{-1}\) band was believed to reflect adsorption at very weakly basic sites and lead to the formation of a thiocarbonate species (CO\(_2\)S\(^2-\)).
There are three types of sites on alumina that could be involved in adsorption or reaction; hydroxyl groups, aluminium ions (Lewis acid sites) or oxide ions. Of these sites, only hydroxyl groups can be observed directly with FTIR techniques [107]. The type of alumina sites molecular COS adsorbs on and the sites involved in hydrolysis have been described in a variety of ways, including:

- COS adsorbs on Lewis acid (Al ion) sites via its sulfur atom (Species B, Figure 6.2 [107]),
- Competitive adsorption of COS and H$_2$O on basic sites [95], increasing the basicity with NaOH doping substantially increased COS hydrolysis (Species C or D, Figure 6.2 [93]),
- COS adsorption on reduction (especially coordinatively unsaturated O$^{2-}$, but bare unsolvated OH$^{-}$ also possible) sites (Species C or D, Figure 6.2), with H$_2$O adsorption and reaction occurring on Lewis acidic (Al ion) sites [94].

Creation of Brønsted acidity, such as by sulfation of alumina, has been found to poison the catalyst and prevent COS adsorption or hydrolysis [97].

### 6.5.2 Hydrogen Thiocarbonate (HCO$_2$S) Formation

The second type of adsorbed COS species requires the presence of surface hydroxyl groups [101] and are found at similar wavenumbers to hydrogen carbonate species, therefore they have been identified as hydrogen thiocarbonate species. Hydrogen thiocarbonate (HTC) species, HCO$_2$S, have bands at around 1550 and 1350 cm$^{-1}$ (measured to be 1572 and 1327 cm$^{-1}$ by reference [101] at room temperature) and may be an intermediate formed between...
adsorbed molecular COS and H₂S gas. Temperature and O₂ levels were found by Fiedorow et al. [95] to affect the exact position and nature of these bands.

Hydrogen thiocarbonate species often form simultaneously with hydrogen carbonates, HCO₃⁻, which have three bands at around 1650, 1450 and 1250 cm⁻¹ [101], when COS is contacted with alumina at near ambient temperatures. These hydrogen carbonate bands were found to disappear at 50°C.

Due to the formation of HTC species and subsequent COS hydrolysis, some hydroxyl group activity is observed when COS adsorbs on alumina. For alumina activated at room temperature, a loss in free hydroxyl groups at 3744 and 3703 cm⁻¹ and a gain at 3620 cm⁻¹ was associated with COS adsorption [101]. Alumina evacuated at 500°C showed a decrease in free OH groups at 3780 and 3711 cm⁻¹ and an increase at 3609 cm⁻¹ with COS adsorption. It has been suggested by Bachelier et al. [97] that the specific OH groups involved in hydrogen thiocarbonate formation are Brönsted basic sites (the most basic OH groups, OH⁴ and OPH⁶ in Figure 6.1). Competitive adsorption of COS and SO₂ was observed on these sites, with SO₂ adsorbing more strongly.

Deuterated alumina experiments determined that hydrogen thiocarbonates on alumina were configured in the manner of Type 1 HTC species in Figure 6.3, since their formation was insensitive to HD substitution. Type 1 HTC species should also have an SH band, which was not detected, but SH bands are known to be weak [101].

Mechanistic IR experiments have therefore established that COS probably adsorbs molecularly first, then forms a hydrogen thiocarbonate species on the alumina surface with a
hydroxyl group, before leaving the surface as H$_2$S. Possible adsorbed species are summarised in Figure 6.2 and Figure 6.3.

### 6.6 Kinetics of COS Hydrolysis

There are some contradictory studies with respect to the kinetics of COS hydrolysis on alumina. One of the most interesting studies of COS hydrolysis from a dry scrubbing point of view was done by Williams et al., who considered 150 ppm COS on $\gamma$-alumina (150 and 300 m$^2$g$^{-1}$) at 30 – 250ºC in a fixed bed microreactor using GC with a pulsed flame photometric detector to measure gas composition [99]. A further study by West et al. [100] at 30ºC of the hydrolysis of COS (150 ppm COS) on $\gamma$-alumina (initial BET surface area 300 m$^2$g$^{-1}$) with an additive (about 3% Na, Fe, Co, Ni, Cu or Zn) was performed using a laboratory microreactor (stainless steel U-tube reactor) and GC with pulsed flame photometric detection for gas analysis. The alumina was doped using the incipient wetness method, where a metal nitrate solution is adsorbed onto the alumina, followed by drying (120ºC in air for 4 hrs) and calcining (500ºC for 5 hrs).

Figure 6.4 shows the COS conversion over time achieved in the Williams et al. [99] study; greatest conversion occurred in the first half an hour. Figure 6.5 shows experimental data on the rate of COS hydrolysis as a function of H$_2$O concentration and compares two different calculated models to determine the limiting step in hydrolysis. Langmuir-Hinshelwood kinetics were proposed for COS hydrolysis, where the reaction products are not strongly adsorbed, with a rate given by:

$$ \text{rate} = \frac{k_1[COS][H_2O]}{(1+K_2[COS]+K_3[H_2O])^2} \quad (6.4) $$

Where $k_1$ is the rate constant and $K_2$ and $K_3$ are the equilibrium constants for the adsorption of COS and H$_2$O respectively.
Figure 6.4: COS conversion as a function of time at 30°C, with 300 ppm COS, 1200 ppm H\textsubscript{2}O, γ-alumina (0.5g, 300 m\textsuperscript{2}g\textsuperscript{-1}) and a gas hourly space velocity of 100,000 h\textsuperscript{-1} [99].

Figure 6.5: Rate of COS hydrolysis as a function of H\textsubscript{2}O concentration at 60°C, with 150 ppm COS γ-alumina (0.5g, 300 m\textsuperscript{2}g\textsuperscript{-1}), and a gas hourly space velocity of 500,000 h\textsuperscript{-1}. Key: ♦ = experimental data, - - - = calculated data for COS adsorption limited model, – = calculated data for surface reaction type model [99].
At high temperatures (250°C), surface hydrolysis of thiocarbonate was rate determining step. At low temperatures (30 – 60°C), the rate determining step was either the adsorption of COS or the surface reaction between adsorbed COS and an H$_2$O-derived intermediate (called the “surface reaction type model” in Figure 6.5, where these two models are compared to the experimental data). At lower temperatures the products were not believed to be strongly adsorbed and the surface area of the alumina became an important design parameter.

There is no clear consensus on the behaviour of H$_2$O kinetically in COS hydrolysis. In the low temperature study (30°C – 60°C [99]), the rate of COS hydrolysis was observed to significantly decrease as the concentration of water was increased, which is illustrated in the results in Figure 6.5. However in several earlier studies at higher temperatures (around 250°C), COS hydrolysis was found to be kinetically zero order with respect to H$_2$O (the strongly adsorbed reactant) and first order with respect to COS [92, 95]. These conflicting results may be due to the temperature and gas composition of each particular study, but in any case the low temperature study is more relevant to dry scrubbing. Fiedorow et al. reported competitive adsorption between COS and H$_2$O [95] and Tong et al. reported that adsorption of water vapour could significantly retard the rate of hydrolysis [98]. An Eley-Rideal surface reaction mechanism has been proposed [95, 98], where H$_2$O is adsorbed first, COS then adsorbs onto adsorbed H$_2$O. It can be concluded that although some H$_2$O is required as a reactant for the hydrolysis of COS, these studies suggest that too much H$_2$O will have a negative impact on the amount of COS hydrolysed, probably due to the stronger adsorption of H$_2$O on alumina compared to COS.

The effect of doping the alumina used for the low temperature, low COS concentration conditions was studied by West et al., who found that doping to about 3 wt% with Na, Fe, Co, Ni, Cu or Zn reduced the BET surface area from 300 m$^2$g$^{-1}$ to 199 – 263 m$^2$g$^{-1}$ [100]. No change in the x-ray diffraction pattern was observed. Additives enhanced the initial intrinsic activity (mol[COS(hydrolysed)]m$^{-2}$hr$^{-1}$), but this rapidly decayed as the experiment progressed in most cases. Only Ni and Zn doped catalysts gave a significant increase in specific activity (mol[COS(hydrolysed)]g$^{-1}$hr$^{-1}$) throughout the timeframe of the experiment compared to undoped alumina. The alumina was observed to retain sulfur in the first 5 hours of COS hydrolysis.
West et al. found that Na doping increased the initial extent of COS hydrolysis compared to undoped alumina, but it did not increase the overall specific activity of alumina towards COS hydrolysis. Another study of the effect of Na on alumina showed different behaviour at different levels of doping. Ivanov et al. found that small amounts of Na (<1000 ppm Na₂O) decreased activity to COS hydrolysis in two ways [102]:

- Na decreased available OH groups, leading to a decrease in activity.
- Na reduced basicity, which was believed to be due to better crystallinity – if Na⁺ migrates into the bulk leading to a charge compensation phenomenon, then fewer defects would be present in the anion subnetwork.

Greater than 2500 ppm Na resulted in increased basicity, increasing the number of sulfation reactions on the surface. Therefore, between 1000 ppm and 2500 ppm was believed to be the optimum Na doping for alumina [102]. However, West et al. did not report a change in sulfation reactions with >1 wt% Na, instead claiming this level of doping produced an active alumina catalyst due to increased surface basicity of the catalyst [100].

Fiedorow et al. observed that basic surface sites were essential to COS hydrolysis [95]. Likewise, George [93] found that the hydrolysis of COS increased with catalyst basicity, although Akimoto and Dalla Lana [94] did not observe basicity to affect COS hydrolysis. High levels of Fe have been reported to increase the acidity of the alumina leading to reduced activity [91]. The presence of Fe, Cu and Ni increased the sulfate species on alumina, while Mo, V and W all reduced the amount of sulfate species (sulfate species poison the catalyst) [91].

Fiedorow et al. reported that the presence of O₂ also reduced the rate of COS hydrolysis [95]. George found that CO₂ poisoning did not affect the rate of COS hydrolysis [92], while Akimoto and Dalla Lana found that both CO₂ and SO₂ temporarily poisoned the catalyst [94]. H₂S presence has been reported to lead to sulfdation, decreasing the number of basic sites on the alumina [103]. A review by Rhodes et al. [91] explained that at greater than 200°C, the oxidation of H₂S into SO₂ becomes significant and the co-existence of SO₂ and O₂ leads to sulfation of the alumina. Sulfation can also occur when SO₂ is chemisorbed on alumina, although this is believed to occur at even higher temperatures. Sulfation increases the acidity.
of the catalyst, resulting in decreased activity towards COS hydrolysis [91]. Doping the alumina catalyst with Na, Cu and Fe has also been reported to increase sulfation [104, 105].

### 6.7 Other Methods for COS Decomposition

The majority of COS-Alumina studies focus on the hydrolysis of COS. Hydrolysis of COS is just one of the options for removal of this gas. Other methods that have been considered include:

(i) Hydrogenation using H$_2$ and a Co-Mo-Al$_2$O$_3$ catalyst.
(ii) Combustion to produce SO$_2$, which is then removed using a CaO absorbent.
(iii) Oxidation using SO$_2$ to produce CO$_2$ and S with a Co-Mo-Al$_2$O$_3$ catalyst or alumina catalyst (prone to deactivation due to CO$_2$ poisoning) [91].

A high temperature study was conducted by Haas and Khalafalla [109], who considered the catalytic thermal decomposition of COS with a variety of alumina-based catalysts and silica gel. The decomposition of COS is possible in several ways:

\[
2\text{COS}(g) \rightarrow \text{CO}_2(g) + \text{CS}_2(g) \tag{6.5}
\]

\[
\text{COS}(g) \rightarrow \text{CO}(g) + \frac{1}{x} \text{S}_x \tag{6.6}
\]

The presence of a catalyst was found to increase the extent of decomposition, so that at 700°C, more than 55% decomposition was obtained. Reaction (6.5) forming CS$_2$ was favoured below 635°C and Reaction (6.6) was favoured above this temperature forming elemental S.

The presence of SO$_2$ was found to increase the decomposition rate at lower temperatures according to the reaction:

\[
2\text{COS}(g) + \text{SO}_2(g) \rightarrow 2\text{CO}_2(g) + \frac{3}{x} \text{S}_x \tag{6.7}
\]
This reaction between COS and SO$_2$ has been investigated by Chuang et al. [107] on γ-alumina using infrared spectroscopy. They postulated that SO$_2$ adsorbed on hydroxyl sites and COS on aluminium ion sites, allowing the reaction to proceed. CO$_2$ chemisorption irreversibly blocked COS adsorption sites. On the other hand, George [93] did not observe CO$_2$ poisoning with the cobalt-molybdate catalyst used.

6.8 SO$_2$ Adsorption on Alumina

The adsorption of SO$_2$ on alumina has been considered extensively with respect to Claus catalysis. The majority of studies have utilised IR or FT-IR spectroscopy to determine the mechanism for adsorption. However, other techniques that have been employed include EPR spectroscopy [108] and thermogravimetric analysis [110-112]. TGA studies have found that the rate of SO$_2$ adsorption is fastest in the first minute, then the rate drops significantly [112]. Irreversible adsorption of SO$_2$ increases with the amount of water lost from the alumina surface [111].

<table>
<thead>
<tr>
<th>Bands (cm$^{-1}$)</th>
<th>Species</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1340-30, 1151-40</td>
<td>Physisorbed SO$_2$</td>
<td>[108, 113-117]</td>
</tr>
<tr>
<td>2499-2470, 2340</td>
<td>Physisorbed SO$_2$ Overtones</td>
<td>[113, 114]</td>
</tr>
<tr>
<td>1090-50</td>
<td>Sulfite (SO$_3^{2-}$)</td>
<td>[108, 111, 115-117]</td>
</tr>
<tr>
<td>1020-800</td>
<td>Hydrogen Sulfite (HSO$_3^-$)</td>
<td>[96, 97, 111]</td>
</tr>
<tr>
<td>1685 – 1090</td>
<td>Other Chemisorbed SO$_2$</td>
<td>[108, 113, 116, 117]</td>
</tr>
<tr>
<td>1400, 1100</td>
<td>Sulfate (SO$_4^{2-}$)</td>
<td>[116]</td>
</tr>
</tbody>
</table>

This review focuses on the mechanism of SO$_2$ adsorption using IR spectroscopy, since it is the aspect of most relevance to the COS-dry scrubbing studies. Several adsorbed SO$_2$ species have been identified (See Table 6.2). Usually γ-alumina has been considered [108, 113-115]; both hydroxylated [111] and dehydrated [116]; and in one case α-alumina has been studied [117]. The effect of activation temperature (300 to 700°C), adsorption temperature, desorption temperature, O$_2$ [112], HF [118], H$_2$S [113, 115, 119], COS (see Section 6.5 [93, 94, 97, 107]) and CO$_2$ [107] presence have all been considered on aluminas which typically
have a surface area of around 100 m$^2$g$^{-1}$ (although one alumina studied is closer to 300 m$^2$g$^{-1}$ [108]).

### 6.8.1 Physisorbed SO$_2$ Species

Adsorption of SO$_2$ on alumina usually leads to bands at around 1330 and 1140 cm$^{-1}$ due to the symmetric and asymmetric stretching vibrations of SO, such as those observed by Deo et al. on $\gamma$-alumina (50 – 100 m$^2$g$^{-1}$) [113]. In this case, SO$_2$ was believed to be physisorbed on the alumina via hydrogen bonding to hydroxyl groups. This adsorbed species was also observed on $\gamma$-alumina (91 m$^2$g$^{-1}$, 400ºC activation) by Liu et al. [114], with bands at 1335 and 1140 cm$^{-1}$ and by Karge and Dalla Lana [115] at 1330 and 1150 cm$^{-1}$, which they believed indicated adsorption on acidic sites (probably like OH$^{664}$ and OH$^{666}$ in Figure 6.1). Only the 1326 cm$^{-1}$ band was observed by Chang et al. [116] for adsorbed SO$_2$ on well-dehydrated alumina (and this species could be removed at 100ºC). Datta et al. [108] observed this species at 1334 and 1148 cm$^{-1}$ (which desorbed after room temperature evacuation for 1 hour, confirming its physisorbed status) and believed it to bond to hydroxyl groups at 3730 cm$^{-1}$ (based on the reappearance of this band after desorption, see species Type 4 in Figure 6.6). Berben et al. [117] observed physisorbed SO$_2$ at 1330 and 1151 cm$^{-1}$ for $\gamma$-alumina and 1340 and 1150 cm$^{-1}$ for $\alpha$-alumina (both aluminas activated at 500ºC), bonded to the acidic hydroxyl groups at 3690 cm$^{-1}$. The overtones of these bands have been detected at 2470 and 2340 cm$^{-1}$ by Deo et al. [113] and at 2499 cm$^{-1}$ by Liu and Dalla Lana [114].

### 6.8.2 Sulfite and Hydrogen Sulfite Species

Chang et al. [116] were the first to observe a dominant low wavenumber band that initially formed at 1060 cm$^{-1}$ when SO$_2$ chemisorbed on well-dehydrated $\gamma$-alumina (96 m$^2$g$^{-1}$, activated at 700ºC), which was assigned to a sulfite species (removed at 600ºC). Karge and Dalla Lana [115] detected a dominant band at 1065 cm$^{-1}$ and assigned it to strongly held SO$_2$ adsorbed on basic sites on $\gamma$-alumina (100 m$^2$g$^{-1}$) and Datta [108] also assigned a broad band at 1050 cm$^{-1}$ to adsorbed SO$_2$ (Type 4 in Figure 6.6). Berben et al. [117] assigned adsorbed sulfite to a band at 1090 cm$^{-1}$ for $\gamma$-alumina, but bands in this region were not assigned for $\alpha$-
alumina (this species is illustrated as Type 4 in Figure 6.6). A broad band in the hydroxyl region at 3500 cm$^{-1}$ was attributed to the presence of a bisulfite species ($\text{HSO}_3^-$).

Lavalley et al. [111] attributed negative bands at 1645, 1437 and 1230 cm$^{-1}$ to the loss of $\text{HCO}_3^-$, caused when $\text{SO}_2$ adsorbed on hydroxylated aluminas (surface area 90 m$^2$g$^{-1}$ activated at 300 to 600°C). Preadsorbed $\text{SO}_2$ also prevented the formation of hydrogen carbonate species, suggesting that $\text{SO}_2$ adsorbed as hydrogen sulfite ($\text{-SO}_3\text{H}$) by attacking free hydroxyl groups. A band at 3500 cm$^{-1}$ was believed to be associated with these groups and it was suggested that they were hydrogen bonded. When alumina was heat treated at 200°C, uptake of $\text{SO}_2$ increased, with sulfite (1050 cm$^{-1}$) and hydrogen sulfite (1020 cm$^{-1}$) forming. The increased uptake was attributed to the formation of $\text{O}_{\text{cus}}$ and $\text{Al}_{\text{cus}}$ ions ($\text{cus} = \text{ coordinatively unsaturated ions}$) with increased temperature, which can also be sites for $\text{SO}_2$ chemisorption. Bachelier et al. [96, 97] suggested that bands in the 800 to 1000 cm$^{-1}$ region were due to the formation of hydrogen sulfite on $\gamma$-alumina (215 m$^2$g$^{-1}$, calcined at 500°C).

Chang et al. [116] found that $\text{SO}_2$ chemisorbed more readily on a well-dehydrated surface, suggesting that the nature of the hydroxyl group population was important in determining the type of $\text{SO}_2$ adsorption. Lavalley et al. [111] observed a reduction in available hydroxyl groups after $\text{SO}_2$ chemisorption at 3785, 3735 and 3700 cm$^{-1}$ and the appearance of a broad band at 3500 cm$^{-1}$, all of which are partly irreversible at room temperature. Datta et al. [108] detected an initial shift of two bands in the hydroxyl region from 3750 to 3735 cm$^{-1}$ and from 3680 to 3550 cm$^{-1}$, suggesting that $\text{SO}_2$ interferes with this hydroxyl group on adsorption, although it does not interact directly with it. $\text{SO}_2$ was believed by Chuang et al. [107] to be hydrogen bonded to surface hydroxyl groups, based on a decrease in 3785 cm$^{-1}$ hydroxyls and the appearance of a broad hydrogen bonding band (3500 cm$^{-1}$). This bonding was believed to occur via the S atom, based on the wavenumber shift (32 cm$^{-1}$) observed for the $\text{SO}$ stretching vibration.

### 6.8.3 Other Chemisorbed $\text{SO}_2$ Species

Other adsorbed $\text{SO}_2$ species can be detected after desorption of the dominant physisorbed species or by changing adsorption conditions. At higher $\text{SO}_2$ pressures (up to 100 torr), Deo et al. [113] observed pairs of bands at 1685 and 1240 cm$^{-1}$ and 1410 and 1090 cm$^{-1}$. On heat
treatment (<400°C), a further pair of bands at 1570 and 1440 cm\(^{-1}\) were observed. After prolonged heat treatment, two chemisorbed species were detected – one with bands at 1375 and 1110 cm\(^{-1}\) and the other with bands at 1570 and 1470 cm\(^{-1}\).

A total of five adsorbed SO\(_2\) species were identified by Datta et al. on catalyst alumina (activated at 400°C to 700°C, BET surface area typically 296 m\(^2\)g\(^{-1}\)) [108], which are summarised in Figure 6.6. In addition to the physisorbed (1334 and 1148 cm\(^{-1}\)) and sulfite (called Type 4, 1050 cm\(^{-1}\)) species already mentioned, a weak band at 1189 cm\(^{-1}\) (desorbed at 200°C) was observed when SO\(_2\) initially adsorbed on alumina activated at 400°C.

After physisorbed species were removed, smaller underlying bands at 1322 and 1140 cm\(^{-1}\) were detected and assigned to chemisorbed SO\(_2\) bonded to 3680 cm\(^{-1}\) hydroxyls, which desorbed at 100°C. This weakly chemisorbed species was also detected by Berben et al. [117], with a band at 1320 cm\(^{-1}\) (for \(\alpha\) - and \(\gamma\)-alumina), but they believed it bonded to weakly acidic hydroxyls (3730 cm\(^{-1}\)) and basic surface sites (negatively charged oxygen ions). Fiedorow et al. [120] observed that the strongest interaction to arise from SO\(_2\) adsorption was between SO\(_2\) and the least acidic hydroxyls. SO\(_2\) adsorption affected the 3720 cm\(^{-1}\) hydroxyl groups, and in some cases, the 3680 cm\(^{-1}\) hydroxyl groups.

![Figure 6.6: Adsorbed SO\(_2\) species assigned by Datta et al. [108]. Types 1 and 4 have been identified in most studies (see Table 6.2) and Types 2 and 4 were also detected by Berben et al. [117].](image)

Datta et al. identified a fourth (1130 and 1050 cm\(^{-1}\), desorbed at 400 to 600°C) species after higher temperature desorption studies, along with 1189 cm\(^{-1}\) band already mentioned, but their assignment was uncertain. Datta et al. found that the third species (see Figure 6.6)
affected the 3750 cm\(^{-1}\) hydroxyls, but was not believed to be directly bonded to these hydroxyls. The fourth species did not affect hydroxyl groups and was therefore assumed to bond to coordinatively unsaturated aluminium or oxygen ions or aluminium ion clusters.

A fifth species was identified on alumina activated at 700\(^{\circ}\)C, with a band at 1255 cm\(^{-1}\), which desorbed at 200\(^{\circ}\)C. Datta et al. [108] concluded that SO\(_2\) adsorbed to both basic and acidic sites. In contrast, Berben et al. [117] also identified a species with bands at 1200 and 1245 cm\(^{-1}\) (\(\gamma\)-alumina) or 1250 cm\(^{-1}\) (\(\alpha\)-alumina), but assigned the 1245 – 1250 cm\(^{-1}\) band to the asymmetric stretching S-O vibration of SO\(_2\) adsorbed on an aluminium cation in an octahedral position. Likewise, the 1200 cm\(^{-1}\) band was the tetrahedral positioned species.

### 6.8.4 Sulfate Formation

Further studies at higher temperatures determined that when \(\gamma\)-alumina was exposed to SO\(_2\) and O\(_2\) above 400\(^{\circ}\)C, a band at 1365 cm\(^{-1}\) was observed in addition to a band at 1060 cm\(^{-1}\) (see Figure 6.6), characterising strongly adsorbed SO\(_2\) [112, 111]. These bands shift to 1400 and 1100 cm\(^{-1}\) with further heating at 500\(^{\circ}\)C, attributed to the formation of aluminium sulfate. Chang et al. [116] found that in the presence of O\(_2\), aluminium sulfate formed at 600\(^{\circ}\)C with bands at 1400 and 1100 cm\(^{-1}\), and subsequently decomposed at 800\(^{\circ}\)C. Below 400\(^{\circ}\)C, O\(_2\) had no effect on SO\(_2\) chemisorption.

Exposure of alumina to SO\(_3\) results in the initial formation of bands at 1326 and 1065 cm\(^{-1}\), which on further exposure develop into sulfate bands at 1400 and 1100 cm\(^{-1}\) [116].

### 6.8.5 Surface Reaction Between SO\(_2\) and H\(_2\)S

Deo and Dalla Lana [113] observed no SO\(_2\) chemisorption bands when a 2:1 ratio of H\(_2\)S and SO\(_2\) were in contact with alumina; only the Claus reaction occurred (Reaction (6.1)).

However, Karge and Dalla Lana [115] later did detect chemisorbed SO\(_2\) on the alumina surface during Claus reaction and found that it was reactive toward H\(_2\)S. Chemisorbed SO\(_2\)
was also detected on alumina pre-exposed to SO₂ before exposure to H₂S and vice versa by Datta and Cavell [119]. Adsorbed H₂S was not detected in these experiments. Physisorbed SO₂ (1327 and 1145 cm⁻¹) was the first to react on addition of H₂S, followed by the 1189 cm⁻¹ species and chemisorbed species (1322 and 1141 cm⁻¹). The species at 1055 cm⁻¹ (sulfite) was unaffected by addition of H₂S. H₂S was found to occupy fewer sites on alumina than SO₂.

George found that for the Claus reaction (Reaction (6.1)), SO₂ was the strongly absorbed reactant and was zero order, while H₂S was first order. Considerable irreversible adsorption was observed in the reaction between SO₂ and H₂S [92].

### 6.8.6 Effect of HF

Khallafalla and Haas [118] believed that SO₂ adsorbed on hydroxyl sites (basic Brönsted sites) and confirmed this by treating the surface with HF. Incorporation of halogens to the alumina surface had been previously shown to increase the acidity of Lewis acid sites and used to promote catalytic activity towards petroleum hydrocarbon cracking, reforming and polymerisation. HF was found to replace the OH⁻ surface ions with which SO₂ forms a surface species and thus hinders adsorption.

### 6.9 H₂S Adsorption on Alumina

H₂S and alumina have a weak interaction, which is one of the reasons that alumina is suitable for Claus catalysis. In relation to Claus catalysis there have been several studies of H₂S adsorption on γ-alumina, with surface areas ranging from 50 to 300 m² g⁻¹ [122, 123] – once again, this review concentrates on mechanistic studies using IR spectroscopy. The effect of SO₂ has also been considered (See Section 6.8.5 [113, 114, 119] and has been found to displace H₂S on the alumina surface [113]. It has been suggested that H₂S adsorbs both dissociatively and undissociatively [123], with a summary of adsorbed H₂S bands shown in Table 6.3.
### Table 6.3: Summary of adsorbed H$_2$S bands and their assignments.

<table>
<thead>
<tr>
<th>Bands (cm$^{-1}$)</th>
<th>Species</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1345-34</td>
<td>Adsorbed H$_2$S bending mode</td>
<td>[113, 114, 123]</td>
</tr>
<tr>
<td>2585-60</td>
<td>Adsorbed H$_2$S stretching mode</td>
<td>[113, 114, 122, 123]</td>
</tr>
<tr>
<td>1568-56, 1420</td>
<td>Associated with adsorbed H$_2$S</td>
<td>[114, 123]</td>
</tr>
</tbody>
</table>

#### 6.9.1 Adsorbed H$_2$S Bands

The bending mode for adsorbed H$_2$S (1290 cm$^{-1}$ for the free molecule [113]) has been reported variously at 1345 cm$^{-1}$ [114], 1335 cm$^{-1}$ (which remained after room temperature evacuation [113]) and 1334 cm$^{-1}$ [123]. But in one case, this adsorbed H$_2$S species was not detected [122].

Likewise, the SH stretching vibrations (2611 and 2684 cm$^{-1}$ for the free molecule) have been reported at 2565 cm$^{-1}$ [114], 2560 cm$^{-1}$ (which remained after room temperature evacuation [113]), 2585 – 2575 cm$^{-1}$ [122] and 2578 cm$^{-1}$ [123] for adsorbed H$_2$S. The first overtone of the bending vibration is believed to contribute to this band [113, 123].

Other bands have also been reported in relation to adsorbed H$_2$S on alumina. Liu et al. reported an adsorbed H$_2$S band at 1568 cm$^{-1}$ (in addition to bands at 2565 and 1345 cm$^{-1}$), but did not assign it to a particular species [114]. Datta and Cavell detected two further bands at 1556 cm$^{-1}$ and a weaker one at 1420 cm$^{-1}$, which they believed were associated with the alumina itself [123].

There have been differing suggestions on the mechanism and adsorption sites for H$_2$S. In Liu et al.’s study of adsorbed H$_2$S on γ-alumina (91 m$^2$g$^{-1}$, activated at 400ºC), H$_2$S was believed to adsorb on Lewis acid (aluminium ions) sites, but basic sites (e.g. surface oxide ions) were also believed to be indirectly involved in subsequent reaction [114]. Deo et al. [113] studied the adsorption of H$_2$S on γ-alumina (50-100 m$^2$g$^{-1}$) and determined that hydrogen bonding occurs between surface hydroxyl groups and H$_2$S molecules. They also concluded that the
shift in wavenumber for the 2560 cm\(^{-1}\) band they detected (compared to the free molecule), meant the S was bound with an OH group, which in turn was bound to an Al.

Saur et al., who only detected the higher wavenumber band, concluded that there was dissociative chemisorption of H\(_2\)S, based on the similarities between H\(_2\)S adsorption on alumina (\(\gamma\)- and \(\delta\)-alumina, 90 m\(^2\)g\(^{-1}\), activated at 600ºC) and CH\(_3\)SH adsorption [122]. Datta and Cavell [123] studied H\(_2\)S adsorption on \(\gamma\)-alumina (296 m\(^2\)g\(^{-1}\), activated at 400 and 700ºC). The bending vibration of water at 1620 cm\(^{-1}\) increased with H\(_2\)S adsorption, suggesting that H\(_2\)S adsorbed dissociatively leading to the formation of water. While the authors concluded that H\(_2\)S is not very strongly adsorbed on the alumina surface, they did determine that there were two forms of adsorbed H\(_2\)S – undissociated and dissociated (see Figure 6.7) adsorption on Al.

![Figure 6.7: Dissociative adsorption of H\(_2\)S on \(\gamma\)-alumina, proposed by Datta and Cavell [123].](image)

6.10 CS\(_2\) Adsorption on Alumina

More recently, attention has focussed on CS\(_2\) hydrolysis with \(\gamma\)-alumina in relation to Claus catalysis. The mechanistic behaviour of CS\(_2\) on catalyst alumina appears to be similar to COS, with the formation of hydrogen carbonates and hydrogen thiocarbonates due to adsorption. A summary of adsorbed CS\(_2\) species and their IR bands is given in Table 6.4.

Physisorbed CS\(_2\) was found to have a band at 1515 cm\(^{-1}\) when Laperdrix et al. studied CS\(_2\) adsorption on \(\gamma\)-alumina (200 m\(^2\)g\(^{-1}\), activated at 450ºC) [124]. This band was confirmed in a further study of CS\(_2\) hydrolysis on \(\gamma\)-alumina (180 m\(^2\)g\(^{-1}\), activated at 450ºC in vacuum) by Sahibed-Dine et al. [125] and both groups found it desorbed after room temperature
evacuation. Sahibed-Dine et al. detected another band at 1166 cm⁻¹, which they believed was
due a new species and this also disappeared after room temperature evacuation.

Table 6.4: Summary of adsorbed CS₂ species.

<table>
<thead>
<tr>
<th>Bands (cm⁻¹)</th>
<th>Species</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1515</td>
<td>Physisorbed CS₂</td>
<td>[124, 125]</td>
</tr>
<tr>
<td>1166</td>
<td>Associated with adsorbed CS₂</td>
<td>[125]</td>
</tr>
<tr>
<td>1650, 1436, 1229</td>
<td>Hydrogen Carbonate (HCO₃⁻)</td>
<td>[124]</td>
</tr>
<tr>
<td>1578, 1345-30</td>
<td>Hydrogen Thiocarbonate (HCO₂S⁻)</td>
<td>[124, 125]</td>
</tr>
</tbody>
</table>

Formation of bands at 1650, 1436 and 1229 cm⁻¹ due to hydrogen carbonates and bands at
1578 and 1330 cm⁻¹ due to hydrogen thiocarbonate have been detected by Laperdrix et al. as
a result of CS₂ adsorption [124]. Sahibed-Dine et al. detected only the 1345 cm⁻¹ hydrogen
thiocarbonate band [125]. These hydrogen thiocarbonate species have also been observed
when adsorbed COS on alumina (See Section 6.5.2 [96]).

Sahibed-Dine et al. believed that CS₂ adsorption occurred on basic O²⁻ sites leading to the
formation of xanthate species (CS₂O)²⁻. Laperdrix observed a reduction in the physisorbed
CS₂ band at 1515 cm⁻¹ and a hydroxyl band at 3767 cm⁻¹, signifying CS₂ hydrolysis had
occurred and they believed that adsorbed COS and hydrogen thiocarbonate were intermediate
species [124]. SO₂ adsorption was found to inhibit CS₂ hydrolysis by reducing available OH
groups.

6.11 Relevance to Dry Scrubbing

There are several aspects of research into COS hydrolysis with respect to Claus catalysis that
are relevant to predicting the behaviour of COS in the dry scrubber:

- H₂O has been shown to compete for adsorption sites with COS on alumina.
- Sulfation or sulfidation of catalyst alumina is caused by reaction with SO₂ or H₂S and
  leads to deactivation of the catalyst. A similar process could result in reduced
  adsorption capacity of smelter-grade alumina with respect to COS.
- The presence of CO₂ has been found to temporarily poison the alumina catalyst.
• HF adsorption diminishes adsorption capacity of catalyst-grade alumina with reference to SO$_2$ adsorption.

• Sodium is a common impurity in all types of alumina. Detailed studies of its affect on catalyst alumina behaviour can be applied to smelter-grade alumina.

• Conditions under which COS hydrolysis to H$_2$S is promoted or discouraged have been studied with catalyst alumina and may also be relevant to smelter-grade.

Additionally, mechanistic studies of COS adsorption on $\gamma$-alumina, particularly using IR techniques, can be applied to smelter-grade alumina studies. The intermediate species, hydrogen thiocarbonate, that has been observed on $\gamma$-alumina proved to be relevant on smelter-grade alumina (see Chapter 9).

While previous COS/alumina studies are useful, there are several important differences between these Claus catalyst studies and the capture of COS using smelter-grade alumina in a dry scrubber:

• Claus catalysis research has frequently been focussed on high COS concentrations and different gas compositions than those encountered in aluminium smelting.

• Catalyst-grade alumina has been used in all cases, which has a much higher surface area than smelter-grade alumina, although much of the work above suggests the same chemistry applies.

• Temperatures considered in these previous studies are often much higher than those in the dry scrubber.
Chapter 7  THERMODYNAMIC CALCULATIONS OF COS STABILITY IN DRY SCRUBBING

The calculations discussed in this chapter predict the equilibrium composition of COS on alumina in both simplified systems and those approaching the complexity of a dry scrubber. Specific reactions that may occur have also been determined.

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7.1 Introduction

Two factors determine how a chemical system may behave – thermodynamics and kinetics. Thermodynamic calculations predict stable species at equilibrium and feasibility of specific reactions, while kinetics determine the rate that these reactions may occur. The software package HSC Chemistry© [82] was used to calculate equilibrium for various species under dry scrubber conditions.

To use HSC Chemistry©, initial conditions were specified by the user and equilibrium was determined using Gibbs Free Energy minimisation. HSC Chemistry© also calculated the Gibbs Free Energy for individual reactions, allowing the feasibility of certain reactions at equilibrium to be determined. The initial gas composition studied for equilibrium was 10 ppm COS in Ar, then other gases were added at relevant concentrations, until all the major dry scrubbing gases had been considered.

Equilibrium was calculated both with and without alumina and several different phases of alumina were considered. Smelter-grade alumina is usually a mixture of $\alpha$-alumina, $\gamma$-alumina, other transition phases and more hydrated phases such as gibbsite (Al(OH)$_3$). The presence of phases like $\gamma$-alumina, contribute to the relatively high surface area of smelter-grade alumina. As well as high surface area, the other factor that increases the activity of the alumina is adsorbed water (surface hydroxyl groups). Due to this, a phase like gibbsite had to be considered, which is a fully hydrated phase of alumina.

Temperature was usually 80°C for equilibrium calculations (although it is specified for each equilibrium calculation) and pressure was always ambient. One variable was always selected for equilibrium calculations – this might be temperature, amount of alumina, or gas composition.
7.2 COS In Isolation

Firstly, the stability of COS was considered when no other species were present (other than inert gas). The calculations show that at equilibrium, COS is not stable, most of it breaking down into CO$_2$ gas and elemental S and C (see the equilibria in Figure 7.1 with increasing COS concentration and Figure 7.2 with increasing temperature). This was called the disproportionation reaction and since the Gibbs free energy for this reaction is negative, the products of the reaction are favoured at 80ºC:

$$2\text{COS (g)} \rightarrow \text{CO}_2 (g) + 2\text{S} + \text{C} \quad \Delta G (80^\circ\text{C}) = -27 \text{kJmol}^{-1} \text{ S} \quad (7.1)$$

![Figure 7.1: The equilibrium composition as COS concentration is increased (diluted in Ar) at 80ºC. Initial composition: [Ar] = 9.6 kmol, [COS] = 1E-06 – 1E-04 kmol (0.1 – 10 ppm), T = 0 – 100ºC.](image-url)
Figure 7.2: Equilibrium composition for S and C species between 0 and 100ºC, with the starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), T = 0 – 100ºC.

7.3 Influence of Alumina

Having seen how COS behaved in isolation, the effect of adding alumina was considered. Three different types of alumina were considered for the adsorption reaction: α- and γ-alumina were chosen because they are common phases in scrubber alumina, gibbsite (Al(OH)₃) was chosen to model adsorbed water on alumina.

7.3.1 α- and γ-Alumina

α- or γ-alumina do not affect equilibrium composition when either is added to COS and Ar gas. Once again, the disproportionation reaction (Reaction (7.1)) is favoured, forming elemental S and C and CO₂ gas at equilibrium. Varying temperature or the concentration of COS or alumina at 80ºC does not change the products formed at equilibrium (see Figure 7.1 and Figure 7.2). Subsequent results are only presented for α-alumina, since α- and γ-alumina behaved in the same way at equilibrium.
7.3.2 Gibbsite (Al(OH)$_3$)

The presence of gibbsite (Al(OH)$_3$) changes the equilibrium composition due to its adsorbed water content. At 80ºC, equal amounts of H$_2$S and CO$_2$ gas are stable at equilibrium as Figure 7.3 shows, so hydrolysis reactions (Reactions (7.2) and (7.3)) are favoured for this system. The hydrolysis reaction can be in the gas phase (Reaction (7.2)) or in the presence of gibbsite (Reaction (7.3)). The Gibbs energy change for both reactions shows that the reaction with gibbsite is slightly more favoured:

\[
\text{COS} (g) + \text{H}_2\text{O} (g) \rightarrow \text{CO}_2 (g) + \text{H}_2\text{S} (g)
\]

\[
\Delta G (80^\circ C) = -33 \text{ kJ mol}^{-1} \text{ S (or } -31 \text{ kJ mol}^{-1} \text{ if } \text{H}_2\text{O (l)}
\]

\[
3\text{COS} (g) + 2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{CO}_2 (g) + 3\text{H}_2\text{S} (g)
\]

\[
\Delta G (80^\circ C) = -39 \text{ kJ mol}^{-1} \text{ S}
\]

Figure 7.3: The S and C equilibrium composition when gibbsite is present for the starting components: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [Al(OH)$_3$] = 0.01 kmol (1 g), T = 0 – 100ºC.
7.3.3 Mixture of phases

Smelter-grade alumina is a mixture of phases, so equilibrium was calculated with about 1% gibbsite and the remainder 50% $\alpha$- and 50% $\gamma$-alumina. Interestingly, hydrolysis was not favoured at all temperatures, as shown in Figure 7.4. Complete hydrolysis occurs if no $\alpha$- or $\gamma$-alumina are present, and the quantities of gibbsite and COS are unchanged from Figure 7.4. The change in equilibrium in Figure 7.4 cannot be explained by the gibbsite breaking down into gaseous $\text{H}_2\text{O}$ and alumina, since this is less favoured at lower temperatures. Therefore it appears that at low temperatures, $\alpha$- and $\gamma$-alumina dominate the equilibrium resulting in disproportionation into elemental S (Reaction (7.1)) and above about 50ºC, gibbsite dominates, resulting in hydrolysis of COS into $\text{H}_2\text{S}$ (Reaction (7.3)). At dry scrubbing temperatures, hydrolysis would be expected to be the dominant reaction. When the gibbsite concentration is varied at 80ºC, hydrolysis is always favoured at equilibrium.

![Figure 7.4: The S and C equilibrium composition as temperature varies with the following starting components: $[\text{Ar}] = 9.6$ kmol, $[\text{COS}] = 1\text{E}-04$ kmol (10 ppm), $[\alpha-\text{Al}_2\text{O}_3] = 0.005$ kmol (0.5 g), $[\gamma-\text{Al}_2\text{O}_3] = 0.005$ kmol (0.5 g), $[\text{Al(OH)}_3] = 0.0001$ kmol (0.01 g), $T = 0 – 100$ºC.](image-url)
7.4 Addition of $\text{H}_2\text{O}$

$\text{H}_2\text{O}$ is present in the dry scrubber and is a reactant in gas phase hydrolysis, so it is important in determining the stable sulfur species at equilibrium. Figure 7.5 shows that when no alumina is present, COS hydrolysis into $\text{H}_2\text{S}$ is favoured at equilibrium above 0.0001 kmol $\text{H}_2\text{O}$ (the initial concentration of COS is also 0.0001 kmol). Below 0.0001 kmol $\text{H}_2\text{O}$, some disproportionation of COS into elemental S occurs. If $\alpha$-alumina is present, complete hydrolysis occurs above 0.00015 kmol $\text{H}_2\text{O}$ because a small amount of available water below 0.00015 kmol $\text{H}_2\text{O}$ is used to form small amounts of more hydrated alumina phases, such as $\text{AlOOH} (<0.0001\text{ kmol})$. However, generally $\alpha$-alumina does not change the equilibrium composition. If gibbsite is present ($\text{Al(OH)}_3$), hydrolysis of COS into $\text{H}_2\text{S}$ is always the favoured reaction.

Figure 7.5: The S and C equilibrium composition as $\text{H}_2\text{O}$ concentration increases and no alumina is present. Starting composition: $[\text{Ar}] = 9.6\text{ kmol}$, $[\text{COS}] = 1\text{E}-04\text{ kmol (10 ppm)}$, $[\text{H}_2\text{O}] = 1\text{E}-05 – 1\text{E}-03\text{ kmol}$, $T = 80^\circ\text{C}$. 
7.5 Addition of $O_2$

When anode gases are mixed with the induced air draft in the cell hood, they are exposed to large amounts of $O_2$. $O_2$ strongly affected the equilibrium composition, as shown in Figure 7.6. In the absence of alumina, oxidation of COS into $SO_2$ occurs in the $0.00005 – 0.0002$ kmol $O_2$ range, when $0.0001$ kmol of COS is initially present. Above $0.0002$ kmol (and up to $1.92$ kmol, or $20\%$ gas) $O_2$, oxidation to $SO_3$ is favoured at equilibrium. $CO_2$ is always the stable carbon species.

Reactions to form $SO_2$ and $SO_3$ included below show that although the formation of $SO_3$ and $CO_2$ are more favoured, the formation of $SO_2$ and/or $CO$ are also possible at $80^\circ C$ in the gas phase:

\[
\begin{align*}
COS_{(g)} + 1.5O_2_{(g)} &\rightarrow SO_2_{(g)} + CO_2_{(g)} \\
\Delta G (80^\circ C) &= -525 \text{ kJmol}^{-1} S \\
\text{COS}_{(g)} + O_2_{(g)} &\rightarrow CO_{(g)} + SO_2_{(g)} \\
\Delta G (80^\circ C) &= -272 \text{ kJmol}^{-1} S \\
\text{COS}_{(g)} + 2O_2_{(g)} &\rightarrow SO_3_{(g)} + CO_2_{(g)} \\
\Delta G (80^\circ C) &= -590 \text{ kJmol}^{-1} S \\
\text{COS}_{(g)} + 1.5O_2_{(g)} &\rightarrow CO_{(g)} + SO_3_{(g)} \\
\Delta G (80^\circ C) &= -338 \text{ kJmol}^{-1} S \\
2SO_2_{(g)} + O_2_{(g)} &= 2SO_3_{(g)} \\
\Delta G (80^\circ C) &= -66 \text{ kJmol}^{-1} S \\
2CO_{(g)} + O_2_{(g)} &= 2CO_2_{(g)} \\
\Delta G (80^\circ C) &= -252 \text{ kJmol}^{-1} C
\end{align*}
\]
Figure 7.6: C and S equilibrium composition when no alumina is present and O₂ concentration is increasing. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [O₂] = 1E-05 – 1E-03 kmol, T = 80°C.

When α-alumina (or γ-alumina) is present, as shown in Figure 7.7, aluminium sulfate (Al₂(SO₄)₃) is the stable sulfur species at equilibrium above 0.0002 kmol O₂. Several reactions could occur, although the formation of CO₂ and Al₂(SO₄)₃ is most favourable:

\[
3\text{COS}(g) + 6\text{O}_2(g) + \text{Al}_2\text{O}_3 \rightarrow 3\text{CO}_2(g) + \text{Al}_2(\text{SO}_4)_3
\]
\[\Delta G (80^\circ C) = -715 \text{ kJ mol}^{-1} \text{ S} \quad (7.10)\]

\[
3\text{COS}(g) + 4.5\text{O}_2(g) + \text{Al}_2\text{O}_3 \rightarrow 3\text{CO}(g) + \text{Al}_2(\text{SO}_4)_3
\]
\[\Delta G (80^\circ C) = -462 \text{ kJ mol}^{-1} \text{ S} \quad (7.11)\]

\[
3\text{SO}_2(g) + \text{Al}_2\text{O}_3 + 1.5\text{O}_2(g) \rightarrow \text{Al}_2(\text{SO}_4)_3
\]
\[\Delta G (80^\circ C) = -190 \text{ kJ mol}^{-1} \text{ S} \quad (7.12)\]
Figure 7.7: The S and C equilibrium composition when α-alumina is present and O₂ concentration increases. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [O₂] = 1E-05 – 1E-03 kmol, [α-Al₂O₃] = 0.01 kmol (1 g), T = 80°C.

If gibbsite is present instead of α-alumina, as shown in Figure 7.8, COS hydrolysis into H₂S is predictably favoured below 0.00005 kmol O₂. At higher O₂ concentrations, the equilibrium is the same as for α-alumina, forming SO₂ and then Al₂(SO₄)₃.

Reactions to form Al₂(SO₄)₃ from gibbsite are more favourable than hydrolysis or oxidation occurring from any other initial composition:

\[
3\text{COS}_\text{(g)} + 6\text{O}_2\text{(g)} + 2\text{Al(OH)}_3 \rightarrow 3\text{CO}_2\text{(g)} + \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}_\text{(g)}
\]  \hspace{1cm} (7.13)  \(\Delta G (80^\circ C) = -720 \text{ kJmol}^{-1} \text{ S}\)

\[
3\text{COS}_\text{(g)} + 4.5\text{O}_2\text{(g)} + 2\text{Al(OH)}_3 = 3\text{CO}_\text{(g)} + \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}_\text{(g)}
\]  \hspace{1cm} (7.14)  \(\Delta G (80^\circ C) = -468 \text{ kJmol}^{-1} \text{ S}\)
The formation of $\text{Al}_2(\text{SO}_4)_3\cdot6\text{H}_2\text{O}$ is also very favourable, although this does not appear as a stable species at equilibrium in Figure 7.8, perhaps because COS is the limiting reactant:

\[
\text{6COS} \ (g) + 12\text{O}_2 \ (g) + 4\text{Al(OH)}_3 \rightarrow 6\text{CO}_2 \ (g) + \text{Al}_2(\text{SO}_4)_3 + \text{Al}_2(\text{SO}_4)_3\cdot6\text{H}_2\text{O} \quad \text{(7.15)}
\]

\[
\Delta G \ (80^\circ \text{C}) = -737 \text{ kJmol}^{-1} \ S
\]

\[
\text{6COS} \ (g) + 9\text{O}_2 \ (g) + 4\text{Al(OH)}_3 \rightarrow 6\text{CO} \ (g) + \text{Al}_2(\text{SO}_4)_3 + \text{Al}_2(\text{SO}_4)_3\cdot6\text{H}_2\text{O} \quad \text{(7.16)}
\]

\[
\Delta G \ (80^\circ \text{C}) = -484 \text{ kJmol}^{-1} \ S
\]

\[
2\text{Al(OH)}_3 + 6\text{O}_2 \ (g) + 3\text{H}_2\text{O} \ (g) + 3\text{COS} \ (g) \rightarrow \text{Al}_2(\text{SO}_4)_3\cdot6\text{H}_2\text{O} + 3\text{CO}_2 \ (g) \quad \text{(7.17)}
\]

\[
\Delta G \ (80^\circ \text{C}) = -754 \text{ kJmol}^{-1} \ S
\]
7.5.1 $H_2O / O_2$

When $H_2O$ is present in levels sufficient for complete hydrolysis of COS, the concentration of $O_2$ determines the stable sulfur species at equilibrium in the absence of alumina, as shown in Figure 7.9. $H_2S$ is stable below $0.00005 \text{ kmol O}_2$, elemental S forms up to $0.00015 \text{ kmol O}_2$ and $SO_2$ forms between $0.00005 – 0.0002 \text{ kmol O}_2$. Above $0.0002 \text{ kmol O}_2$, a mixture of $H_2SO_4$ and $SO_3$ gases are stable at equilibrium. Adding further $H_2O$ has no effect on equilibrium, since excess $H_2O$ is stable at equilibrium. $H_2SO_4$ formation occurs by the following reaction:

$$\text{COS} (\text{g}) + H_2O (\text{g}) + O_2 (\text{g}) \rightarrow H_2SO_4 (\text{g}) + CO_2 (\text{g})$$  \hspace{1cm} (7.18)

$\Delta G (80^\circ C) = -636 \text{ kJmol}^{-1} \text{ S}$

![Equilibrium Composition Diagram](image)

Figure 7.9: The S and C equilibrium composition when no alumina is present. Starting composition: $[Ar] = 9.6 \text{ kmol}$, $[COS] = 1E-04 \text{ kmol (10 ppm)}$, $[H_2O] = 2E-04 \text{ kmol}$, $[O_2] = 1E-05 – 1E-03 \text{ kmol}$, $T = 80^\circ C$. 
When $\alpha$-alumina is added, the same reactions occur at low $O_2$ concentrations, but $Al_2(SO_4)_3$ is favoured over $H_2SO_4$ and $SO_3$ at higher $O_2$ concentrations (see Figure 7.10). The presence of gibbsite results in a similar equilibrium composition to the one with $\alpha$-alumina.

![Figure 7.10: The S and C equilibrium composition when $H_2O$ and $\alpha$-alumina are present and $O_2$ concentration is increasing. Starting composition: $[Ar] = 9.6$ kmol, $[COS] = 1E-04$ kmol (10 ppm), $[H_2O] = 2E-04$ kmol, $[O_2] = 1E-05 – 1E-03$ kmol, $[\alpha-Al_2O_3] = 0.01$ kmol, $T = 80^\circ C$.](image-url)
7.6 Addition of CO$_2$

CO$_2$ is the major species present in anode gas, but is still present in significant quantities entering the dry scrubber (after dilution with air). As CO$_2$ concentration increases to 40 mol% in the absence of alumina, disproportionation of COS into elemental S is initially favoured (see Figure 7.11). COS becomes completely stable above about 0.5 kmol of CO$_2$ (about 5% of total gas). This explains why COS is the dominant sulfur gas to form at the anode, but is less stable on leaving the cell. The presence of $\alpha$-alumina has no effect on equilibrium, but the presence of gibbsite leads to complete hydrolysis of COS at all CO$_2$ concentrations. The following reactions demonstrate how COS is stable at 80ºC:

$$\text{COS} (g) + 2\text{CO}_2 (g) \rightarrow 3\text{CO} (g) + \text{SO}_2 (g) \quad \Delta G (80^\circ C) = 233 \text{kJmol}^{-1} \text{S} \quad (7.19)$$

$$\text{CS}_2 (g) + \text{CO}_2 (g) \rightarrow 2\text{COS} (g) \quad \Delta G (80^\circ C) = -2 \text{kJmol}^{-1} \text{S} \quad (7.20)$$

![Figure 7.11: The S and C equilibrium composition (excluding CO$_2$) as CO$_2$ concentration increases. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol, [CO$_2$] = 0.0384 – 3.84 kmol, T = 80°C.](image-url)
7.6.1 $H_2O / CO_2$

In the absence of alumina, with enough $H_2O$ present to enable complete hydrolysis of COS and an increasing level of $CO_2$, Figure 7.12 shows that $H_2S$ is the major sulfur species at equilibrium up to 0.01 kmol $CO_2$. Some formation of elemental $S$ occurs up to 0.5 kmol $CO_2$, but COS is major stable sulfur species above 0.3 kmol.

![Figure 7.12: The S equilibrium composition at 80ºC when $H_2O$ is present and $CO_2$ concentration is increasing. Starting composition: $[Ar] = 9.6$ kmol, $[COS] = 1E-04$ kmol (10 ppm), $[H_2O] = 2E-04$ kmol, $[CO_2] = 1E-06 – 5$ kmol, $T = 80$ºC.](image-url)
7.7 Addition of CO

CO is another important anode gas, but Figure 7.13 shows that it doesn’t change the equilibrium composition when it is present in the absence of alumina, with COS disproportionating into elemental S. α-alumina does not affect this equilibrium composition, but the presence of gibbsite leads to complete hydrolysis of COS. Possible reactions involving CO include:

\[
\text{COS (g) + CO (g) } \rightarrow \text{CO}_2 (g) + S + C \quad \Delta G (80^\circ \text{C}) = -82 \text{ kJmol}^{-1} \text{ S} \quad (7.21)
\]

\[
S + CO (g) \rightarrow \text{COS (g)} \quad \Delta G (80^\circ \text{C}) = -28 \text{ kJmol}^{-1} \text{ S} \quad (7.22)
\]

Figure 7.13: The S and C equilibrium composition with varying CO concentration when no alumina is present at 80°C. Starting composition: $[\text{Ar}] = 9.6 \text{ kmol}$, $[\text{COS}] = 1E-04 \text{ kmol (10 ppm)}$, $[\text{CO}] = 1E-05 – 1E-03 \text{ kmol}$, $T = 80^\circ \text{C}$. 
7.7.1 H₂O / CO

In the presence of H₂O and increasing CO, Figure 7.14 shows that COS hydrolysis into H₂S is favoured below 0.002 kmol CO and above this CO concentration, disproportionation into elemental S is favoured.

Figure 7.14: S Composition at equilibrium when H₂O is present and CO concentration is increasing. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [H₂O] = 2E-04 kmol, [CO] = 1E-04 – 1E-02 kmol, T = 80°C.
7.7.2 Changing CO₂ / CO Ratio

The ratio of CO₂ to CO can change at the anode depending on the operation of the cell. In the absence of alumina, elemental S was the favoured sulfur species at equilibrium with a changing CO₂ to CO ratio (as shown in Figure 7.15) at all but very high CO₂/CO ratios, where COS was stable.

![Figure 7.15: S equilibrium composition as the CO₂/CO ratio changes from 100% CO₂ to equal quantities of CO₂ and CO. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [CO₂] = 6 – 3 kmol, [CO] = 0 – 3 kmol, T = 80°C.](image-url)
7.8 Addition of SO$_2$

SO$_2$ is usually the major sulfur gas entering the dry scrubber [5]. It can be adsorbed on alumina, but is not usually removed to a significant extent due to competitive adsorption of HF [21]. The equilibrium composition in Figure 7.16 shows that as SO$_2$ concentration increases in the absence of alumina, COS has most likely reacted to form elemental S. When $\alpha$-alumina is present, SO$_2$, elemental S and Al$_2$(SO$_4$)$_3$ are all stable at equilibrium, but it is difficult to determine which of these species formed from COS (Figure 7.17). Hydrolysis to H$_2$S occurs at low SO$_2$ concentrations with gibbsite, but the stable equilibrium species become SO$_2$, elemental S and Al$_2$(SO$_4$)$_3$ as SO$_2$ levels increase Figure 7.18. The stability of SO$_2$ is reduced in the presence of gibbsite, but is least stable in the presence of $\alpha$-alumina.

![Figure 7.16: S and C equilibrium composition with increasing SO$_2$ concentration. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [SO$_2$] = 1E-05 – 1E-03 kmol, T = 80°C.](image)
Figure 7.17: S and C equilibrium composition for SO\(_2\) concentrations up to 0.001 kmol. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [SO\(_2\)] = 1E-05 – 1E-03 kmol, [\(\alpha\)-Al\(_2\)O\(_3\)] = 0.01 kmol (1 g), T = 80°C.

Figure 7.18: S and C equilibrium composition in the presence of gibbsite, with SO\(_2\) concentration increasing up to 0.001 kmol. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [SO\(_2\)] = 1E-05 – 1E-03 kmol, [Al(OH)\(_3\)] = 0.01 kmol (1 g), T = 80°C.
7.8.1 $H_2O/ SO_2$

When $H_2O$ and $SO_2$ are present, COS hydrolysis into $H_2S$ only occurs below 0.00005 kmol $SO_2$, then disproportionation is favoured, forming elemental $S$ (see Figure 7.19). When $\alpha$-alumina or gibbsite is added, some $Al_2(SO_4)_3$ forms at equilibrium in addition to the other species (see Figure 7.20 for $\alpha$-alumina). $SO_2$ is most stable in the absence of alumina and less stable in the presence of $\alpha$-alumina than gibbsite.

Figure 7.19: $S$ and $C$ equilibrium composition when $SO_2$ concentration is changing and $H_2O$ is present. Starting composition: $[Ar] = 9.6$ kmol, $[COS] = 1E-04$ kmol (10 ppm), $[H_2O] = 2E-04$ kmol, $[SO_2] = 1E-05 - 1E-03$ kmol, $T = 80^\circ C$. 
Figure 7.20: S and C equilibrium composition when H₂O is present and SO₂ concentration is changing. Starting composition: [Ar] = 9.6 kmol, [COS] = 1E-04 kmol (10 ppm), [H₂O] = 2E-04 kmol, [SO₂] = 1E-05 – 1E-03 kmol, [α-Al₂O₃] = 0.01 kmol, T = 80ºC.

7.9 Addition of Other Smelter Gases

H₂S and CS₂: H₂S and CS₂ are other sulfur gases that can be present in small concentrations entering the dry scrubber and H₂S is also the product of COS hydrolysis. H₂S is stable at equilibrium and when it is present, COS disproportionates into elemental S. This equilibrium composition is unchanged in the presence of α-alumina, but COS hydrolysis into H₂S still occurs in the presence of gibbsite. CS₂ behaves in a similar way at equilibrium to COS – in the absence of alumina or the presence of α-alumina, disproportionation of COS and CS₂ occurs to form elemental S. In the presence of gibbsite, hydrolysis of COS and CS₂ leads to the formation of H₂S at equilibrium.

HF and H₂: HF does not change the equilibrium composition with respect to COS. In the presence of H₂, COS is hydrolysed to form H₂S at equilibrium. The following reaction between H₂ and COS is possible:
\[
\text{COS}_2(g) + \text{H}_2(g) \rightarrow \text{H}_2\text{S}_2(g) + \text{CO}_2(g) \quad \Delta G (80^\circ C) = -7.131 \text{ kJmol}^{-1} S \quad (7.23)
\]

### 7.10 Addition of Air

An induced air draft leaving the smelting cell dilutes the anodes gases significantly and is believed to lead to oxidation of the majority COS into SO\(_2\) [4]. As the concentration of dry air increases in the presence of COS, COS becomes increasingly oxidised into SO\(_2\) and then SO\(_3\) gas, as shown in Figure 7.21. So, the effect of adding dry air is the same as the effect of pure O\(_2\) gas. Likewise, when \(\alpha\)-alumina or gibbsite is present, Al\(_2\)(SO\(_4\))\(_3\) forms instead of SO\(_3\) gas.

![Figure 7.21: S and C equilibrium composition as air concentration increases. Starting composition: [Ar] = 9.6 – 9.595 kmol, [CH\(_4\)] = 1.71E-10 – 8.54E-09 kmol, [CO\(_2\)] = 3.52E-08 – 1.76E-06 kmol, [COS] = 9.76E-05 kmol, [He] = 5.13E-10 – 2.57E-08 kmol, [Kr] = 1.10E-10 – 5.50E-09 kmol, [N\(_2\)] = 7.63E-05 – 3.82E-03 kmol, [Ne] = 1.78E-09 – 8.90E-08 kmol, [O\(_2\)] = 2.05E-05 – 1.03E-03 kmol, T = 80^\circ C.](image-url)
7.11 Stability of Dry Scrubbing Gas

Having individually considered the effect common dry scrubbing gases might have on COS, calculations were performed to see how the complete dry scrubbing system behaved at equilibrium. Gibbsite was the only alumina phase considered for these equilibrium calculations, since it usually affected COS stability more than α- or γ-alumina at equilibrium. Typical values of inlet dry scrubber gas composition were supplied by ALSTOM Power and used for equilibrium calculations of the complete dry scrubber system. The mid-points in the ranges given below were used for calculations:

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</tr>
<tr>
<td>N₂</td>
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</tr>
<tr>
<td>H₂O</td>
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<tr>
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<tr>
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<td>[SO₂] = 0.0079 m³</td>
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<tr>
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</tr>
<tr>
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<td>100 m³</td>
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<td></td>
</tr>
</tbody>
</table>

Figure 7.22: S and C equilibrium composition in the temperature range 80 – 130°C. Initial composition: [O₂] = 19 m³, [N₂] = 77 m³, [H₂O] = 2 m³, [CO₂] = 0.75 m³, [CO] = 0.075 m³, [SO₂] = 0.0079 m³, [HF] = 0.0336 m³, [COS] = 0.00035 m³, [Ar] = 1.133 m³, Total Gas = 100 m³, T = 80 – 130 ºC.
With no alumina present and a temperature range of 80°C – 130°C, equilibrium results in Figure 7.22 show that the dominant sulfur species is $\text{H}_2\text{SO}_4\cdot3\text{H}_2\text{O}$ at lower temperatures and $\text{H}_2\text{SO}_4$ gas at higher temperatures, formed by oxidation reactions with either COS or SO$_2$. CO$_2$ is the stable carbon species and HF the stable fluorine species at equilibrium. A transition occurs at about 104°C and beyond this temperature all species at equilibrium are gaseous.

Reactions (7.24) – (7.29) were proposed for COS reacting to form the sulfur species that are present at equilibrium and the change in Gibbs Free Energy for each of these reactions was calculated between 80°C and 130°C. From these calculations, the most favourable reaction for COS is the formation of $\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}$ at all temperatures (Reaction (7.24)).

\[
\begin{align*}
\text{COS} \ (g) + \text{H}_2\text{O} \ (g) + 2\text{O}_2 \ (g) & \rightarrow \text{H}_2\text{SO}_4 \ (g) + \text{CO}_2 \ (g) \\
\Delta G \ (80^\circ\text{C}) &= -636 \text{ kJmol}^{-1} \text{ S}, \quad \Delta G \ (105^\circ\text{C}) = -628 \text{ kJmol}^{-1} \text{ S}, \\
\Delta G \ (130^\circ\text{C}) &= -620 \text{ kJmol}^{-1} \text{ S} \\
\text{COS} \ (g) + 4\text{H}_2\text{O} \ (g) + 2\text{O}_2 \ (g) & \rightarrow \text{H}_2\text{SO}_4\cdot3\text{H}_2\text{O} + \text{CO}_2 \ (g) \\
\Delta G \ (80^\circ\text{C}) &= -713 \text{ kJmol}^{-1} \text{ S}, \quad \Delta G \ (105^\circ\text{C}) = -692 \text{ kJmol}^{-1} \text{ S}, \\
\Delta G \ (130^\circ\text{C}) &= -672 \text{ kJmol}^{-1} \text{ S} \\
\text{COS} \ (g) + 5\text{H}_2\text{O} \ (g) + 2\text{O}_2 \ (g) & \rightarrow \text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O} + \text{CO}_2 \ (g) \\
\Delta G \ (80^\circ\text{C}) &= -720 \text{ kJmol}^{-1} \text{ S}, \quad \Delta G \ (105^\circ\text{C}) = -696 \text{ kJmol}^{-1} \text{ S}, \\
\Delta G \ (130^\circ\text{C}) &= -674 \text{ kJmol}^{-1} \text{ S} \\
\text{COS} \ (g) + \text{H}_2\text{O} \ (g) + 2\text{O}_2 \ (g) & \rightarrow \text{H}_2\text{SO}_4 + \text{CO}_2 \ (g) \\
\Delta G \ (80^\circ\text{C}) &= -665 \text{ kJmol}^{-1} \text{ S}, \quad \Delta G \ (105^\circ\text{C}) = -654 \text{ kJmol}^{-1} \text{ S}, \\
\Delta G \ (130^\circ\text{C}) &= -643 \text{ kJmol}^{-1} \text{ S} \\
\text{COS} \ (g) + 2\text{O}_2 \ (g) & \rightarrow \text{SO}_3 \ (g) + \text{CO}_2 \ (g) \\
\Delta G \ (80^\circ\text{C}) &= -590 \text{ kJmol}^{-1} \text{ S}, \quad \Delta G \ (105^\circ\text{C}) = -586 \text{ kJmol}^{-1} \text{ S}, \\
\Delta G \ (130^\circ\text{C}) &= -582 \text{ kJmol}^{-1} \text{ S} \\
\text{COS} \ (g) + 2\text{O}_2 \ (g) + \text{HF} \ (g) & \rightarrow \text{HSO}_3\text{F} \ (g) + \text{CO}_2 \ (g) \\
\Delta G \ (80^\circ\text{C}) &= -628 \text{ kJmol}^{-1} \text{ S}, \quad \Delta G \ (105^\circ\text{C}) = -620 \text{ kJmol}^{-1} \text{ S}, \\
\Delta G \ (130^\circ\text{C}) &= -613 \text{ kJmol}^{-1} \text{ S}
\end{align*}
\]
When gibbsite is added to the dry scrubbing gas and temperature is varied, \( \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} \) is always the favoured sulfur species in the temperature range 80 – 130°C. Two reactions (Reactions (7.30) and (7.31)) were proposed for COS and of these the formation of \( \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} \) from COS in the presence of gibbsite (Reaction (7.30)) is most favoured in the relevant temperature range.

\[
\begin{align*}
3\text{H}_2\text{O} (g) + 6\text{O}_2 (g) + 3\text{COS} (g) + 2\text{Al(OH)}_3 & \rightarrow \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} + 3\text{CO}_2 (g) & (7.30) \\
\Delta G (80^\circ\text{C}) &= -754 \text{ kJmol}^{-1} \text{ S, } \Delta G (105^\circ\text{C}) = -741 \text{ kJmol}^{-1} \text{ S, } \\
\Delta G (130^\circ\text{C}) &= -729 \text{ kJmol}^{-1} \text{ S} \\
6\text{O}_2 (g) + 3\text{COS} (g) + 2\text{Al(OH)}_3 & \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{CO}_2 (g) + 3\text{H}_2\text{O} (g) & (7.31) \\
\Delta G (80^\circ\text{C}) &= -720 \text{ kJmol}^{-1} \text{ S, } \Delta G (105^\circ\text{C}) = -715 \text{ kJmol}^{-1} \text{ S, } \\
\Delta G (130^\circ\text{C}) &= -710 \text{ kJmol}^{-1} \text{ S}
\end{align*}
\]

After varying temperature with and without gibbsite, the gas composition was altered by changing various species one at a time:

**Varying \([\text{Al(OH)}_3]\):** At all but very low gibbsite concentrations at 105°C, \( \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} \) is the most stable sulfur species at equilibrium. Below about 0.0002 kmol (0.016 kg) of Al(OH)\(_3\), the dominant species is H\(_2\)SO\(_4\) gas. Below 0.0005 kmol (0.039 kg) of Al(OH)\(_3\), HF is the stable fluorine species, then AlF\(_3\) is favoured at equilibrium. CO\(_2\) gas is stable at all Al(OH)\(_3\) concentrations.

**Varying \([\text{H}_2\text{O}]\):** Without alumina and below 0.10 kmol H\(_2\)O (3.1 m\(^3\)), H\(_2\)SO\(_4\) gas is the favoured sulfur species at equilibrium. Above 0.10 kmol H\(_2\)O, more hydrated sulfur species such as H\(_2\)SO\(_4\)\(_3\)H\(_2\)O and H\(_2\)SO\(_4\) gas are stable. Carbon and fluorine species are not affected by changing H\(_2\)O concentration. When gibbsite is present and as the H\(_2\)O concentration changes, \( \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} \) is always the stable sulfur phase at equilibrium.

**Varying \([\text{SO}_2]\):** As SO\(_2\) concentration increases with no alumina present, H\(_2\)SO\(_4\) gas is always the most stable sulfur species. When gibbsite is present, the stable sulfur phase is \( \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O} \).
7.12 Summary

A summary table of the important thermodynamic results from this chapter is shown in Table 7.1. Thermodynamic calculations showed that COS was generally not stable at equilibrium at a typical dry scrubbing temperature of 80ºC. This is not unexpected, since smelter measurements of COS concentration leaving the anode and entering the dry scrubber described in Section 2.4, suggested that COS became unstable on leaving the smelting cell. However, these smelter measurements also showed that some COS did survive into the dry scrubber, highlighting the importance of kinetics, as well as thermodynamics, in predicting the stability of COS in the smelter. The thermodynamics generally showed that COS would be oxidised in the gas phase in the presence of O, and this is borne out by smelter measurements, which show that COS is largely oxidised in the gas ducting to SO₂.

Table 7.1: Summary of thermodynamic results, with respect to COS stability at equilibrium under different conditions typical of a dry scrubber at 80ºC.

<table>
<thead>
<tr>
<th>Species Present</th>
<th>Stability of COS</th>
</tr>
</thead>
<tbody>
<tr>
<td>COS, Ar</td>
<td>Disproportionates into S, C and CO₂</td>
</tr>
<tr>
<td>COS, Ar, α- or γ-alumina</td>
<td>Disproportionates into S, C and CO₂</td>
</tr>
<tr>
<td>COS, Ar, gibbsite</td>
<td>Hydrolyses into H₂S and CO₂</td>
</tr>
<tr>
<td>COS, Ar, H₂O</td>
<td>Hydrolyses into H₂S and CO₂</td>
</tr>
<tr>
<td>COS, Ar, O₂, α-alumina</td>
<td>Oxidised into SO₂ or SO₃ (depends on O₂ concentration)</td>
</tr>
<tr>
<td>COS, Ar, O₂, gibbsite</td>
<td>Oxidised into SO₂ or Al₂(SO₄)₃ (depends on O₂ concentration)</td>
</tr>
<tr>
<td>COS, Ar, O₂, H₂O</td>
<td>Oxidised into SO₂ or Al₂(SO₄)₃ (depends on O₂ concentration)</td>
</tr>
<tr>
<td>COS, Ar, O₂, H₂O, α-alumina or gibbsite</td>
<td>Oxidised into SO₂ or Al₂(SO₄)₃ (depends on O₂ concentration)</td>
</tr>
<tr>
<td>COS, Ar, CO</td>
<td>Stable species H₂S, SO₂ or H₂SO₄ (depends on O₂ concentration)</td>
</tr>
<tr>
<td>COS, Ar, CO₂, H₂O</td>
<td>Stable species H₂S or COS (depends on CO₂ concentration)</td>
</tr>
<tr>
<td>COS, Ar, CO</td>
<td>Disproportionates into S, C and CO₂</td>
</tr>
<tr>
<td>COS, Ar, CO₂, H₂O</td>
<td>Stable species H₂S or S (depends on CO₂ concentration)</td>
</tr>
<tr>
<td>COS, Ar, CO₂, CO</td>
<td>Stable species COS or S (depends on CO₂/CO ratio)</td>
</tr>
<tr>
<td>COS, Ar, SO₂</td>
<td>Stable species SO₂</td>
</tr>
<tr>
<td>COS, Ar, SO₂, H₂O</td>
<td>Stable species H₂S or SO₂ (depends on SO₂ concentration)</td>
</tr>
<tr>
<td>COS in typical smelting duct gases</td>
<td>Stable species H₂SO₄*xH₂O</td>
</tr>
<tr>
<td>COS in dry scrubber (with gibbsite)</td>
<td>Stable species Al₂(SO₄)₃*xH₂O</td>
</tr>
</tbody>
</table>
The thermodynamic results also show the importance of humidity on the thermodynamic stability of COS, which could be crucial to determining the overall COS emissions in a smelter, due to seasonal variations in humidity levels. Thermodynamic calculations show that this strong influence of humidity could also have an impact in the dry scrubber, where adsorbed water on the scrubbing alumina could determine the extent of any COS conversion.

There are three important reactions found from the thermodynamic calculations using HSC Chemistry computer package:

1. The disproportionation reaction breaks COS into elemental sulfur, elemental carbon and CO₂ gas and is favourable at 80°C (Reaction (7.1)). This equilibrium reaction occurs:
   a. With a COS – argon mixture
   b. When additional CO is present (in the absence of gibbsite)
   c. At low CO₂ concentrations (in the absence of gibbsite), but as CO₂ concentration increases COS is stable at equilibrium.

2. The hydrolysis reaction forms H₂S and CO₂ from COS and H₂O (or gibbsite) and is also favourable at 80°C (Reactions (7.2) and (7.3)). This equilibrium reaction occurs:
   a. Provided enough H₂O is present, in the absence of reactants such as O₂
   b. If gibbsite is present, due to the water contained in gibbsite.

3. Several different oxidation reactions also occur commonly, forming CO₂ and SO₂ (Reaction (7.4)), SO₃ (Reaction (7.6)), Al₂(SO₄)₃ (Reaction (7.10) and (7.13)) and Al₂(SO₄)₃•6H₂O (Reaction (7.15)), depending on whether alumina is present or not.
   a. The presence of O₂ alone results in SO₂ or SO₃ to form depending on the initial O₂ concentration
   b. When α- or γ-alumina is present, Al₂(SO₄)₃ forms at equilibrium
   c. The presence of gibbsite causes a mixture of Al₂(SO₄)₃ and Al₂(SO₄)₃•6H₂O to form.

The thermodynamics of the sulfur gas species at dry scrubbing (low) temperatures are quite different from the thermodynamics at high temperatures as the gas leaves the anode in the
cell. In the dry scrubber, the presence of H₂O or hydrated alumina (e.g. Al(OH)₃, gibbsite),favours H₂S and H₂SO₄ formation from COS. The presence of O₂ favours SO₂, SO₃ andaluminium sulfates at equilibrium. COS is not stable even on its own, decomposing into S and CO₂ at equilibrium.
Chapter 8  EXPERIMENTAL METHODS USED FOR COS/ALUMINA STUDIES

Two major experimental methods were used to study the interaction between COS gas and smelter-grade alumina. The first was a fluidised bed reactor connected to a mass spectrometer and the second a heatable DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) cell containing alumina. Both methods are described in this chapter. The aluminas tested during these experiments are also fully characterised.
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8.1 Introduction

Two major sets of experiments were performed to determine the behaviour of COS on smelter-grade alumina. One set of experiments was performed in a fluidised bed reactor, where the gases were analysed by mass spectrometry before and after the reactor. While this was a successful way of determining changes in gas composition, it provided no direct evidence of the interaction between COS and alumina, because the reaction products formed at the alumina surface were not stable outside of the reactor. The second set of experiments, using DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy), analysed the adsorbed species on the alumina surface in a fixed alumina bed, after exposure to COS and other gases.

In addition to studying the COS/alumina interaction, the behaviour of SO₂ and H₂S on alumina were also investigated, since they are the other major sulfur gases to enter the aluminium smelter dry scrubber (see Chapter 2). A number of different gas compositions were investigated to study the effect of SO₂, H₂O, HF, O₂ and CO₂ on the COS/alumina system. As well as varying gas composition, the type of alumina used in experiments was also studied. In addition to primary smelter-grade alumina, secondary smelter-grade alumina, laboratory-fluorinated smelter grade alumina, impurity doped aluminas (doped with Na, Fe and Ca) and catalyst γ-alumina were considered.

8.2 Fluidised Bed Studies

For the fluidised bed reactor studies, a specific gas composition diluted in Ar at a total flow rate of 0.4 Lmin⁻¹ was passed through a 15 mm diameter fluidised bed reactor containing 0.5 g of alumina. The gas composition was controlled using mass flow controllers and could be monitored at the reactor inlet and outlet using a mass spectrometer, which was calibrated for COS, SO₂ and H₂S gases.

In on-site smelter measurements, COS concentrations are about 4000 ppm at the face of the anode and about 5 ppm entering the dry scrubber [4]. COS concentrations of 50 – 240 ppmv
were used in the fluidised bed experiments, which were high enough to ensure detection in the mass spectrometer and low enough to minimise safety risks.

Temperature was maintained at 80°C in the reactor and most of the gas tubing by enclosing the system in an oven and using heating cords on exposed tubing. Gases were preheated in tubing coils in the oven before entering the reactor. For H₂O experiments, the temperature throughout the apparatus was increased to 100°C to prevent condensation. Pressure throughout the apparatus was ambient and a pressure relief valve was installed in case of reactor blockage due to alumina fines. The layout of the apparatus is shown in Figure 8.1.

H₂S was compatible with most materials of construction in the temperature range used, but SO₂ was incompatible with aluminium, manganese and chromium [126], COS was suspected to react with stainless steel according to one report [36] and all sulfur gases were more corrosive when wet. Therefore, due to the corrosive nature of sulfur gases and HF, Teflon (PTFE) was used for all tubing and most valves that were exposed to these gases. However, two valves on the COS line were aluminium (which has acceptable compatibility [126]) and mass flow controllers and much of the mass spectrometer itself were stainless steel.

### 8.2.1 Gases Used

All gases used for adsorption experiments were supplied by BOC Gases. COS, H₂S and SO₂ were usually supplied at nominally 200 ppm in Ar. BOC tested these mixtures to ensure stability for eight weeks after preparation and before delivery. High purity special gas regulators were used to control addition of each gas to the apparatus. CO₂ and O₂ were supplied at 5% diluted in Ar. Additional Ar was used as a dilutant in the adsorption experiments and this was supplied as Zero Grade Ar.
Figure 8.1: Layout of the experimental apparatus used for fluidised bed reactor/mass spectrometer studies.
COS, SO₂ and H₂S are all poisonous gases causing respiratory paralysis in high enough levels [127-130]. The workplace short term exposure limit for SO₂ is 5 ppm (14 (mg)m⁻³). The maximum recommended concentration of H₂S is 10 ppm (14 (mg)m⁻³) for 10 minutes [126, 131, 132]. While safe working limits for COS have never been determined, its toxic mechanism is to break down into H₂S in the body [133], so working limits for H₂S were followed. All gases in the apparatus were contained in tubing (which was routinely leak tested) before disposal in the fume cupboard using alcoholic KOH solution (or deionised water was used if HF was present). Sulfur gases were supplied diluted in Ar or N₂, with a maximum concentration of 240 ppm.

### 8.2.2 Fluidised Bed Reactor Design

![Schematic of the fluidised bed reactor](image)

The fluidised bed reactor used for experiments was based on a design described in [134]. A schematic of this design is shown in Figure 8.2. Conditions in the fluidised bed had to be selected to ensure effective fluidisation of the alumina in the reactor. Figure 8.3 shows that
theoretically, as superficial velocity (velocity of the gas) increases, the pressure drop across the bed ($\Delta p$) should become constant once fluidisation has been reached. Thereafter, the bed height, $L$, should increase linearly with increasing superficial velocity. Bed height and pressure drop can vary depending on whether superficial velocity is increasing or decreasing.

![Diagram showing relationship between bed height, pressure drop, and superficial velocity](image)

**Figure 8.3: Bed height and pressure drop versus superficial velocity for a bed of solids [135].**

To study fluidisation, a second reactor was made of transparent acrylic tubing (identical-sized to the one in Figure 8.2), so that the fluidised bed could be observed over a variety of conditions. Ar gas of increasing velocity ($0 – 0.325$ m s$^{-1}$ or $0 – 2.5$ L min$^{-1}$) was passed through a bed containing $0.5 – 2$ g smelter-grade alumina, then the final bed height was measured. Pressure drop across the reactor was measured using a water manometer and total pressure using a pressure gauge.

The linear change in bed height with superficial velocity, in Figure 8.4, shows that fluidisation was reached at very low gas velocities ($0.3$ L min$^{-1}$) when $0.5$ g alumina was present in the reactor. Although total pressure was always close to atmospheric, pressure drop was observed to increase by $3$ kPa with increasing superficial velocity (Figure 8.5), contrary to theory (Figure 8.3). It was concluded that pressure drop was very small over the superficial velocities studied and the bed height measurements were then used to ensure fluidisation conditions. Since a limited amount of gas supply was available, $0.5$ g alumina and a gas flow rate of $0.4$ L min$^{-1}$ were chosen for future fluidised bed experiments.
Figure 8.4: Measurements of alumina bed height versus Ar gas velocity.

Figure 8.5: Pressure drop versus gas velocity for fluidised bed containing 0.5 g alumina.
8.2.3 \( \text{H}_2\text{O} \) and HF Experiments

\( \text{H}_2\text{O} \) was injected into a PTFE mixing tee to provide controlled levels of humidity to the gas, using a syringe pump fitted with a 30 mL syringe and a 25 gauge needle. A one metre heating coil ensured the \( \text{H}_2\text{O} \) injected was vaporised before entering the reactor. Calibration of the syringe pump is shown in Figure 8.6. Relative humidities used for experiments were usually 4 \%RH (0.2 mLhr\(^{-1}\) pumping rate) or 16 \%RH (1.0 mLhr\(^{-1}\)).

![30 mL Syringe Pump Calibration 3/00](image)

**Figure 8.6: The syringe pump calibration.**

For addition of HF solution, a “needle” made out of PTFE with an internal diameter of 1 mm was connected to a PTFE tee, allowing mixing with the gas flow. For HF gas experiments, a 10.6 gL\(^{-1}\) HF solution was pumped at 0.2 mLmin\(^{-1}\) to produce 90 mgNm\(^{-3}\) HF and 4 \%RH in the COS/Ar gas. For fluorinated alumina experiments (1.2 mLhr\(^{-1}\) pump rate), 330 mgNm\(^{-3}\) HF and 4 \%RH were present in a 2 Lmin\(^{-1}\) \( \text{N}_2 \) gas. For fluorinated alumina experiments, COS or \( \text{SO}_2 \) were added in a separate experiment. Appendix D outlines humidity and HF calculations.
8.2.4 Quadrupole Mass Spectrometer

A quadrupole mass spectrometer was used to measure gas composition entering and exiting the fluidised bed reactor. Commercially available mass analysers fall into one of two categories; beam transport and ion trapping. A quadrupole mass spectrometer is of the beam transport variety, which involves the movement of ions through space over which electric or magnetic fields are applied. In this way a separation can be achieved according to the mass to charge ratio (m/z) [136].

A schematic for the operation the mass spectrometer is shown in Figure 8.7 [137]. Neutral gas molecules enter through a fine silica capillary, controlling the total pressure in the mass spectrometer, which must remain below $10^{-5}$ torr (or < 0.001 Pa). On entering, gas molecules are ionised and then separated using a quadrupole analyser, which is a mass filter that creates an oscillating electric field with dc and rf components. The field is created by four precisely machined rods that the ions must pass between to reach the detector, so that only ions of a selected mass-to-charge ratio (m/z) are transmitted to the detector [138]. The mass spectrometer measures the current of ionised molecules at any given m/z and converts this to a partial pressure.

Figure 8.7: A schematic of a quadrupole mass spectrometer. [137]
Atmospheric background gases are always present in the analysis chamber, particularly \( \text{H}_2\text{O}, \text{N}_2, \text{O}_2, \text{CO}_2 \) and Ar, totalling about \( 1 \times 10^{-8} \) torr. A single species can be fragmented into several different \( m/z \)'s in the mass spectrometer with predictable relative proportions. Usually, the \( m/z \) corresponding to the parent molecular mass of the species is far larger than any fragmentation peaks. However, a species can be identified by it’s particular fragmentation pattern of \( m/z \)'s and partial pressures, if the major peak cannot be resolved, such as \( \text{N}_2 \) and \( \text{CO} \ (m/z \ 28) \) and \( \text{O}_2 \) and \( S \ (m/z \ 32) \).

The reactor gas entered the Ametek Dycor MA100 mass spectrometer at a pressure \( 1 \times 10^{-5} \) torr through a 50\( \mu \)m diameter fused silica capillary (about 3 cm long), controlled by a vacuum-safe valve. Gas sampling could occur at the fluidised bed reactor inlet or outlet. Data acquisition from the mass spectrometer was controlled by computer, using a program developed by Clover [137]. Selected \( m/z \) ratios (shown in Table 8.1) were measured every 10 minutes to allow longer dwell times at each \( m/z \) ratio, since some gases were present in very low concentrations (10 ppmv).

<table>
<thead>
<tr>
<th>Channel</th>
<th>( m/z ) Ion</th>
<th>Dwell (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>34</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>44</td>
<td>2.0</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>8.0</td>
</tr>
<tr>
<td>8</td>
<td>64</td>
<td>4.0</td>
</tr>
</tbody>
</table>

8.2.5 Sensitivity to Ionisation

Measurements of smelter gas composition have usually reported sulfur gas concentrations in ppmv [4, 5]. Therefore, it was desirable to convert partial pressure (in torr) measured by the mass spectrometer into concentrations in ppmv (parts per million by volume). At the low pressures encountered in the mass spectrometer, Dalton’s law should apply:
\( P_a = y_a P_T \) \hspace{1cm} (8.1)

\( p_a = \) partial pressure of gas \( a \)
\( y_a = \) mole fraction of gas \( a \)
\( P_T = \) total pressure

However, total pressure is measured independently of partial pressures in the mass spectrometer and is not necessarily the sum of all partial pressures measured [137]. Additionally, the partial pressure of a specific gas is dependant on the sensitivity of the quadrupole to ionisation efficiency of that gas. This means that two gases of equal concentration may have different partial pressures in the mass spectrometer.

As a result, COS, SO\(_2\) and H\(_2\)S were calibrated in the mass spectrometer by introducing known concentrations (in ppmv) of a particular sulfur gas through the mass spectrometer and measuring partial pressures (torr) of all sulfur gases. Although it only takes a few seconds for gas to pass through the apparatus and be detected in the mass spectrometer, the time is sufficient for small amounts of gas phase reaction. So iterative calculations were used to ensure that the measured sulfur gas composition (COS and H\(_2\)S and SO\(_2\) in the mass spectrometer) accounted for the inlet sulfur gas levels (COS or H\(_2\)S or SO\(_2\)). Then an ionisation conversion factor (I) in torr/ppm could be calculated for each sulfur gas. See Appendix G for detailed calculations of ionisation factor.

When calculating concentration (ppmv) levels from partial pressure (torr) data for experiments, the background pressure for a specific gas (at a specific m/z ratio) must be subtracted, before dividing by the ionisation factor. The resulting number must also be corrected by another factor to account for daily fluctuations in mass spectrometer measurement at that particular m/z ratio. This daily correction factor is the ratio of partial pressure at a specific m/z at the time of calibration experiments with the partial pressure at the same gas concentration measured for the current experiment. Conversion (torr into ppmv) calculations can be summarised with the following equations:

\[ C_a = \frac{P_a - P_{ab}}{ID} \] \hspace{1cm} (8.2)
\[ D = \frac{p_{ac}}{p_a} \]  

\( C_a \) = concentration of gas a (ppmv)  
\( p_a \) = partial pressure of gas a (torr)  
\( p_{ab} \) = background partial pressure of gas a (torr), measured on the same day  
\( I \) = ionisation factor, or the sensitivity of gas a towards ionisation in the mass spectrometer \((\text{torr/ppmv})\)  
\( D \) = daily correction factor, to account for fluctuations in partial pressure from day to day  
\( p_{ac} \) = partial pressure of gas a at the time of calibration (torr)

Despite all the corrections for sensitivity to ionisation and day-to-day changes in the mass spectrometer, it was found that after filament replacement in 2001 there were some differences in the quantification of sulfur gases, particularly H\(_2\)S. Therefore, although an attempt has been made to quantify gas composition results, the focus of experimental analysis is on relative trends rather than exact gas concentrations (see Chapter 9).

### 8.2.6 Procedure for Fluidised Bed Experiments

For all fluidised bed experiments, the apparatus was allowed to heat up to temperature (usually 80 – 100\(^{\circ}\)C) for about an hour prior to the experiment. During this time, the gas lines, reactor and mass spectrometer were purged with 0.4 L\(\text{min}^{-1}\) \(\text{Ar}\) to minimise contaminants in the gas phase. Following this, the background gas composition (with \(\text{Ar}\) flowing) was measured in the mass spectrometer, to standardise the gas measurement from one day to the next. The reactor inlet gas composition was also measured immediately before the experiment commenced.

In selected fluidised bed experiments, the total percentage of sulfur adsorbed on the alumina surface over the experiment duration was calculated. To calculate this, the concentration of adsorbed COS (in ppmv) was summed over the experiment duration, converted into a mass using the density of COS at 80\(^{\circ}\)C (or the appropriate temperature), and divided by the total mass of alumina in the fluidised bed.
Specific details for each experiment are included with the results (Chapter 9), but an outline of experiments performed using the fluidised bed reactor is included here. Gas phase only calibrations and experiments (with no alumina present in the reactor) were performed before experiments with different alumina types with the various different gas mixtures. The experiments performed included:

- **Gas stability experiments.** Gas phase only experiments with: H₂O in Ar, O₂ in Ar, COS in N₂/Ar, COS/H₂O in N₂/Ar, COS/O₂ in Ar, COS/SO₂ in N₂/Ar, COS/HF in N₂/Ar, SO₂ in Ar, SO₂/H₂O in Ar, SO₂/O₂ in Ar, H₂S in Ar, H₂S/H₂O in Ar, H₂S/O₂ in Ar

- **The influence of primary smelter-grade alumina experiments.** Primary smelter-grade alumina with: COS, SO₂, COS/SO₂, H₂S, COS/H₂O, COS/CO₂, COS/O₂

- **The influence of adsorbent type experiments.** Secondary smelter-grade alumina with COS, Laboratory fluorinated primary alumina with: COS, SO₂, COS/SO₂, γ-Alumina with COS

- **The influence of doping agent experiments.** Na, Fe and Ca doped aluminas each with COS

### 8.3 DRIFTS

A Perkin Elmer 2000 FTIR system was used for experiments. In FTIR (Fourier Transform Infrared), the interferogram of a sample is measured using an interferometer, then a Fourier transform is performed to turn this into an infrared spectrum. An interferometer causes two beams of light to travel difference distances, known as the optical path difference. The interferogram is the constructive or destructive combination of the two beams of light against the variation of optical path difference [139]. Each gas (COS, SO₂ and H₂S) was first studied using FTIR in a gas cell, with a MIRTGS detector. The spectrum measured for each gas was the average of 8 scans in the wavenumber range 6000 – 400 cm⁻¹.

All alumina DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) experiments were performed using a Harrick high temperature vacuum chamber with ZnSe windows and Harrick DRA-3C5 diffuse reflectance accessory (see Figure 8.8 and Figure
8.9). The 4000 – 580 cm\(^{-1}\) region was measured using an MCT detector with a resolution of 4 cm\(^{-1}\) and taking an average of 16 scans (according to reference [140]).

![Figure 8.8: Praying mantis accessory for diffuse reflectance spectrometry. The sample holder is the cylindrical part in the centre of the drawing. Ellipsoidal focusing mirrors and collection mirrors shown carry the IR beam from the source to the detector [141].](image)

![Figure 8.9: Heatable evacuable cell to fit in the praying mantis accessory [141].](image)

Several factors were adjusted to maximise the energy of the IR beam reaching the detector [140, 142]:

- The sample was ground to reduce particle size.
- The sample holder was packed with powder to a sufficient density.
- The instrument B-stop (maximum variable IR beam intensity) was set to maximum position (21.2 cm).
• The mirrors of the DRIFTS cell were adjusted prior to each experiment with the sample in position.
• The appropriate dilutant was chosen (CaF$_2$ in this case) at the appropriate concentration.

![Diagram of DRIFTS cell for alumina adsorption studies](image)

**Figure 8.10:** Diagram of DRIFTS cell for alumina adsorption studies [140].

Gases were injected or flowed through the cell in the manner shown in Figure 8.10. For COS and H$_2$S adsorption studies, a mixture of 50% alumina and 50% CaF$_2$ was used, while for SO$_2$ adsorption studies 30% alumina diluted in CaF$_2$ was used (see discussion in Appendix E). Temperature was controlled in the DRIFTS cell at 80ºC during adsorption and was capable of heating to 500ºC for calcining and desorption studies.

### 8.3.1 Gases Used

H$_2$S was supplied at 2.5% in H$_2$ and SO$_2$ was supplied as a pure gas. Due to time constraints and problems with the COS gas supplied, it was prepared in the laboratory according to the following reaction [143]:

$$
\text{KCNS (s)} + \text{H}_2\text{SO}_4 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{COS (g)} + \text{KHSO}_4 (\text{aq}) + \text{NH}_4\text{HSO}_4 (\text{aq}) \quad (8.4)
$$
COS was collected in a gas tight syringe and its presence and stability were checked using FT-IR. Syringe samples of COS appeared to be stable for several days. A sample of the gas produced was also analysed using mass spectrometry (15 mL COS was injected into the gas tight bottle for analysis, referenced to atmospheric air). The results of the mass spectrometer analysis in Figure 8.11 show an increase in all sulfur gases (compared to background air), as well as CO$_2$. However, COS is present in levels at least one order of magnitude higher (in terms of partial pressure) than these other species. Determining the composition with a greater degree of accuracy cannot be achieved without calibration of the gases in the mass spectrometer.

![Mass Spectrometer: COS gas](image)

Figure 8.11: Mass spectrometer scan showing the change in gas composition between atmospheric air and COS in air. Note logarithmic scale.

FT-IR spectra of COS, SO$_2$ and H$_2$S gases are included in Appendix F.

### 8.3.2 Artefacts and Features in the IR Spectrum

Adsorbed water and hydrogen carbonate species are usually observed on alumina in IR studies [88-90]. When water is removed during heating (or the drying effect of argon flow),
the structural hydroxyl groups to which they were co-ordinated are free to vibrate ("liberated"), so in DRIFTS spectra it appears that there is an increase in hydroxyl groups. These OH groups are usually located at wavenumbers between 3500 and 4000 cm\(^{-1}\), while adsorbed water appears as a broad band centred around 3000 cm\(^{-1}\), with a sharper band at 1640 cm\(^{-1}\). The bands of adsorbed hydrogen carbonate were determined experimentally and are included in Chapter 9.

Due to the instrument set-up during the collection of DRIFTS spectra, most of the IR beam path is through air in the open atmosphere, with only a small amount of the beam path in the closed cell containing the alumina sample (see Figure 8.8). As a result, the presence of species such as CO\(_2\) gas depends more on the open atmosphere than the conditions in the cell, so little information about the reactions in the cell are revealed by a change in concentration of this species. CO\(_2\) gas has a strong set of bands around 2350 cm\(^{-1}\) (see Chapter 9).

When gas is adsorbed onto the alumina surface with no change in structure (physisorbed), the adsorption band is shifted only a few wavenumbers from the pure gas, e.g. COS. Gas bands can be distinguished from adsorbed species bands, because the gas band is usually a doublet, while the adsorbed species is usually a single sharp band with a slight change in wavenumber [96]. It is important to have argon gas flow to ensure the injected gas is flushed out of the cell in order to detect the adsorbed species band.

### 8.3.3 Summary of DRIFTS Experiments

Gas IR spectra (no alumina) were measured using an FT-IR gas cell, then DRIFTS experiments were performed where sulfur gases were contacted with alumina. The experiments performed included:

- **Gas phase experiments.** The IR spectra of COS, SO\(_2\) and H\(_2\)S were measured.
- **Adsorbed species on primary alumina.** Primary alumina with: CO\(_2\), COS, SO\(_2\), H\(_2\)S, COS/SO\(_2\), COS/Air
- **The influence of adsorbent type.** Calcined primary alumina with: COS, SO\(_2\), H\(_2\)S, Secondary alumina with: COS, SO\(_2\), Calcined secondary alumina with COS, γ-Alumina with COS
• The influence of doping agent. Na, Fe and Ca doped aluminas, each with COS

8.4 Alumina Analysis

All of the aluminas used for fluidised bed and DRIFTS experiments are described and characterised in Section 8.5. A number of methods and techniques were used to characterise aluminas, including:

1. Particle size distribution
2. BET Surface Area
3. XRF (X-Ray Fluorescence)
4. XRD (X-Ray Diffraction)
5. XPS (X-ray Photoelectron Spectroscopy)
6. SEM (Scanning Electron Microscopy) with EDS (Energy Dispersive Spectroscopy).

8.4.1 Particle Size Distribution

A sieve analysis of the primary smelter-grade alumina was performed to determine its particle size distribution, using sieves with 38, 53, 63, 75, 90, 106, 125 and 150 µm mesh sizes. The sieves were cleaned in an ultrasonic water bath for at least 10 minutes followed by cleaning with compressed air before being used for size distribution measurements.

8.4.2 BET Surface Area

To measure surface area, a 0.06 g sample of alumina was held in a U-tube with flowing N₂/He gas. Adsorption of N₂ gas on cooling the U-tube (with a liquid N₂ bath) and desorption on warming to room temperature again were measured for a range of N₂/He ratios. This data was used to construct a nitrogen adsorption isotherm, which was then used to determine specific surface area using BET (Brunauer-Emmett-Teller) theory [134]. Primary and secondary alumina samples were heated to 80°C overnight in flowing N₂/He gas to remove adsorbed water prior to measurement.
8.4.3 XRD (X-Ray Diffraction)

When monochromatic x-rays are diffracted from atoms on a number of equally spaced parallel planes (i.e. crystals), then constructive interference can occur [144]. The angle of diffraction (θ) of x-rays from the crystalline planes in a sample can be related to the interplanar spacing (d in Å) of the crystalline planes in the sample according to Bragg’s Law:

\[ \lambda = 2dsin\theta \]  
(8.5)

\( \lambda \) = wavelength of the x-rays, 1.5405 Å for a Cu x-ray source.

XRD can be used to determine the nature of crystalline species present in a sample (by comparing with standards from JCPDS or Joint Committee on Powder Diffraction Standards) and can give an indication of the proportion of crystalline to amorphous species present, by measuring the radiation emitted from the sample (counts) with changing angle of diffraction (2θ). All diffractogram results are presented for a Cu anode x-ray source (some were converted from a Co source), usually measured in the range of 10 – 90° 2θ, with a step size of 0.05° and 5 s/step on a Bruker AXS D8 Advance instrument using Diffrac Plus V1.01 software.

8.4.4 XRF (X-Ray Fluorescence)

XRF (X-Ray Fluorescence) allows identification of an element by measurement of its characteristic x-ray emission wavelength or energy, following irradiation by x-rays. The method permits quantitative estimation of a given element by first measuring an emitted characteristic line intensity and then relating this intensity to elemental concentration [145].

XRF of a fused bead (0.5 g alumina, 7.5 g flux powder) was used to determine the %F in fluorinated alumina and a full elemental composition of primary and secondary smelter-grade alumina. The elemental composition of primary and secondary alumina was also determined.
using a 10 g alumina pressed powder sample, which gives more accurate results for elements other than F. XRF measurements were performed on a Siemens SRS300 Sequential X-ray Spectrometer, with a limit of detection for the pressed powder method of 190 ppm and a limit of determination of 380 ppm. Siemens Spectra 3000 V2.0 was the software used for fused bead analysis and pressed powders were analysed by a semiquant analysis using the software Bruker Spectraplus V1.51.

8.4.5 XPS (X-ray Photoelectron Spectroscopy)

XPS involves irradiating a solid under vacuum with monoenergetic x-rays and analysing the kinetic energy (KE) of the emitted electrons. A spectrum is obtained as a plot of the number of detected electrons per energy interval versus their binding energy. Each element has a unique set of binding energies (BE) for core electron levels, allowing identification of the elements at the surface. BE (binding energy) relates to the measured KE (kinetic energy) by the Einstein equation (hν is the energy of the x-ray source):

\[
\text{BE} = h\nu - \text{KE} \quad (8.6)
\]

XPS is a surface sensitive method that analyses at most the top 5 nm of a surface and provides semiquantitative elemental analysis from the peak areas of peaks of interest. Using a Kratos XSAM 800 XPS instrument, a “wide scan” spectrum (0 – 1100 eV) determined which elements were present and the approximate binding energy for each element. Detailed narrow scans (measured over about a 20 eV range) over particular peaks of interest were collected to measure the BE with accuracy and provide “chemical shift” information allowing chemical states to be determined [146].

As well as a sample of primary alumina, an analysis of fines from the sieving process were characterised to check that the sieves were not contaminating the alumina. In each case a wide scan was done of the alumina sample, but narrow scans were only performed for selected samples. The XPS was set up using Al Kα x-rays, and the analyser set for low magnification, with a pass energy of 65 eV for wide scans and 38 eV for narrow scans. Wide scans were done between 1100 and 0 eV, with a step size of 1 eV and a dwell time of 4500
ms. Narrow scans of C 1s, Al 2p, O 1s, S 2p, Na 1s F 1s were performed, with a step size of 0.2 eV and dwell times ranging from 4000 ms (for O 1s) to 20 000 ms (for S 2p). Binding energies were referenced to adventitious hydrocarbon at 285.0 eV.

The Na Auger parameter can be used to give extra information about the chemical state of Na. The Na Auger Parameter can be calculated from the equation:

$$\alpha' + \hbar \nu = \text{BE}_p + \text{KE}_A$$  \hspace{1cm} (8.7)

$\alpha'$ = modified Auger parameter  
$\text{BE}_p$ = binding energy for the Na 1s photoelectron (eV)  
$\text{KE}_A$ = kinetic energy of the Auger Na KLL line  
$\hbar \nu$ = the photon energy of the x-ray source ($\text{Al K}_\alpha$ anode = 1486.6eV)

### 8.4.6 SEM with EDS

To produce an SEM (Scanning Electron Microscopy) image, an electron beam rasters over a rectangular area of the specimen surface, causing several types of energetic emissions, including backscattered electrons, secondary electrons, Auger electrons (a type of secondary electron), continuous x-rays and characteristic x-rays. Usually the secondary electrons are detected and used to collect the image, because they come from the area directly under the beam and their yield depends strongly on the surface topography (so the intensity of the secondary electrons reflects the surface topography), therefore giving the image very high resolution. For EDS (Energy Dispersive [X-ray] Spectroscopy), Characteristic x-rays emitted from the atoms in the sample can be collected over varying energies producing a spectrum, where peaks correspond to elements present in the sample [144].

SEM with EDS was used to study local elemental composition of the different aluminas, using a Philips XL30S instrument at an accelerating voltage of 10.0 kV and an SiLi (lithium drifted silicon) EDS detector. For primary, secondary, fluorinated and $\gamma$-aluminas, samples were gold coated for imaging and carbon coated for EDS measurements. Impurity doped aluminas were platinum coated, which allows for good imaging, while the coating is thin.
enough to allow EDS analysis. EDS is useful for determining the composition of heavier elements (such as Al, Ca, Fe and Na), but is relatively light element insensitive, therefore measurements of O concentration are less quantitative.

8.5 Aluminas Tested

A number of different aluminas were considered for fluidised bed and DRIFTS experiments and these were characterised to determine their bulk and surface properties.

8.5.1 Primary Smelter-Grade Alumina

QAL smelter-grade primary alumina was used for the majority of both fluidised bed and DRIFTS experiments. Particle size distribution, BET surface area, XRD, XRF, XPS and SEM with EDS were all employed to characterise the primary smelter-grade alumina used for experiments. The particle size distribution was measured and is shown in Figure 8.12. Undersize (< 45 μm diameter) and oversize (> 150 μm diameter) particles were removed by
sieving to ensure good bed fluidisation in the reactor and minimise blockages [134]. The BET surface area of the primary smelter-grade alumina studied was 74.7 m$^2$g$^{-1}$.

Figure 8.15 (Section 8.5.2) shows the XRD diffractogram of the primary alumina (along with secondary and lab-fluorinated alumina) used for experiments. The major crystalline phase in primary alumina was $\alpha$-$\text{Al}_2\text{O}_3$, although it constitutes less than 15% of the sample (depending on the refining process used), along with lesser amounts of transition $\text{Al}_2\text{O}_3$ phases and gibbsite ($\text{Al(OH)}_3$).

### Table 8.2: XRF elemental analysis (mass%) of primary alumina.

<table>
<thead>
<tr>
<th>Species</th>
<th>Fused Bead mass %</th>
<th>Pressed Powder mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>99.4</td>
<td>99.4</td>
</tr>
<tr>
<td>$\text{F}$</td>
<td>$&lt;0.39$</td>
<td>0.047</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>0.39</td>
<td>0.31</td>
</tr>
<tr>
<td>$\text{S}$</td>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>0.12</td>
<td>0.086</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>0.039</td>
<td>0.024</td>
</tr>
<tr>
<td>All other species</td>
<td>$&lt;0.01$ wt%</td>
<td></td>
</tr>
</tbody>
</table>

The elemental composition of a sample of the primary alumina was determined using XRF and the results are shown in Table 8.2. Composition was measured using both fused bead and pressed powder method – the fused bead method has been calibrated for F in alumina, but the pressed powder is considered more reliable for other elements. The analysis shows that Na is the major impurity in the alumina, as expected for smelter grade alumina.

XPS (X-ray Photoelectron Spectroscopy) was used to semi-quantitatively determine the element composition for the alumina and to check for surface contamination of the alumina due to the sieving process. Wide scan results (Figure 8.13 and Table 8.3) show that alumina, adventitious carbon and small amounts of Na and F are present on the sample surface. Narrow scans for Al 2p, O 1s, Na 1s and C 1s (due to adventitious hydrocarbon) regions determined that a single Al species (alumina) and a single Na species are present (see Table 8.3 for Narrow scan BE’s). The BE for the Na species and the Na Auger parameter indicate Na-F bonding [147, 148]. C 1s and O 1s scans show several species each. The narrow scan
results are similar to those obtained by Gillespie [134] for smelter-grade alumina. No contamination of the alumina fines was observed after sieving, according to XPS analysis.

![XPS analysis for primary smelter-grade alumina.](image)

**Figure 8.13:** XPS analysis for primary smelter-grade alumina.

**Table 8.3:** XPS elemental quantification for primary alumina (BE values are from narrow scans).

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding Energy (eV)</th>
<th>Atomic Conc. (%)</th>
<th>Mass Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285.0</td>
<td>17.75</td>
<td>11.5</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.2</td>
<td>51.99</td>
<td>44.9</td>
</tr>
<tr>
<td>Al 2p</td>
<td>74.6</td>
<td>28.57</td>
<td>41.6</td>
</tr>
<tr>
<td>Na 1s</td>
<td>1071.5</td>
<td>0.51</td>
<td>0.6</td>
</tr>
<tr>
<td>F 1s</td>
<td>685.0</td>
<td>1.18</td>
<td>1.2</td>
</tr>
<tr>
<td>Na Auger Parameter</td>
<td>2060.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A primary alumina sample was studied using SEM with EDS, which allows local elemental composition to be related to features on the surface of the sample. The results, in Figure 8.14 and Table 8.4, show that primary alumina is made up of clean, crystalline particles, usually about 100 μm in size, with no particulate impurities (apart from Na and F detected in XPS and XRF) detected in the EDS scan.

Figure 8.14: SEM image (1140X magnification) for primary smelter-grade alumina.

<table>
<thead>
<tr>
<th>Scan</th>
<th>Al mass%</th>
<th>O mass%</th>
<th>Na mass%</th>
<th>F mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>71.27</td>
<td>28.13</td>
<td>0.36</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>68.73</td>
<td>30.84</td>
<td>0.35</td>
<td>0.09</td>
</tr>
</tbody>
</table>

To summarise, the primary smelter-grade alumina studied had a surface area of about 75 m²g⁻¹, with α-alumina and lesser amounts of transition aluminas and gibbsite the major crystalline phases. The major impurity in the bulk was Na, which may be bonded with NaF on the surface. A typical alumina particle is crystalline in appearance and 100 μm in size.
8.5.2 Secondary Alumina Characterisation

Secondary alumina is alumina that has been used in the dry scrubbing process. A sample of secondary alumina was obtained from dry scrubbers at Karmøy, Norway for these studies and a full characterisation of the secondary alumina sample was completed by measuring BET surface area and using XRD, XRF, XPS and SEM with EDS. Although this secondary alumina was not from the same source as the primary alumina used, the BET surface area of secondary alumina was $74.6 \text{m}^2\text{g}^{-1}$, which is almost identical to the primary alumina studied.

The crystalline (and amorphous) phases of the secondary alumina sample were compared with those of primary (see Section 8.5.1) and laboratory-fluorinated alumina (see Section 8.5.3) using XRD, as shown in Figure 8.15. Secondary alumina shows an increase in sub-crystalline material, although generally the same crystalline phases were present. There is perhaps an additional broad peak around $67^\circ$, but this is not indicative of additional cryolite or other similar species (e.g. Chiolite, CaF$_2$, NaAlF$_4$, AlF$_2$(OH), AlF$_3$$\cdot$3H$_2$O) that might be expected in secondary alumina.

![XRD Results](image)

**Figure 8.15:** XRD diffractograms of primary, lab fluorinated and secondary alumina.
XRF analysis of secondary alumina using fused bead method (for F analysis) and pressed powder method (for other elements) is given in Table 8.5 and shows that more F and S were detected in secondary alumina compared to primary.

Table 8.5: XRF elemental analysis (mass%) of secondary alumina.

<table>
<thead>
<tr>
<th>Species</th>
<th>Fused Bead mass %</th>
<th>Pressed Powder mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>97</td>
<td>95.9</td>
</tr>
<tr>
<td>F</td>
<td>1.8</td>
<td>2.84</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.54</td>
<td>0.69</td>
</tr>
<tr>
<td>S</td>
<td>0.42</td>
<td>0.426</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.095</td>
<td>0.073</td>
</tr>
<tr>
<td>CaO</td>
<td>0.072</td>
<td>0.055</td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td>0.017</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>&lt;0.0088</td>
<td>0.015</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>0.01</td>
</tr>
</tbody>
</table>

All other species <0.01 wt%

XPS wide scan results are shown in Figure 8.16, elemental composition (with BE values from narrow scan results) is shown in Table 8.6. A small amount of S was also identified in the secondary alumina sample that had a binding energy consistent with aluminium sulfate [149].

Table 8.6: Elemental composition of secondary alumina determined using XPS.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding Energy (eV)</th>
<th>Atomic Conc. (%)</th>
<th>Mass Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>285.0</td>
<td>23.06</td>
<td>15.1</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.5</td>
<td>36.94</td>
<td>32.4</td>
</tr>
<tr>
<td>Al 2p</td>
<td>74.6 77.5</td>
<td>20.66 30.6</td>
<td></td>
</tr>
<tr>
<td>Na 1s</td>
<td>1072.4</td>
<td>3.70 4.6</td>
<td></td>
</tr>
<tr>
<td>F 1s</td>
<td>686.1</td>
<td>14.53 15.1</td>
<td></td>
</tr>
<tr>
<td>S 2p</td>
<td>169.9</td>
<td>1.10 1.9</td>
<td></td>
</tr>
<tr>
<td>Na Auger Parameter</td>
<td>2059.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Compared to primary alumina, secondary alumina has significantly more surface Na and F present, as expected. This is due to adsorption of HF and collection of fine bath particulates. A second form of aluminium was detected from a narrow scan of the Al 2p region in
secondary alumina compared to primary. This second high binding energy species (see Table 8.6) corresponds with a species with Al-F bonding (such as NaAlF₄, for example). The Na Auger parameter is 1eV smaller for secondary alumina compared to primary, but surprisingly does not indicate a species such as NaF or cryolite [147]. The BE of Na indicates that Na₂O is probably present [150].

![XPS results for secondary alumina from Karmøy, Norway.](image)

**Figure 8.16:** XPS results for secondary alumina from Karmøy, Norway.

SEM with EDS was performed on the secondary alumina sample to determine how surface features related to local elemental composition, e.g. bath particulates vs. alumina. The SEM image Figure 8.17 shows how typically, the secondary alumina surface looked dirtier than primary alumina. Using EDS (see Table 8.7) it was determined that impurities such as F, Na, S, Si and Ca on the secondary alumina surface tended to be present together in smaller non-crystalline particles.
Figure 8.17: SEM image (5000X magnification) of secondary alumina.

Table 8.7: Selected EDS results of elemental composition of secondary alumina. Scans 1, 3 and 8 were of bigger, more crystalline particles and scans 6 and 10 were of smaller particles.

<table>
<thead>
<tr>
<th>Scan</th>
<th>Al mass%</th>
<th>O mass%</th>
<th>Na mass%</th>
<th>F mass%</th>
<th>S mass%</th>
<th>Si mass%</th>
<th>Ca mass%</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>62.74</td>
<td>30.24</td>
<td>0.95</td>
<td>0.64</td>
<td>0.71</td>
<td>3.82</td>
<td>0.9</td>
</tr>
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<td>3</td>
<td>62.62</td>
<td>29.98</td>
<td>2.6</td>
<td>1.97</td>
<td>1.71</td>
<td>0.77</td>
<td>0.36</td>
</tr>
<tr>
<td>8</td>
<td>58.21</td>
<td>32.27</td>
<td>3.04</td>
<td>2.27</td>
<td>2.03</td>
<td>0.77</td>
<td>0.36</td>
</tr>
<tr>
<td>6</td>
<td>38.36</td>
<td>24.98</td>
<td>12.07</td>
<td>8.08</td>
<td>7.37</td>
<td>1.3</td>
<td>0.78</td>
</tr>
<tr>
<td>10</td>
<td>30.55</td>
<td>21.6</td>
<td>22.13</td>
<td>21.13</td>
<td>2.45</td>
<td>0.81</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Although the surface area of secondary alumina was the same as primary, it was more amorphous than primary alumina, with impurities present on the alumina particle surface. Higher levels of Na, F, S, Ca and Si were present and they tended to be co-located in smaller particles. A second type of Al bonding was observed compared to primary, in the form of AlF₃, and S was present in the form of sulfate on the alumina surface according to the XPS analysis.
8.5.3 Laboratory Fluorinated Primary Smelter-Grade Alumina

Fluorination is expected to change the properties of the alumina surface with respect to sulfur gas adsorption or reaction [21]. To study the influence of F species, rather than bath particulates (as on secondary alumina), alumina with about 3 wt% F was prepared in the fluidised bed reactor in the laboratory to use for adsorption experiments. According to Gillespie [134], the fluorinated alumina phase should be in the form AlF$_x$OH$_{(3-x)}$$\cdot$yH$_2$O, where $y = 6$ or 12 and $x + (3-x) = 3$, rather than as AlF$_3$, although the structure of both phases is the same. Alumina was fluorinated in 4 g batches, using a 2 Lmin$^{-1}$ N$_2$ stream carrying 4 %RH and an HF concentration of about 327 mgNm$^{-3}$. Fluorination took two hours and the final F concentration was determined using XRF (X-Ray Fluorescence). The 4 g samples of alumina produced from each fluorination trial were combined to reduce any fluctuations in experimental conditions. A sample of this alumina was analysed using XRF and 3.0 wt% F was present on the surface.

As fluorinated alumina ages, usually in humid conditions, the surface fluoride species crystallise and this is seen in the alumina as fine crystals aggregated on the surface. Aging was minimised by storing the prepared fluorinated alumina in dry, plastic containers. XRD analysis (see Figure 8.15) at the time the fluorinated alumina was used for experiments with COS, showed that the AlF$_x$OH$_{(3-x)}$$\cdot$yH$_2$O was amorphous, since the diffractogram was identical to that of the primary alumina sample. No crystalline fluoride species were identified in laboratory fluorinated alumina, so the initial fluorinated species were amorphous.

Table 8.8: Selected EDS results showing the elemental composition at selected spots on a laboratory-fluorinated alumina sample.

<table>
<thead>
<tr>
<th>Scan</th>
<th>Al mass%</th>
<th>O mass%</th>
<th>Na mass%</th>
<th>F mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.41</td>
<td>34.39</td>
<td>0.40</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>65.44</td>
<td>31.63</td>
<td>2.21</td>
<td>0.71</td>
</tr>
<tr>
<td>4</td>
<td>64.82</td>
<td>33.77</td>
<td>1.07</td>
<td>0.34</td>
</tr>
<tr>
<td>5</td>
<td>61.63</td>
<td>36.63</td>
<td>0.54</td>
<td>1.20</td>
</tr>
<tr>
<td>7</td>
<td>66.12</td>
<td>31.36</td>
<td>1.82</td>
<td>0.70</td>
</tr>
</tbody>
</table>
SEM with EDS analysis of laboratory fluorinated alumina was performed to determine how local elemental composition related to surface features. Laboratory fluorinated alumina looked very similar to primary alumina (see Figure 8.14), however, the EDS point scan results in Table 8.8 shows that some F could be detected on the surface.

To summarise, laboratory fluorinated primary alumina contained 3 wt%F in the form of aluminium hydroxy fluorides, but otherwise resembled untreated primary alumina.

### 8.5.4 Impurity Doped Aluminas

![XRD Results](image)

**Figure 8.18:** XRD (X-Ray Diffraction) results comparing the different alumina types studied.

As well as adsorbed HF, secondary alumina contains cation (Ca, Fe and Na [10]) impurities that, if present at the surface, may affect COS adsorption and reaction. Doped alumina samples were prepared by shaking a 30 g primary alumina sample with 200 mL nitrate solution containing the metal ion of interest. The liquid was then decanted off and the alumina sample dried at 100°C for a minimum of 4 hours, followed by calcining at 500°C for 5 hours [100]. In case this doping process was changing phases present in the alumina, a
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COS / Alumina Studies Experimental Method

“primary treated alumina” sample was prepared using deionised water instead of nitrate
solution with the same heat treatment process. Samples of each doped alumina were used in
fluidised bed and DRIFTS studies to examine COS adsorption.
XRD results for three doped aluminas and two primary aluminas are given in Figure 8.18.
The untreated primary alumina XRD had two extra peaks not observed in the treated one
(Figure 8.18 at about 42º and 49º), which were due to a mixture of alumina phases (such as κAl2O3). The loss of these peaks may have been due to the calcining process. The treated
primary alumina sample has a small peak at about 61º, which may be present in the untreated
sample (this is a noisier spectrum).
The Fe treated sample has peaks at 36º and 54º, which are due to the Fe2O3. The Ca treated
sample has extra peaks at 30º and 11º, the former of these peaks is due to CaCO3, while the
latter peak could be due to CaAl2(CO3)4(OH)8•6H2O. Overall, the XRD results indicate that
no distinct crystalline species have been formed by the heat treatment process used for
doping. However, there are additional crystalline species present in the Fe (Fe2O3) and Ca
(CaCO3) doped aluminas.
An XRF elemental analysis, shown in Table 8.9, gives the doping level of each alumina,
which were 0.78 mass% Na, 6.11 mass% Fe and 10.9 mass% Ca respectively.

Table 8.9: XRF elemental compositions of various doped aluminas.
Na Doped Alumina
Species
Fused Bead
mass %
Al2O3
98.720

Fe Doped Alumina
Species
Fused Bead
mass %
Al2O3
93.550

Na2O

0.780

Fe2O3

6.110

SiO2

0.270

Na2O

Fe2O3

0.020

CaO
Ga2O3

0.150

Ca Doped Alumina
Species
Fused Bead
mass %
Al2O3
88.680
10.900

0.190

CaO
SO3

SiO2

0.074

Na2O

0.120

0.031

SiO2

0.063

0.015

CaO
Ga2O3

0.014

Fe2O3

0.017

SO3

0.013

CoO

0.010

Ga2O3

0.015

Cl

0.011
All other species < 0.01 wt%

0.150


An SEM image of the treated primary alumina sample studied in Figure 8.19 shows that the alumina appears no different after heat treatment than untreated primary alumina (see Figure 8.14). A typical SEM image of the Na treated alumina (Figure 8.20) shows that the surface is similar to primary alumina (Figure 8.19). EDS (Energy Dispersive Spectroscopy) quantitative results from spot scans at various places on the Na doped sample are summarised in Table 8.10 and show that surface Na levels varied between 0.51 wt% and 0.62 wt%.

![Figure 8.19: SEM image of primary alumina at a magnification of 10000X.](image1)

![Figure 8.20: SEM image of Na treated alumina at a magnification of 20000X.](image2)
Table 8.10: EDS results of spot scans of the Na doped alumina sample.

<table>
<thead>
<tr>
<th>Scan</th>
<th>Al (wt%)</th>
<th>O (wt%)</th>
<th>Na (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.54</td>
<td>39.84</td>
<td>0.62</td>
</tr>
<tr>
<td>2</td>
<td>59.35</td>
<td>40.14</td>
<td>0.51</td>
</tr>
<tr>
<td>3</td>
<td>63.64</td>
<td>35.79</td>
<td>0.58</td>
</tr>
</tbody>
</table>

An SEM image of the Fe doped alumina surface (Figure 8.21) shows that a large number of small particles appear to be attached to the alumina surface. This may indicate that some of the Fe is present as oxide particles on the surface, rather than as adsorbed species. SEM analysis of secondary alumina also determined the presence of smaller particles on the alumina surface (see Figure 8.17). The amount of Fe on the surface varied from 4.75 to 12.98 wt% using EDS analysis (see Table 8.11), although one point analysis of a smaller particle contained 40.32 wt% Fe and 49.95% Al.

Figure 8.21: SEM image of Fe treated alumina at a magnification of 10000X.

Table 8.11: EDS results of spot scans of the Fe doped alumina sample.

<table>
<thead>
<tr>
<th>Scan</th>
<th>Al (wt%)</th>
<th>O (wt%)</th>
<th>Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.32</td>
<td>35.93</td>
<td>4.75</td>
</tr>
<tr>
<td>2</td>
<td>56.57</td>
<td>36.35</td>
<td>7.08</td>
</tr>
<tr>
<td>3</td>
<td>49.95</td>
<td>9.73</td>
<td>40.32</td>
</tr>
<tr>
<td>4</td>
<td>55.99</td>
<td>31.03</td>
<td>12.98</td>
</tr>
<tr>
<td>5</td>
<td>53.49</td>
<td>37.69</td>
<td>8.81</td>
</tr>
</tbody>
</table>
An SEM image of the Ca doped alumina (Figure 8.22) shows that needle-like crystals were present on the alumina particles, most likely calcium carbonate (from XRD results). EDS spot scans determined 2.76 to 11.12 wt% Ca was present on the surface (see Table 8.12), with one scan showing 60.17 wt% Ca (this was once again a small particle).

![Figure 8.22: SEM image of Ca treated alumina at a magnification of 10000X.](image)

<table>
<thead>
<tr>
<th>Scan</th>
<th>Al wt%</th>
<th>O wt%</th>
<th>Ca wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53.01</td>
<td>39.87</td>
<td>7.12</td>
</tr>
<tr>
<td>2</td>
<td>51.50</td>
<td>41.89</td>
<td>6.61</td>
</tr>
<tr>
<td>3</td>
<td>57.72</td>
<td>31.16</td>
<td>11.12</td>
</tr>
<tr>
<td>4</td>
<td>61.37</td>
<td>35.87</td>
<td>2.76</td>
</tr>
<tr>
<td>5</td>
<td>10.52</td>
<td>29.31</td>
<td>60.17</td>
</tr>
</tbody>
</table>

To summarise, the doping process itself did not significantly alter the crystalline phases present in the alumina. Na doped alumina contained 0.78 mass% Na, but otherwise the particles resembled untreated primary alumina. Fe doped alumina contained 6.11 mass% Fe; Fe containing crystals were observed on the alumina surface under SEM and identified as Fe$_2$O$_3$ using XRD. The Ca doped alumina had 10.9 mass% Ca, with crystals present on the surface that were most likely due to CaCO$_3$. 

![Table 8.12: EDS results of spot scans of the Ca doped alumina sample.](image)
8.5.5 γ-Alumina

The alumina types considered so far all originated from primary smelter-grade alumina, of which γ-alumina is a relatively minor component. The very high surface area of this transition alumina, hundreds of $m^2\cdot g^{-1}$, makes it important in the overall surface area of smelter aluminas, but the major use is elsewhere as a catalyst or catalyst support. It was supplied as sintered beads, about 1 mm in diameter and specified as 340 $m^2\cdot g^{-1}$. It was thought that the effect that smelter-grade primary alumina had on COS stability would be magnified with γ-alumina, and therefore it would provide a more active model for the COS/alumina system.

Table 8.13: Composition of the catalyst grade γ-alumina studied.

<table>
<thead>
<tr>
<th>Component</th>
<th>Assay (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>95.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.02</td>
</tr>
<tr>
<td>NaO</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The γ-alumina studied was HF-200 activated alumina (Alcoa) with amorphous, χ- and γ-alumina phases (detected by XRD by the manufacturer), with a crush strength of 25 kg and a bulk density of 750 kgm$^3$. The composition, as supplied by the manufacturer is given in Table 8.13.

Table 8.14: XRF analysis of catalyst-grade γ-alumina.

<table>
<thead>
<tr>
<th>Species</th>
<th>Fused Bead $mass \ %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>99.0</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.62</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.25</td>
</tr>
<tr>
<td>CaO</td>
<td>0.07</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.06</td>
</tr>
<tr>
<td>NiO</td>
<td>0.02</td>
</tr>
</tbody>
</table>
XRF analysis (using the fused bead method) was used to confirm the elemental composition supplied by the manufacturer. The results, shown in Table 8.14, suggest a much more pure alumina (99 mass%), with the major impurity being Na (0.62 mass%).

![XPS wide scan for catalyst γ-alumina.](image)

**Figure 8.23:** XPS wide scan for catalyst γ-alumina.

**Table 8.15:** XPS elemental composition of γ-alumina.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding Energy (eV)</th>
<th>Atomic Conc. (%)</th>
<th>Mass Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>284.9</td>
<td>28.59</td>
<td>20.0</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.4</td>
<td>49.77</td>
<td>46.5</td>
</tr>
<tr>
<td>Al 2p</td>
<td>74.4</td>
<td>20.13</td>
<td>31.7</td>
</tr>
<tr>
<td>Na 1s</td>
<td>1064.9</td>
<td>0.31</td>
<td>0.4</td>
</tr>
<tr>
<td>F 1s</td>
<td>684.4</td>
<td>1.19</td>
<td>1.3</td>
</tr>
</tbody>
</table>

XPS analysis of this alumina detected elements C, O, Al and F on the alumina surface, as shown in Figure 8.23. The elemental composition in Table 8.15 shows that F is the most
significant impurity. Narrow scans (not shown) of C 1s, O 1s, Al 2p, F 1s and S 2p were also completed and it was determined from these that C, O, Al and F were present in only one chemical form each (no S was detected).

SEM with EDS analysis of the \(\gamma\)-alumina detected small amounts of Na and F (see Table 8.16) and a typical image of a fractured alumina bead is shown in Figure 8.24.

![SEM image of the sintered \(\gamma\)-alumina particles observed inside a catalyst bead](image)

**Figure 8.24:** SEM image of the sintered \(\gamma\)-alumina particles observed inside a catalyst bead [Source: \(\gamma\)-alumina sample exposed to 240ppm COS for 5 hours]. The image looks at the edge between a broken face (bottom right) and the surface of the bead (top left).

<table>
<thead>
<tr>
<th>Scan</th>
<th>Al mass%</th>
<th>O mass%</th>
<th>Na mass%</th>
<th>F mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>58.68</td>
<td>40.54</td>
<td>0.52</td>
<td>0.26</td>
</tr>
<tr>
<td>2</td>
<td>56.42</td>
<td>42.42</td>
<td>0.62</td>
<td>0.53</td>
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<td>3</td>
<td>65.48</td>
<td>33.81</td>
<td>0.46</td>
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<td>39.04</td>
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<tr>
<td>5</td>
<td>59.43</td>
<td>38.9</td>
<td>0.99</td>
<td>0.68</td>
</tr>
</tbody>
</table>

To summarise, the \(\gamma\)-alumina sintered beads contained similar elemental impurities to primary alumina (e.g. Na) but had an increased surface area of 340 m\(^2\) g\(^{-1}\).
8.5.6 Summary of Alumina Characterisation

Characterisation of all the aluminas used in fluidised bed and DRIFTS experiments were performed to determine their bulk and surface properties. Primary smelter-grade alumina (QAL) had a surface area of about 75 m$^2$g$^{-1}$, and typical alumina particles were crystalline in appearance and about 100 µm in size, with the major crystalline phase being α-alumina. The major impurity in the bulk was Na, which may be bonded with NaF on the surface. Laboratory fluorinated primary alumina contained 3 wt%F as amorphous aluminium hydroxy fluorides, but otherwise resembled untreated primary alumina.

A sample of secondary alumina was obtained from a dry scrubber at Karmøy, Norway. The surface area of secondary alumina was the same as primary, but it was more amorphous than primary alumina. Impurities were present on the alumina particle surface, including Na, F, S, Ca and Si and they tended to be co-located in smaller particles. A second type of Al bonding was observed on secondary alumina, in the form of AlF$_3$ and S was present in the form of sulfate on the alumina surface.

Several primary alumina samples were doped with the impurities Na, Fe and Ca. Na doped alumina contained 0.78 mass% Na, but otherwise the particles resembled untreated primary alumina. Fe and Ca doped aluminas contained 6.11 mass% Fe and 10.9 mass% Ca respectively, and Fe$_2$O$_3$ or CaCO$_3$ crystals were detected on the alumina surface.

HF-200 activated alumina (Alcoa), which was catalyst-grade alumina (γ-alumina) in the form of sintered beads, was also studied. This alumina contained similar elemental impurities to primary alumina (e.g. Na) but had a significantly increased surface area of 340 m$^2$g$^{-1}$. 
Chapter 9  THE ACTIVITY OF SMELTER-GRADE ALUMINA TOWARDS COS GAS

This chapter reports the results of fluidised bed and DRIFTS experiments to determine the adsorbed species and reaction products after COS has contacted smelter-grade primary alumina in a fluid bed reactor such as a dry scrubber. The interaction between COS and primary alumina usually involves a mixture of COS adsorption, followed by incomplete hydrolysis forming H$_2$S. The dry scrubber is a complex system to predict, containing a number of gases and impurities from the smelting process. As a result, there are several factors in particular, that could affect reaction between COS and smelter-grade alumina in the scrubber. Some of the factors considered include the presence of humidity and other gases like O$_2$, HF and SO$_2$, and changes to the alumina activity, due to the alumina phase, fluorination and impurities.

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<th>Title</th>
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<td>9.7</td>
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</tr>
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<td>SO₂ Fluidised Bed Studies</td>
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<td>Effect of γ-Alumina</td>
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<td>Fluidised Bed Studies of γ-Alumina Activity</td>
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<td>9.11.2</td>
<td>DRIFTS Studies with γ-Alumina</td>
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</tbody>
</table>
9.1 Gas Phase Experiments

Before the effect of contact with smelter-grade alumina on COS stability could be studied, COS and several other gases important to these studies were measured using mass spectrometry and FT-IR (the two major methods for determining gas composition). FT-IR spectra of COS, SO$_2$ and H$_2$S are included for reference in Appendix F.

Gas phase measurement of COS, SO$_2$ and H$_2$S in the mass spectrometer are included in Appendix G. Mass spectrometer measurements were used to calibrate for these sulfur gases (also detailed in Appendix G), which allowed conversion from partial pressure (torr) into concentration (ppmv) and also allowed a sulfur mass balance to be calculated across the fluid bed reactor. Mass spectrometer measurements were performed for an additional reason – to check the stability of COS, SO$_2$ and H$_2$S in isolation and in the presence of other gases, such as humidity and O$_2$.

The most important of these gas phase experiments is the stability of COS in the gas phase in isolation and this is shown in Figure 9.1. The mass balance (in ppmv) from this COS gas phase experiment, shows that the extent of hydrolysis of COS in the gas phase with increasing COS concentration was a linear relationship. In this case, when the maximum COS supply was 187 ppm, the COS outlet concentration was about 171 ppmv, with less than 1 ppm SO$_2$ and approximately 12 ppm H$_2$S forming. The hydrolysis of COS in the gas phase is thermodynamically favourable (see Chapter 7) and occurs according to the reaction:

\[
\text{COS} (g) + \text{H}_2\text{O} (g) \rightarrow \text{H}_2\text{S} (g) + \text{CO}_2 (g)
\]  

(9.1)

It was concluded that while COS is not predicted to be thermodynamically stable, residual water present in the apparatus was sufficient to allow only a small amount of gas phase COS hydrolysis to occur in the absence of alumina. COS was largely stable in isolation, compared to its change in stability in the presence of alumina. Likewise H$_2$S and SO$_2$ were also stable in the apparatus in isolation.
9.2 Effect of Smelter Grade Alumina on COS Gas

COS gas was relatively stable in the gas phase when in isolation (Figure 9.1), with only a small amount of hydrolysis occurring to H$_2$S and no oxidation to SO$_2$. Although the products of disproportionation, elemental sulfur and carbon, could not be detected in the mass spectrometer, there was no evidence of disproportionation in the fluidised bed (in the form of sulfur or carbon deposits). The thermodynamic calculations (see Chapter 7) predicted that in the presence of alumina, the hydrolysis and oxidation of COS would become more favourable at equilibrium.

9.2.1 Fluidised Bed Studies of COS on Alumina

Experiments at 60 and 120 ppmv COS (diluted in Ar) on smelter-grade primary alumina in the fluidised bed reactor were performed at a dry scrubbing temperature of 80ºC. The outlet gas composition was tracked until the system approached steady state (4 – 5.5 hours), as
shown in Figure 9.2 and Figure 9.3 at 60 ppmv COS and Figure 9.4 and Figure 9.5 at 120 ppmv COS. The reactor inlet composition was tracked just prior to the start of the experiment and this is shown at –2 minutes.

Figure 9.2: Sulfur species composition when 60 ppmv COS was passed through a fluidised bed of primary alumina (T = 80ºC, Total Gas = 0.4 Lmin⁻¹, Dilutant = Ar, Mass Alumina = 0.5 g, before September 2001). The reactor inlet gas composition is shown at –2 minutes.

The results at 60 ppmv COS, shown in Figure 9.2, reveal that COS was partially hydrolysed on primary alumina to form H₂S. Studies of COS on Claus catalyst alumina confirm that hydrolysis into H₂S occurs (see Chapter 6 [98, 99, 101]). A mass balance of sulfur gases entering and exiting the reactor determined that some COS was retained in the reactor. This was most likely as adsorbed COS on the alumina surface and is labelled as such in Figure 9.2, which agrees with mechanistic studies into COS hydrolysis on Claus catalyst alumina [94-96]. The rate of COS hydrolysis decreased over time. It was highest during the initial stages of the experiment, where complete conversion of COS was achieved and high levels of adsorbed COS were calculated. The formation of H₂S peaked about 60 minutes into the experiment, and at about 90 minutes unreacted COS levels started to increase. An increase in unreacted COS corresponded to a decrease in adsorbed COS and H₂S formed.
Following filament replacement in September 2001, mass spectrometer measurements of sulfur gases changed slightly, even after the sulfur gases were recalibrated (see Appendix G). The COS on primary alumina experiments were repeated and the results are shown in Figure 9.3 and Figure 9.5. For a 60 ppmv COS inlet (see Figure 9.3), the general trends were the same as in Figure 9.2, except the outlet COS concentration at 300 minutes had increased from 22 ppmv to 34 ppmv. Maximum H$_2$S levels also increased from 30 ppmv to nearly 40 ppmv, but as the system approached steady state, H$_2$S levels were comparable. Filament replacement could have implications for the ioniser in the mass spectrometer with regard to temperature and build up of adsorbed material. These later experiments show that the mass spectrometer results are qualitative rather than fully quantitative, so although an attempt has been made to quantify gas compositions, there is a degree of uncertainty. These results nevertheless show that the relative trends are accurate.

![Graph showing sulfur species composition](image)

**Figure 9.3:** Sulfur species composition when 60 ppmv COS was passed through a primary alumina fluidised bed (after September 2001).

With an inlet COS concentration of 120 ppmv (prior to September 2001), shown in Figure 9.3, complete conversion of COS into adsorbed COS and H$_2$S was also observed. However at this higher inlet concentration, unreacted COS levels increased at about 30 minutes into the
experiment (sooner than the 60 ppmv experiment). Later experiments varying the relative humidity (Section 9.3.1) suggest that this change in the extent of hydrolysis was almost certainly related to the availability of water. The initial high rate of H$_2$S formation was the result of hydrolysis with adsorbed water on the alumina surface. As this adsorbed water on the alumina surface was depleted, residual water in the apparatus was the only source of water, so the extent of COS hydrolysis started to approach that of gas phase hydrolysis (see Figure G.12). As the rate of hydrolysis decreased, adsorbed COS remains on the alumina surface, gradually saturating it and leading to an increase in unreacted COS in the reactor outlet.

![Figure 9.4: Sulfur species composition when 120 ppmv COS is passed through a fluidised bed of primary alumina (before September 2001).](image)

At 120 ppmv COS inlet concentration (after September 2001, see Figure 9.5), outlet COS concentrations were within 10 ppmv at 200 minutes of the previous experiment (see Figure 9.4). The major difference between the two experiments was maximum H$_2$S levels, which were about 60 ppmv prior to September 2001 and about 110 ppmv afterwards. However, as the system approached steady state at 200 minutes, the H$_2$S levels were within 5 ppmv of each other.
Figure 9.5: Sulfur species composition when 120 ppmv COS was passed through a primary alumina fluidised bed (after September 2001).

The total amount of adsorbed COS was calculated for each experiment and converted into a mass percentage of S on the alumina surface. Before September 2001, total adsorbed COS was calculated to be 1.3 mass% of the primary alumina at 60 ppmv COS inlet (Figure 9.2) and 1.6 mass% at 120 ppmv COS inlet (Figure 9.4) over the first 223 minutes of each experiment. After September 2001, total COS adsorbed was calculated at only 0.8 mass% at 60 ppmv COS (Figure 9.3) and 0.3 mass% at 120 ppmv COS experiment (Figure 9.5) in the first 223 minutes of the experiment.

Whereas the adsorbed COS levels are about 20 ppmv approaching steady state in the two experiments prior to September 2001 (Figure 9.2 and Figure 9.4), in experiments after this date adsorbed COS levels are calculated to be zero approaching steady state. Since adsorbed COS is measured indirectly, changes to the calibration of COS and H$_2$S levels affect the mass balance and therefore the amount of adsorbed COS calculated. However, it is likely that adsorbed COS (Al$_2$O$_3$•COS) is still forming as an intermediate in the hydrolysis reaction:

\[
\text{Al}_2\text{O}_3 + \text{COS(g)} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S(g)} + \text{CO}_2 \text{(g)} + \text{Al}_2\text{O}_3 \quad (9.2)
\]
\[
\frac{d\text{COS}_{\text{ad}}}{dt} = r_1 - r_2
\]  \hspace{1cm} (9.3)

Therefore, changes to the amount of adsorbed COS calculated can also be explained by the reaction rates of adsorption and hydrolysis. When the rate of the adsorption step \((r_1)\) is faster than the rate of the hydrolysis reaction \((r_2)\), there will be an accumulation of adsorbed COS, measured as an imbalance across the reactor. If the opposite is true, then according to Equation (9.3) the change in adsorbed COS with time could become negative, until there is no adsorbed COS accumulating in the system.

No significant oxidation of COS to \(\text{SO}_2\) was detected during these experiments. \(\text{CS}_2\) (m/z 76) and \(\text{SO}_3\) (m/z 80) were monitored for several experiments, but there was no change in partial pressure detected for either of these gases during a typical experiment. Gases were sampled at the inlet and outlet 20 minutes after the start of a 60 ppmv COS experiment and measured using an \(\text{H}_2\text{S}\) calibrated GC (Gas Chromatograph at the School of Environmental and Marine Sciences, The University of Auckland). The results of the reactor inlet gas indicated that it contained no \(\text{H}_2\text{S}\), but large amounts of COS were detected. The outlet gas contained no COS and 13 ppmv \(\text{H}_2\text{S}\). These GC results were consistent with mass spectrometer measurements.

Within each period (either before or after September 2001), the 60 and 120 ppmv COS experiments were repeated with very similar composition results. Two major sets of experiments, investigating the effects of \(\text{O}_2\) and alumina impurities, were performed after September 2001. For these experiments, the results must be compared to those in Figure 9.3 and Figure 9.5. All other experiments, including investigations into the effect of humidity, fluorination, \(\text{SO}_2\), \(\text{CO}_2\), \(\text{H}_2\text{S}\), secondary alumina and \(\gamma\)-alumina, the results should be compared to experiments in Figure 9.2 and Figure 9.4.

For one 60 ppmv COS on alumina experiment (prior to September 2001), desorption of gases adsorbed on the primary alumina were tracked in the mass spectrometer after turning off the COS gas flow (prior to September 2001). The results, in Figure 9.6, show that COS concentration levels drop as soon as flow was turned off. \(\text{H}_2\text{S}\) concentration levels were slower to respond, dropping from 21 to 8 ppmv after 30 minutes, then remaining between 5 and 8 ppmv for the next 40 minutes. These results show that COS is more than just physisorbed on the alumina, since it is not desorbed when COS flow is turned off (desorption
would result in much higher COS gas readings after COS flow was turned off). Additionally, the reaction to form \( \text{H}_2\text{S} \) appears to involve the adsorbed COS species, since it took about 30 minutes for \( \text{H}_2\text{S} \) levels to reach steady state after COS adsorption had been halted. This reaction between adsorbed COS and \( \text{H}_2\text{O} \) is slow given the length of time it takes for \( \text{H}_2\text{S} \) levels to reach steady state.

![Figure 9.6: Desorption of sulfur gases following a 60 ppmv COS on primary alumina fluidised bed experiment.](image_url)

**9.2.2 DRIFTS Studies of COS on Alumina**

Based on a sulfur mass balance across the reactor in fluidised bed experiments, it was presumed that some COS was adsorbing onto the alumina surface. Alumina from these fluidised bed experiments was analysed *ex-situ*, using XPS (which gives elemental and chemical state information about the top 5 nm of the alumina surface), but no adsorbed sulfur species were detected. This suggested that any adsorbed species were not strongly enough adsorbed to be retained under the high vacuum conditions of the XPS.
In order to conclusively observe any adsorbed species, a DRIFTS study of COS adsorption on primary alumina was completed. Using a DRIFTS cell, changes to the alumina surface could be observed *in-situ* when COS was added. Pure COS gas was injected into an Ar gas flow (50 mL min\(^{-1}\)), which then passed through a closed DRIFTS cell containing a fixed bed of 0.25 g primary alumina (diluted with 50% CaF\(_2\) to optimise IR absorbance) at 80ºC. By injecting a fixed quantity of gas, the cell cleared quickly and DRIFTS spectra were recorded following each injection until the alumina surface had stabilised. The results of an experiment where 1 mL of COS was injected into the cell containing primary alumina, are shown in Figure 9.7. The spectra were ratioed to a spectrum of the alumina/CaF\(_2\) surface prior to injection (at –2 minutes 22 seconds (-2m22s), in Figure 9.7). The number at the left of each spectrum indicates the time elapsed since injection. Each band is labelled with its wavenumber and likely species assignment, which is either an adsorbed species (ad) or gaseous species (g).

![DRIFTS spectra of primary alumina following a 1 mL injection of COS](image)

*Figure 9.7: DRIFTS spectra of primary alumina following a 1 mL injection of COS (time elapsed after injection is labelled on the left of each spectrum, the injection occurred at 0m0s).*
In Figure 9.7, the main spinning side bands for COS gas were at 2071 and 2051 cm\(^{-1}\), due to the C=O bond, with a smaller band at 2924 cm\(^{-1}\). The C=S bond appears at a lower wavenumber and was not observed in the COS gas phase FT-IR spectrum or the DRIFTS spectra. The gas cleared from the cell after about 7 minutes and the remaining bands at 2098 and 2057 cm\(^{-1}\), slightly different in shape and wavenumber to COS gas, were due to adsorbed COS. An increase in wavenumber of COS on adsorption, as observed here, can be due to an increase in surface Lewis acidity [101]. Adsorbed COS has been reported at 2070 cm\(^{-1}\), in addition to two bands at 1570 – 1470 cm\(^{-1}\) [95], and at 2000 cm\(^{-1}\) [107] in agreement with these findings. However, one conflicting study reported a “slightly perturbed COS” species [101] with bands at 1990 and 1960 cm\(^{-1}\). It was believed in this case that a reduction in electron density of the CO bond in COS after adsorption, resulted in a downwards shift in wavenumber, since O was bonded to the surface.

Further bands observed at 2573, 1582 and 1355 cm\(^{-1}\) were attributed to a hydrogen thiocarbonate (HTC, HCO\(_2\)S\(^-\)) species. Adsorbed HTC has been previously reported after COS adsorption on γ-alumina with similar bands to those observed here [96, 101]. The 2573 cm\(^{-1}\) band was unstable and disappeared after several minutes, while the 1582 and 1355 cm\(^{-1}\) bands were more stable and still present after 15 minutes. This may have been because the 1582 and 1355 cm\(^{-1}\) bands were due to the CO stretch and tended to show strongly in IR, whereas the 2573 cm\(^{-1}\) band was due to the SH stretch, which was not as strong [101]. Alternatively, it could have indicated the conversion of hydrogen thiocarbonate into a thiocarbonate species, or indicate desorbing H\(_2\)S gas – adsorbed H\(_2\)S has been reported with a band at about 2570 cm\(^{-1}\) [114].

Bands at 2342 and 2360 cm\(^{-1}\) were due to CO\(_2\) gas, which may have been due to atmospheric changes outside of the cell. The formation of an unstable adsorbed hydrogen carbonate species (HCO\(_3^+\)) at 1653, 1430 and 1227 cm\(^{-1}\) indicated either that CO\(_2\) adsorbed directly from the injected gas, or was a reaction product from COS hydrolysis. The positions of these hydrogen carbonate bands were confirmed by a DRIFTS experiment in which CO\(_2\) was allowed to adsorb on alumina, with the main bands observed at 1653, 1436 and 1228 cm\(^{-1}\). An increase in OH\(^-\) groups on the alumina surface was indicated by the band at 3750 cm\(^{-1}\). Water loss allows detection of hydroxyl groups on the surface that would otherwise be
invisible to IR due to bonding with water molecules. The broad negative band at around 3000 cm\(^{-1}\) is consistent with this water loss.

As shown in Figure 9.8, a further injection of COS strengthened HTC bands at 1582 and 1355 cm\(^{-1}\) and resulted in an extra band at 1469 cm\(^{-1}\), which was also attributed to adsorbed HTC. Adsorbed COS bands at 2091 and 2058 cm\(^{-1}\) were also stronger after the second injection. Additional activity in the hydroxyl group region (3600 – 3800 cm\(^{-1}\)) and loss of water (broad band between 2500 – 3500 cm\(^{-1}\)) indicated the surface was drying out.

Heat treatment of the reacted alumina sample \textit{in-situ} at 200\(^\circ\)C and 500\(^\circ\)C was performed to check the stability of adsorbed COS species, as shown in Figure 9.9. Each heat treatment involved heating the sample up to temperature in flowing argon and holding at temperature for 30 minutes, before cooling back down to 80\(^\circ\)C to record IR spectra. The adsorbed HTC species were removed at 200\(^\circ\)C, but the adsorbed COS species (with bands at 2089 and 2063 cm\(^{-1}\)) were stable. Subsequent heat treatment at 500\(^\circ\)C removed this latter species. Considerable water (3500 – 3000 cm\(^{-1}\)) and hydrogen carbonate (1700 – 1200 cm\(^{-1}\)) loss

Figure 9.8: Successive DRIFTS spectra following a second 1 mL COS injection on primary alumina (50% in CaF\(_2\)). See Figure 9.7 for the first injection in this experiment.
occurred at both temperatures. Negative bands at 1127 and 996 cm$^{-1}$ could not be assigned to a specific species, but these were frequently observed after heat treatment.

Figure 9.9: DRIFTS spectra before (47m10s) and after heating COS exposed alumina to 200ºC (3h11m) and 500ºC (4h37m).

Figure 9.10: Possible mechanism for COS adsorption and hydrolysis on alumina. Orientation of hydrogen thiocarbonate (HCO$_2$S$^-$) on alumina in the fourth reaction step from [101].

Figure 9.10 shows a possible mechanism for COS adsorption and hydrolysis on alumina, based on the evidence from both fluidised bed and DRIFTS experiments. In this mechanism, COS is first adsorbed on primary alumina, partly as hydrogen thiocarbonate species. This is the likely reaction intermediate for the hydrolysis of COS into H$_2$S, which is then desorbed
from the alumina surface. It appears that water is the limiting reactant, since hydrolysis relies upon adsorbed water on the alumina surface. As a result, in the absence of added humidity, the rate of COS hydrolysis decreases with time and COS begins to saturate the alumina surface.

There is no evidence for H$_2$S reabsorbing, however it appears that CO$_2$, the other product of hydrolysis, does have some short-lived affinity for the alumina surface. Translating these results to a commercial dry scrubber suggests that the hydrolysis of COS into H$_2$S, while potentially controlling the COS emission problem, creates a potential H$_2$S emission problem if H$_2$S does not also adsorb on the scrubbing alumina surface. The interaction between CO$_2$ and alumina is discussed in more detail in Section 9.9 and between H$_2$S and alumina in Section 9.10.

The extent of COS hydrolysis in a commercial dry scrubber must be reasonably small, considering that smelter emission measurements have shown very little, if any, change in COS emission levels before and after dry scrubbing (see Section 2.4). However, if hydrolysis is the dominant COS decomposition reaction in the scrubber, this may partly explain the large variation in measured COS emission levels (approximately 1 – 7 ppmv, see Section 2.4.3), as the humidity at the time of measurement may be significant in determining the final COS concentration leaving the scrubber. Humidity levels were generally not reported in studies of COS emissions from aluminium smelters. The effect of humidity on COS hydrolysis in the dry scrubber is studied in greater detail in the following section.

### 9.3 Effect of H$_2$O

The results in Section 9.2 suggested that humidity levels in the gas phase and adsorbed water on the alumina surface are crucial in COS hydrolysis. Thermodynamic calculations also predicted that the presence of water and alumina together would further reduce the stability of COS (Chapter 7). Humidity and therefore moisture content in the alumina are subject to seasonal changes in the dry scrubber. Experiments were done to investigate the levels of COS hydrolysis that could be achieved with added humidity and to see how depleting the alumina surface of adsorbed water would affect this hydrolysis. Prior to these experiments, the stability of COS together with humidity in the gas phase only was checked and these results
are detailed in Appendix G. To summarise, COS, SO₂ and H₂S each remained largely stable in the gas phase with increasing humidity up to 20 %RH.

### 9.3.1 Effect of Humidity in the Fluidised Bed

Fluidised bed experiments at 100°C with primary alumina at low humidity, 4 %RH, are shown in Figure 9.11 for 60 ppmv COS inlet concentration and Figure 9.12 for 120 ppmv COS. High humidity experiments, at 16 %RH, are shown in Figure 9.13 and Figure 9.14 for 60 and 120 ppmv inlet COS. At high humidity, the data became noisier, but the trends in COS reactivity with humidity are still clear. These results can be compared to experiments with no humidity shown in Figure 9.2 and Figure 9.4.

At 4 %RH, almost no COS was detected exiting the fluidised bed reactor at either COS concentration over the entire duration of the experiment. The results agreed well with thermodynamics which predicted that both hydrated alumina and humidity would decrease the stability of COS approaching equilibrium. The presence of low levels of humidity (Figure 9.11 and Figure 9.12) increased the overall rate of conversion of COS compared to the situation with no humidity present (Figure 9.2 and Figure 9.4).

As the experiment progressed at 4 %RH (Figure 9.11 and Figure 9.12), the level of H₂S detected in the outlet gas stream increased, while the calculated adsorbed COS decreased. This suggests that while adsorption on the alumina surface was fairly rapid, there was a time delay before COS was hydrolysed and desorbed in the form of H₂S.
Figure 9.11: Sulfur species composition when 60 ppmv COS and 4 %RH were passed through a primary alumina fluidised bed.

Figure 9.12: Sulfur species composition when 120 ppmv COS and 4 %RH were passed through a primary alumina fluidised bed.
Figure 9.13: Sulfur species composition when 60 ppmv COS and 16 %RH were passed through a primary alumina fluidised bed.

Figure 9.14: Sulfur species composition when 120 ppmv COS and 16 %RH were passed through a primary alumina fluidised bed.
As the inlet COS concentration increased from 60 (Figure 9.11) to 120 ppmv (Figure 9.12), H₂S levels surpassed adsorbed COS levels sooner, suggesting that the overall rate of hydrolysis had increased.

As humidity was raised to 16 %RH (Figure 9.13 and Figure 9.14), there was clearly less COS conversion, since COS could be detected in the outlet gas even from the start of the experiments. The reduced activity may be due to water competing with COS for active sites on the alumina surface [95].

These results show there is an optimum level of moisture in the gas stream for COS hydrolysis. If the level is too low, the rate of supply of water to the alumina surface limits the hydrolysis. When the level is too high, the water competes with COS for surface sites.

Table 9.1 summarises the calculated percentage of COS adsorbed on alumina over the first 223 minutes of each experiment for various inlet gas compositions, based on the sulfur mass balances (0 %RH results are from Figure 9.2 and Figure 9.4). These calculations show a general increase in the amount of sulfur adsorbed as the inlet COS concentration increases from 60 ppmv to 120 ppmv. The amount of COS adsorbed also appeared to increase with humidity at the higher COS concentration, but there was no trend at the lower COS concentration.

Table 9.1: Calculated mass percentages of COS adsorbed on alumina over the duration of experiments (the first 223 minutes of the experiment, in all cases) and with varying inlet gas compositions.

<table>
<thead>
<tr>
<th>COS Inlet ppmv</th>
<th>Humidity %RH</th>
<th>Adsorbed COS mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>60</td>
<td>4</td>
<td>1.2</td>
</tr>
<tr>
<td>60</td>
<td>16</td>
<td>1.3</td>
</tr>
<tr>
<td>120</td>
<td>0</td>
<td>1.6</td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>2.0</td>
</tr>
<tr>
<td>120</td>
<td>16</td>
<td>2.8</td>
</tr>
</tbody>
</table>
A short experiment to investigate the initial hydrolysis of 60 ppmv COS on dried alumina was performed. A sample of primary smelter-grade alumina was dried at 300°C for 2 hours and then immediately placed in the fluidised bed reactor that had been preheated to 80°C. The results of this experiment, in Figure 9.15, can be compared to those in Figure 9.2 for untreated primary alumina. The maximum H$_2$S levels were not as high as in experiments using untreated alumina. The amount of H$_2$S formed appears to start decreasing towards the end of the experiment, so the steady state concentration is most likely lower than the level reached at the end of the experiment. Adsorbed COS levels remained relatively high throughout the experiment, which probably reflects the reduced competition between water and COS for adsorption sites. Overall, the results show that moisture-depleted alumina reduced the overall hydrolysis of COS into H$_2$S, although COS removal and adsorption on the alumina surface still occurred, probably due to residual moisture present in the apparatus and gas.
9.3.2 Effect of Calcined Primary Alumina Using DRIFTS

DRIFTS experiments to investigate the effect of moisture-depleted primary alumina have an advantage over fluidised bed experiments, because the alumina can be dried *in-situ* at high temperature in a controlled atmosphere before being exposed to COS, reducing the chance for re-adsorption of atmospheric moisture. In addition to removing adsorbed water and changing the surface hydroxyl group population, hydrogen carbonates are also removed, making it easier to identify changes in bands that are in the same wavenumber range, due to COS adsorption and desorption.

A 50% primary alumina sample (ground with 50% CaF$_2$) was calcined *in-situ* with Ar flowing at 500°C for 30 minutes. Following this, the adsorption of a 1 mL injection of COS at 80°C was studied. The results in Figure 9.16 show that the interaction between COS and calcined alumina resulted in narrower bands than in uncalcined (Figure 9.7), because calcining resulted in more specific sites for COS adsorption.

![Successive DRIFTS spectra before and after a 1 mL injection of COS into a cell containing calcined primary alumina (time is 0m0s at injection).](image)

Figure 9.16: Successive DRIFTS spectra before and after a 1 mL injection of COS into a cell containing calcined primary alumina (time is 0m0s at injection).
The adsorbed COS band at around 2060 cm\(^{-1}\) was very small and almost disappeared after 1 hour. The adsorbed COS band at 2094 cm\(^{-1}\) was more stable, but also started to disappear after 1 hour. Of these two bands, the 2060 cm\(^{-1}\) band dominated spectra of uncalcined primary alumina, but this situation reversed for calcined alumina. This shift in wavenumber of the dominant C=O band in the adsorbed COS reveals that the C=O band is weaker in the uncalcined sample, perhaps because it is more strongly bound to the surface.

No 2575 cm\(^{-1}\) band was observed in the calcined sample. Regardless of whether this band is due to adsorbed H\(_2\)S or its precursor, HTC, its absence suggests that less hydrolysis occurs on the calcined surface. Calcining removes hydrogen carbonates, so on subsequent injection of COS, the hydrogen carbonates that reform are more stable (1653, 1434 and 1228 cm\(^{-1}\)) on the calcined alumina compared to the uncalcined sample. HTC species had bands at 1578 and 1328 cm\(^{-1}\), but these were unstable over the hour duration of the experiment. There was another slow-forming band at 1506 cm\(^{-1}\); its identity was unknown. Generally, the formation of hydrogen carbonates dominated over hydrogen thiocarbonate formation during adsorption on calcined (moisture depleted) alumina and the stability of adsorbed COS was reduced overall compared to hydrated alumina.

Overall, these experiments studying the effect of humidity addition or loss to the alumina surface, show how important the concentration of humidity or adsorbed water is in determining the extent of COS hydrolysis. Some smelters have suggested seasonal variations in COS emission levels, indicating that changing humidity levels between summer and winter are affecting the stability of COS in the gas ducting and scrubbing equipment. One group reported COS emission levels were inversely related to SO\(_2\) levels [38]. Meanwhile, the measurement in smelters of H\(_2\)S concentration levels have frequently been neglected, although one study indicates that H\(_2\)S can be present in the gas entering the scrubbing system [5].
9.4 Effect of O$_2$ Gas

Thermodynamic calculations showed that the presence of O$_2$ gas would lead to oxidation of COS into SO$_2$ and SO$_3$ at equilibrium. If alumina was present, then the formation of Al$_2$(SO$_4$)$_3$ was possible at equilibrium. It has been observed that COS exiting the smelting cell with the other anode gases at high temperature is largely oxidised into SO$_2$ on contacting the induced air draft in the cell hood [36]. Therefore, experiments investigating the effect of O$_2$ were conducted under dry scrubbing conditions. COS and SO$_2$ were stable in the gas phase in the presence of O$_2$ gas in the apparatus, however H$_2$S measurement in the mass spectrometer was affected (see Appendix G).

9.4.1 Effect of O$_2$ in the Fluidised Bed

The effect of O$_2$ concentration on the stability of COS in a primary alumina fluidised bed (0.5 g) at 80°C was investigated at 60 ppmv and 120 ppmv COS and O$_2$ concentrations of 0.5%, 1.75% and 3.375% (60ppmv COS only) O$_2$. The results of these experiments can be compared to the COS/primary alumina experiments shown in Figure 9.3 and Figure 9.5.

At 0.5% O$_2$, the results at 60 ppmv COS (see Figure 9.17) and 120 ppmv COS (see Figure 9.18) show that the presence of O$_2$ has not changed the conversion of COS throughout the duration of the experiment (see Figure 9.3 and Figure 9.5 for comparison without O$_2$). The amount of SO$_2$ present increased from 0 ppmv with no O$_2$ to 1 – 2 ppmv at 60 ppmv inlet COS and 3 – 4 ppmv at 120 ppmv inlet COS. There appeared to be an overall reduction in H$_2$S formed, which resulted in increased adsorbed COS at both COS concentrations, more noticeably at 120 ppmv inlet COS.
Figure 9.17: Sulfur species composition when 60 ppmv COS and 0.5% O₂ were passed through a primary alumina fluidised bed.

Figure 9.18: Sulfur species composition when 120 ppmv COS and 0.5% O₂ were passed through a primary alumina fluidised bed.
As the O\textsubscript{2} concentration increased from 0.5% O\textsubscript{2} to 1.75% O\textsubscript{2}, the results at 60 ppmv inlet COS (see Figure 9.19) and 120 ppmv inlet COS (see Figure 9.20) show once again little change in the total amount of COS conversion. The total amount of SO\textsubscript{2} formed has increased at both COS inlet concentrations, but only by a few ppmv. There appears to be a significant reduction in the amount of H\textsubscript{2}S formed.

Figure 9.21 shows the results of an experiment at an O\textsubscript{2} concentration of 3.375% and a COS inlet concentration of 60 ppmv. There did appear to be a small overall reduction in the stability of COS at this O\textsubscript{2} concentration, but with little change in the amount of H\textsubscript{2}S and SO\textsubscript{2} formed (compared to 1.75% O\textsubscript{2}), resulting in an increase in the total amount of COS adsorbed.

SO\textsubscript{3} formation is thermodynamically possible from COS in the presence of high levels of O\textsubscript{2}. SO\textsubscript{3} pressure levels were monitored for one O\textsubscript{2} experiment and although SO\textsubscript{3} was not calibrated for in the mass spectrometer, levels did not appear to change more than background gas levels, indicating that little, if any, SO\textsubscript{3} formed.

Figure 9.19: Sulfur species composition when 60 ppmv COS and 1.75% O\textsubscript{2} were passed through a primary alumina fluidised bed.
Figure 9.20: Sulfur species composition when 120 ppmv COS and 1.75% O₂ were passed through a primary alumina fluidised bed.

Figure 9.21: Sulfur species composition when 60 ppmv COS and 3.375% O₂ were passed through a primary alumina fluidised bed.
The presence of O\textsubscript{2} seems to have had little affect on the stability of COS generally or increase the amount of SO\textsubscript{2} formed, despite thermodynamic predictions that SO\textsubscript{2} formation would be favourable at equilibrium. Although it was difficult to measure H\textsubscript{2}S levels with any accuracy in the presence of O\textsubscript{2}, the results do indicate that less H\textsubscript{2}S formed with increasing O\textsubscript{2} concentrations, leading to increased levels of adsorbed COS, which is shown in Table 9.2.

Table 9.2: Calculated mass percentages of COS adsorbed on alumina over the first 223 minutes of each O\textsubscript{2} experiment, with varying inlet gas compositions.

<table>
<thead>
<tr>
<th>COS Inlet ppmv</th>
<th>O\textsubscript{2} Concentration %</th>
<th>Adsorbed COS mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>60</td>
<td>0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>60</td>
<td>1.75</td>
<td>1.5</td>
</tr>
<tr>
<td>60</td>
<td>3.375</td>
<td>1.8</td>
</tr>
<tr>
<td>120</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>120</td>
<td>0.5</td>
<td>1.6</td>
</tr>
<tr>
<td>120</td>
<td>1.75</td>
<td>1.6</td>
</tr>
</tbody>
</table>

9.4.2 Effect of Air Using DRIFTS

Fluidised bed results suggested that more COS remained adsorbed on the primary alumina surface in the presence of O\textsubscript{2}. The effect of air on the adsorbed COS species on primary alumina (where humidity and O\textsubscript{2} are the active species) was studied. COS was injected (2 mL) onto primary alumina (50% in CaF\textsubscript{2}) in a closed cell at 80ºC with no Argon flow. Successive air injections (50 mL, atmospheric, ambient conditions) commenced 1 minute after injection of COS. Air injections continued until no COS gas remained in the cell.

In the results shown in Figure 9.22, the adsorbed COS band at 2055 cm\textsuperscript{-1} appeared to be stronger compared to the experiment without air (see Figure 9.7) after the same length of time. Initially hydrogen thiocarbonate formation was observed (with bands at 1564 and 1361 cm\textsuperscript{-1}), but this was quickly eclipsed by loss of hydrogen carbonate (with negative bands at 1641, 1505 and 1391 cm\textsuperscript{-1}). Generally, there was much less activity in this region (1650 – 1300 cm\textsuperscript{-1}) than observed without air. The adsorbed COS band at 2055 cm\textsuperscript{-1} was removed after in-situ heat treatment at 500 ºC.
Chapter 9

COS in Air on Primary Al₂O₃

Figure 9.22: DRIFTS spectra of primary alumina following a 2 mL injection of COS and successive injections (50 mL) of air.

The experimental observations, particularly the lack of hydrogen thiocarbonates, suggested that COS stabilised as either unreacted adsorbed COS or was released as H₂S (which was not measured). There are several factors in this experiment that may have impacted the results. Firstly, there was no Ar flow, which may have stabilised adsorbed COS bands more (although there were frequent, relatively large injections of air and COS gas disappeared within 2 minutes). Secondly, atmospheric humidity was present, which would be expected to reduce the stability of adsorbed COS, due to hydrolysis. Thirdly, O₂ was present in the air and this might have stabilised the unreacted adsorbed COS observed.

9.5 Activity of Secondary Alumina Towards COS

Secondary alumina is smelter-grade alumina that has been through the dry scrubbing system. During dry scrubbing, the alumina adsorbs HF, SO₂ and other smelter gases and collects entrained bath and impurities present in the duct gases. Secondary alumina is recycled to the smelting cell, so adsorbed species and impurities are also returned to the cell. It was expected
that these compositional differences would change the activity of the alumina. Secondary alumina experiments can compared to the primary alumina experiments shown in Figure 9.2 and Figure 9.4.

### 9.5.1 Fluidised Bed Studies with Secondary Alumina

An inlet concentration of 60 ppmv COS was passed through a secondary alumina (0.5 g) fluidised bed at 80°C and the outlet gases were tracked for an hour using mass spectrometry, before performing a sulfur mass balance across the reactor. The results in Figure 9.23 show that unreacted COS was detected in the reactor outlet at levels equal to those entering the reactor for the duration of the experiment. The experiment was repeated measuring only COS partial pressure to allow fast sampling times (every 90 seconds), which confirmed that no COS was captured or reacted in the secondary alumina fluidised bed. The low level of hydrolysis into H$_2$S throughout the experiment was consistent with gas phase hydrolysis.

![Figure 9.23](image-url)

**Figure 9.23:** Sulfur species composition when 60 ppmv COS was passed through a secondary alumina fluidised bed. The first data point (at −2 minutes) represents the sulfur species composition prior to contacting secondary alumina.
The results show that there are very few sites for COS adsorption on the secondary alumina surface and that it is inactive towards COS. This is most likely due to adsorbed HF, SO$_2$ and impurities on the secondary alumina surface and these factors were investigated individually in experiments that follow.

### 9.5.2 DRIFTS Studies with Secondary Alumina

With argon gas flowing through the cell, COS adsorption (2 mL injection) on secondary alumina (50% in CaF$_2$) was studied at 80°C. The DRIFTS results, shown in Figure 9.24, show little interaction between COS and secondary alumina, as expected based on fluidised bed experiments. The negative band at 1635 cm$^{-1}$ was a result of water loss over the course of the experiment, due to the drying effect of argon flow rather than the effect of COS injection. After about 10 minutes a band also formed at 1278 cm$^{-1}$, which may represent a type of carbonate or thiocarbonate formation. However, this seems unlikely, given the fluidised bed results, which indicated no adsorption of COS on alumina.

![Figure 9.24: DRIFTS spectra following injection of COS (2 mL) onto secondary alumina (50% in CaF$_2$).](image-url)
The inactivity of secondary alumina, which is alumina that has come from a commercial dry scrubber, shows that additional interactions are occurring to just the simple hydrolysis of COS into H₂S. This is not perhaps unexpected, since the dry scrubber environment is a complicated system, with a number of gases, particulates and adsorbed species on the scrubbing alumina surface present. Two likely species to affect the adsorption and hydrolysis of COS are SO₂ and HF gas. Bearing in mind that smelter grade alumina is not specifically designed for scrubbing, like a catalyst grade alumina would be, the impurities present on the smelter grade alumina surface could also affect the ability of the alumina to adsorb COS and water. All of these factors are studied in the following sections; influence of HF in Section 9.6, influence of SO₂ in Section 9.7 and influence of alumina impurities in Section 9.8.

### 9.6 Effect of HF Gas and Fluorinated Alumina

It has been established that HF adsorption occurs in preference to adsorption of SO₂ on alumina [21]. Adsorption of HF gas in the dry scrubber results in a change to the alumina surface that could also affect the adsorption of COS. Secondary alumina experiments (Section 9.5) indicate that adsorbed HF may prevent COS adsorption. Fluidised bed experiments were carried out to investigate this, where either gaseous HF was added or fluorinated alumina was used in the fluidised bed. These experiments can be compared with primary alumina fluidised bed experiments shown in Figure 9.2 and Figure 9.4.

#### 9.6.1 Fluidised Bed Studies with HF Gas

HF was added using a 10.6 gL⁻¹ solution of HF in H₂O pumped at 0.2 mLmin⁻¹ using a syringe pump to produce around 90 mgNm⁻³ HF and 4 %RH in the gas stream (calculation of HF concentration and humidity are included in Appendix D). Figure 9.25 shows that COS gas was stable in the gas phase in the presence of HF and H₂O at these concentrations (first data point at –18 min). However, after passing through the alumina bed, COS was initially completely converted into primarily adsorbed COS and some H₂S. The concentration of unreacted COS increased much sooner than the equivalent experiment in the absence of H₂O and HF (Figure 9.2). The presence of 4 %RH without HF resulted in complete conversion of
COS within the timeframe studied (Figure 9.11). Therefore, it was concluded that the presence of HF led to a reduction in the total amount of COS adsorbed and reacted.

![Graph showing sulfur species composition](image)

**Figure 9.25:** Sulfur species composition when 60 ppmv COS, 90 mg/Nm$^3$ HF and 4 %RH were passed through a primary alumina fluidised bed.

### 9.6.2 Fluidised Bed Studies with Fluorinated Alumina

By fluorinating a sample of primary alumina to 3 mass% F and then carrying out a separate experiment with COS, humidity did not need to be added during the COS experiment. 60 ppmv COS was passed through a bed of alumina containing 3 mass% F and exit sulfur gases were monitored for just over 3 hours.

The results, shown in Figure 9.26, indicate that the activity of fluorinated alumina lies somewhere between the activity of primary and secondary alumina, confirming the HF gas experiment results. The detected presence of H$_2$S showed that some hydrolysis was occurring, although not to the same extent as for primary alumina (Figure 9.2). In the case of fluorinated alumina, H$_2$S concentration reached a maximum of about 20 ppmv at about 40 minutes. An increase in unreacted COS in the exit gases was observed, with about 30 ppmv
COS detected after 180 minutes (Figure 9.26), compared to less than 10 ppmv COS for the same length of time for the primary alumina experiment (Figure 9.2). Only a small decrease was calculated in the amount of COS attributed to adsorption on fluorinated alumina compared with primary alumina. Overall, COS adsorption was calculated to be about 0.9 mass% S on the alumina over 185 minutes.

![Graph](image)

**Figure 9.26:** Sulfur species composition when 60 ppmv COS was passed through a 3 mass% F alumina fluidised bed.

These results suggest that fluorination reduces the number of sites available for COS adsorption on alumina to a small extent, but more significantly, it inhibits the hydrolysis reaction. However, fluorinated alumina is still more active than secondary alumina with respect to COS, suggesting that other compositional changes on the secondary alumina surface are also affecting COS adsorption and reaction.

### 9.7 Effect of SO₂ Gas

Studies of the Claus process show that sulfation of the alumina surface reduces its activity towards hydrolysis of COS [91, 106]. Fluorinated alumina experiments showed decreased
conversion of COS compared to primary, while secondary alumina was inactive towards adsorption or conversion of COS. SO$_2$ gas is usually present at concentrations an order of magnitude larger than COS entering the dry scrubber [4, 5]. Therefore, adsorbed SO$_2$ could be an important additional factor on the secondary alumina surface contributing to its inactivity towards COS conversion. All SO$_2$ related fluidised bed experiments can be compared with the COS/primary alumina experiments shown in Figure 9.2 and Figure 9.4. Gas phase experiments with COS and SO$_2$, determined that COS was stable in the presence of SO$_2$ (see Appendix G).

### 9.7.1 SO$_2$ Fluidised Bed Studies

Before studying the effect SO$_2$ had on COS adsorption on alumina, SO$_2$ adsorption on alumina was studied in isolation. The concentration of SO$_2$ entering the dry scrubber is usually higher than the concentration of COS by a factor of about 10 [5, 36]. An SO$_2$ inlet concentration of 10$^3$ ppmv was chosen for SO$_2$ experiments; this was nearly twice the COS inlet concentration, but low enough to still observe the competitive adsorption between COS and SO$_2$.

Figure 9.27 shows the sulfur species composition when 10$^3$ ppmv SO$_2$ (diluted in Ar at 0.4 Lmin$^{-1}$) was passed through a fluidised bed of primary alumina (0.5 g) at 80ºC. SO$_2$ saturated the alumina surface rapidly, with the bulk of SO$_2$ adsorption occurring in the first 7 minutes of the experiment. Unlike COS, it was not hydrolysed on the alumina surface. The small amount of H$_2$S present is consistent with gas phase reaction only.

SO$_2$ adsorption on laboratory fluorinated primary alumina (3 mass% F) was also studied and is shown in Figure 9.28. Saturation of the alumina surface was even faster when the alumina was fluorinated, with the bulk of SO$_2$ adsorption occurring in the first 4 minutes of the experiment. This confirmed that fluorination of the alumina surface affected SO$_2$ adsorption [21].
Figure 9.27: Sulfur species composition when 103 ppmv SO$_2$ was passed through a primary alumina fluidised bed.

Figure 9.28: Sulfur species composition when 103 ppmv SO$_2$ was passed through a 3 mass% F alumina fluidised bed.
9.7.2 SO₂ DRIFTS Studies

The adsorption of SO₂ on alumina was also studied using the DRIFTS cell. Although strong gas bands appeared in the FT-IR gas spectrum (Figure F.10), SO₂ gas bands were not as strong in the DRIFTS spectra, which may be because the gas reacted quickly with the alumina surface. Four successive injections of SO₂ (first of 0.2 mL, second - fourth of 0.5 mL) into an Ar stream (50 mL min⁻¹) were passed over primary alumina (30 wt% in CaF₂) at 80°C. DRIFTS spectra were collected immediately after each injection and then repeatedly measured until the spectrum had stabilised, prior to the next injection.

Figure 9.29: DRIFTS spectra of four successive SO₂ injections (1st 0.2 mL, 2nd-4th 0.5 mL) on primary alumina (30% in CaF₂). (-04m33s = prior to injection, 00m00s = immediately after 1st injection (0.2 mL), 12m42s = stable surface after first injection, 22m13s = immediately after 3rd injection (0.5 mL), 35m20s = stable surface after four injections.)

The results (Figure 9.29) of this experiment show the spectrum immediately after the first injection (00m00s) and then successive spectra over the course of the experiment (see Figure 9.29 for details). All spectra were ratioed to the alumina sample prior to injection of any SO₂.
The alumina surface changed quickly on exposure to the first 0.2 mL injection of SO₂ (12m42s, SO₂ gas is at 1371 cm⁻¹), but successive injections did not significantly change the surface further. One of the first things observed was the formation of three negative bands at 1658, 1515 and 1401 cm⁻¹, which corresponded to loss of hydrogen carbonate from the alumina surface.

At the same time a broad band appeared at 1003 cm⁻¹, which was most likely due to the formation of an SO₂ surface species, replacing the hydrogen carbonate on the surface. On subsequent injections, this broad band was partly resolved into several bands.

Aluminium sulfate has bands at 1400 and 1100 cm⁻¹, and is unlikely to form until high temperatures are reached (> 400 ºC) with O₂ present [112]. A low wavenumber band has been reported at around 1060 cm⁻¹ resulting from SO₂ adsorption on γ-alumina and was believed to be a strongly bonded sulfite species [116]. The 1060 cm⁻¹ band was reported to shift to a lower wavenumber (1000 – 900 cm⁻¹) if γ-alumina was substituted with an α-alumina phase. Another study reported a 1020 cm⁻¹ band, which was observed to replace hydrogen carbonate species and was therefore attributed to the formation of a HSO₃⁻ species [111].

An HSO₃⁻ species seems the most likely species to explain the 1003 cm⁻¹ band in the current experiments. The lower wavenumber band observed on smelter grade alumina (1003 cm⁻¹ compared to 1060 cm⁻¹ on γ-alumina) probably reflects adsorption on the different alumina phases present in smelter-grade alumina.

Water loss (2500 – 3000 and 1640 cm⁻¹) was observed over the experiment, due either to SO₂ adsorption or surface drying. The effect of SO₂ injection on OH groups (around 3700 cm⁻¹) was twofold. A loss of free OH groups at 3708 cm⁻¹ was observed over the duration of the experiment, which was probably due to the formation of an adsorbed species at the OH site. A gain in free OH⁻ groups at 3746 cm⁻¹ was also observed at the start of the experiment and this was probably the result of water removal.

Calcining the alumina after SO₂ exposure (500ºC for 30 minutes), led to water and hydrogen carbonate loss and a change in the hydroxyl group population, as shown in Figure 9.30. A
change was also observed in the low wavenumber bands that were believed to be due to SO$_2$ adsorbed species. The dominant bands at 1105 and 1009 cm$^{-1}$ have been shifted to 1027 and 918 cm$^{-1}$ and additional bands have formed at 1281 and 1173 cm$^{-1}$. An HSO$_3^-$ adsorbed species would be less stable at 500ºC, so it is likely to have been converted into a SO$_3^-$ (sulfite) adsorbed species, however very little information is available on bands below 1000 cm$^{-1}$.

![Figure 9.30: Spectra before and after 500ºC heat treatment of primary alumina that has been exposed to SO$_2$. (35m20s = stable surface after four SO$_2$ injections from Figure 9.29, 1h58m = surface after calcining at 500º for 30 minutes.)](image)

A secondary alumina experiment was performed in the same manner as primary alumina experiments to determine the effect of SO$_2$. The results in Figure 9.31 after SO$_2$ injection (2 1 mL injections), show a band formed at 1008 cm$^{-1}$. This band was also observed on primary alumina and was assigned to an HSO$_3^-$ adsorbed species. An unstable band at 1122 cm$^{-1}$ was probably due to gas phase SO$_2$ (see Figure F.10). A series of bands around 1326 cm$^{-1}$ were observed on secondary alumina but not on primary. A number of adsorbed SO$_2$ species are reported to have bands in this range, including physisorbed SO$_2$ (1334 and 1148 cm$^{-1}$), weakly chemisorbed SO$_2$ (1322 and 1140 cm$^{-1}$) [108] and strongly chemisorbed SO$_2$ (1365 and 1060 cm$^{-1}$) [112]. A band at 1326 cm$^{-1}$ has been reported due to adsorbed SO$_2$, which
was removed at 100ºC [116]. Since bands remain at 1374 and 1311 cm\(^{-1}\) after calcining at 500ºC (results not shown), at least some of the bands observed in this experiment must have been due to more strongly adsorbed species. The percentage transmittance of the adsorbed peaks indicated generally that adsorption of SO\(_2\) was not as strong on secondary alumina as it was on primary.

\[\text{Figure 9.31: DRIFTS spectra of secondary alumina (30\% alumina in CaF}_2\text{) before and after SO}_2\text{ injection. (-03m34s = Surface prior to injection, 00m00s = surface immediately after injection, 17m32s = stable surface after injection.)}\]

Despite thermodynamic calculations predicting that SO\(_2\) would form a sulfate species on alumina at equilibrium, this kind of species was not observed experimentally with DRIFTS. Claus catalysis studies suggest that sulfate formation requires a temperature greater than 400ºC and the presence of O\(_2\) in order to occur [112]. Since dry scrubbing temperature is usually much cooler than this, it seems reasonable to discover that sulfation does not occur. The formation of hydrogen sulfite species instead, as predicted from Claus catalysis studies, is more in line with the behaviour of COS and CO\(_2\) (see Section 9.9) on smelter grade alumina. Calcining of the alumina surface after SO\(_2\) exposure, showed that some adsorbed SO\(_2\) species were quite stable, indicating fairly strong adsorption. Therefore, in the absence of HF (which displaces SO\(_2\) on the alumina surface), the alumina surface does have some
limited scrubbing capacity to reduce $SO_2$ emissions. This has implications for recycling the secondary alumina back to the cell as alumina feed, since any stable adsorbed $SO_2$ would also be recycled, potentially increasing the sulfur impurity in the cell.

### 9.7.3 Effect of $SO_2$ on COS Adsorption in the Fluidised Bed

Experiments with $SO_2$ on primary alumina showed that $SO_2$ adsorbed and saturated the available sites on alumina very quickly. Reduced adsorption was observed on fluorinated and secondary alumina. Having established how $SO_2$ behaved in isolation, COS was added into the gas composition to determine how the presence of $SO_2$ would affect COS conversion on alumina.

The results of an experiment conducted in a primary alumina fluidised bed with 60 ppmv COS and 103 ppmv $SO_2$ present in the gas phase at 80°C are shown in Figure 9.32. The results show that there is little change in the total amount of $SO_2$ adsorbed compared to when COS is not present (see Figure 9.27). However, there is a dramatic change in the amount of...
COS adsorbed, with unreacted COS equalling inlet COS concentration after only about 5 minutes. COS concentration increased sooner than SO$_2$, suggesting that SO$_2$ not only reduced the sites available for COS adsorption, but also adsorbed on additional sites compared to COS. As a result of the low levels of COS adsorption, no hydrolysis into H$_2$S was believed to have occurred on the alumina surface – the H$_2$S present was probably from gas phase reactions.

A similar experiment was performed with fluorinated alumina. Experiments between COS and fluorinated alumina showed reduced adsorption (see Figure 9.26) compared to primary alumina (see Figure 9.2). Likewise, SO$_2$ adsorption substantially reduced the adsorption and reaction of COS on the primary alumina surface (see Figure 9.32). When 103 ppmv SO$_2$ and 60 ppmv COS are passed through a 3 mass%F alumina fluidised bed, the combination of these effects can be observed. The results, in Figure 9.33, show that virtually no COS adsorption occurred in this experiment. These results confirmed the hypothesis that the inactivity of secondary alumina towards COS adsorption was due to both adsorbed HF and SO$_2$.

![Figure 9.33: Sulfur species composition when 60ppmv COS and 103 ppmv SO$_2$ were passed through a 3 mass% F alumina fluidised bed.](image-url)
Further experiments with SO\textsubscript{2} were carried out to determine whether SO\textsubscript{2} would displace COS on the alumina surface (or vice versa). The results of one of these experiments in Figure 9.34, show the sulfur species composition when 120 ppmv COS was passed through a fluidised bed containing alumina. The COS gas flow was turned off at 225 minutes and then 103 ppmv SO\textsubscript{2} was passed through the reactor. In Figure 9.34, the inlet gas composition for COS is shown at –2 minutes and the inlet gas composition for SO\textsubscript{2} is at 325 minutes. The results show that after COS flow was turned off and SO\textsubscript{2} supply turned on, the H\textsubscript{2}S concentration rapidly returned to a level consistent with that of gas phase SO\textsubscript{2}. COS concentration also rapidly returned to zero after COS flow had been turned off, therefore there was no evidence that SO\textsubscript{2} replaced COS on the alumina surface. This agreed with the simultaneous COS/SO\textsubscript{2} experiment (see Figure 9.32) where some COS adsorption (although significantly reduced) was observed in the presence of SO\textsubscript{2}.

![Figure 9.34: Sulfur species composition when 120 ppmv COS and then 103 ppmv SO\textsubscript{2} (after 235 min) were successively passed through a primary alumina fluidised bed. The inlet gas composition for COS is at –2 min, and for SO\textsubscript{2} at 325 min. CO\textsubscript{2} gas levels are given as partial pressures (in torr) on the right hand y axis.](image-url)
SO\textsubscript{2}. From DRIFTS results (see Figure 9.29), it was concluded that adsorbing SO\textsubscript{2} displaced adsorbed CO\textsubscript{2} (in the form of hydrogen carbonate) on the alumina surface, so this spike in CO\textsubscript{2} levels was probably due to hydrogen carbonates being released as CO\textsubscript{2}. The spike in adsorbed COS concentration is due to zero gas flow as the gas is switched from COS to SO\textsubscript{2} (adsorbed COS is not measured directly), so does not indicate displacement of adsorbed COS. SO\textsubscript{2} adsorbed and saturated the alumina within 20 minutes or less, but the fact that CO\textsubscript{2} displacement was observed, confirmed that SO\textsubscript{2} did adsorb to a certain extent. Therefore, there must be more sites for SO\textsubscript{2} adsorption on primary alumina, than there are sites for COS adsorption.

Figure 9.35: Sulfur species composition when 103 ppmv SO\textsubscript{2} and then 120 ppmv COS (after 20 min) were successively passed through a primary alumina fluidised bed. The inlet gas composition for SO\textsubscript{2} is at –2 min, and for COS at 96 min.

The reverse experiment, where 103 ppmv SO\textsubscript{2} was passed through a primary alumina fluidised bed for 20 minutes and then 120 ppmv COS was for another 70 minutes, is shown in Figure 9.35. The amount of SO\textsubscript{2} was sufficient to saturate the alumina surface, since outlet levels returned to the inlet concentration of SO\textsubscript{2}. When the gas flow was switched to COS, no reduction in COS levels was detected across the reactor, showing that no COS adsorption
occurred on the alumina surface. These results confirmed that SO$_2$ adsorbed on the same sites as COS and COS did not displace adsorbed SO$_2$ on the alumina.

The results show that SO$_2$, CO$_2$ and COS all adsorbed on the same sites. However, while SO$_2$ displaced CO$_2$ on smelter-grade alumina, there was no evidence that it displaced COS. While some SO$_2$ adsorption can occur after alumina has been exposed to COS, the reverse is not true.

### 9.7.4 Effect of SO$_2$ on COS Adsorption using DRIFTS

![DRIFTS spectra](image)

Figure 9.36: Change in DRIFTS spectra after an injection of COS (5 mL) then SO$_2$ (5 mL). (-02m22s = Background spectrum, 00m00s = Immediately after COS injection, 1h40m = Stable surface after COS injection (sample was left overnight after COS injection), 18h22m = Immediately after SO$_2$ injection, 18h25m = Stable surface after SO$_2$ injection.)

Several DRIFTS experiments were performed to determine whether COS and SO$_2$ adsorb on smelter grade alumina competitively. In the first experiment, 5 mL COS was injected in the cell containing smelter grade alumina (50% in CaF$_2$), then the sample was left overnight to
equilibrate. The following day 5 mL SO\textsubscript{2} was injected. Although the sample was left overnight after COS injection, there was little change to the surface, apart from some water and hydrogen carbonate gain. Leaving the sample overnight did not affect the adsorbed COS peak.

The results (see Figure 9.36) show changes to the alumina surface after COS injection (immediately after injection = 00m00s, stable surface after injection = 1h40m05s), after SO\textsubscript{2} injection (immediately after injection = 18h22m26s, stable surface after injection = 18h25m00s). The results show that while adsorbed COS (2100 and 2060 cm\textsuperscript{-1}) was not displaced by SO\textsubscript{2}, SO\textsubscript{2} did change the alumina surface and a band forms 990 cm\textsuperscript{-1} due to additional adsorption of SO\textsubscript{2}. There was substantial hydrogen carbonate loss on injection of SO\textsubscript{2}, so hydrogen thiocarbonates are probably displaced by hydrogen sulfites, due to their structural similarity.

![Figure 9.37: DRIFTS spectra following injections of SO\textsubscript{2} (6 mL) and COS (6 mL) on primary alumina (50% in CaF\textsubscript{2}). (-02m22s = Background spectrum, 00m00s = Immediately following SO\textsubscript{2} injection, 18m10s = Stable surface after SO\textsubscript{2} injection, 21m07s = Immediately following COS injection, 35m41s = Stable surface after COS injection.)](image-url)
A similar experiment, where 6 mL SO$_2$ followed by 6 mL COS was injected onto primary alumina (50% in CaF$_2$) was performed. In this case, no changes to the alumina surface were observed after COS injection (see Figure 9.37), indicating no COS adsorption occurred.

On the basis of these two experiments, it can be concluded that COS and SO$_2$ share some of the same adsorption sites, but SO$_2$ can adsorb on more sites than COS (maybe because SO$_2$ can displace hydrogen carbonates, but COS cannot). The adsorbed species from COS and SO$_2$ gas do not appear to displace each other on the alumina surface. These DRIFTS results agree well with observations from the fluidised bed experiments.

These results show that in addition to the effect of adsorbed HF, adsorbed SO$_2$ reduces the adsorption and hydrolysis of COS, helping to explain why secondary alumina was so inactive towards COS. Importantly, these results show once again that it is unlikely that COS hydrolysis would occur in a commercial dry scrubber to any significant extent. Therefore, most of the COS gas that survives through the cell ducting will pass through the scrubbing system and stack of a smelter unreacted.

### 9.8 Effect of Alumina Impurities

Secondary alumina contains impurities other than adsorbed F and S species. Pressed powder XRF analysis of primary and secondary alumina samples, showed that secondary alumina had approximately twice the levels of Na, Fe and Ca as primary (see Chapter 8). Primary alumina samples were doped with Na, Fe and Ca to determine how impurities affected the conversion of COS. Characterisation of these aluminas, as well as details on how these samples were prepared are included in Chapter 8.

#### 9.8.1 Fluidised Bed Studies of Alumina Impurities

Fluidised bed experiments with Na, Fe and Ca doped aluminas can be compared to the primary alumina experiments shown in Figure 9.3 (60 ppmv COS) and Figure 9.5 (120 ppmv COS).
Figure 9.38: Sulfur species composition when 60 ppmv COS was passed through a Na treated (0.78 mass% Na) primary alumina fluidised bed.

Figure 9.39: Sulfur species composition when 120 ppmv COS was passed through a Na treated (0.78 mass% Na) primary alumina fluidised bed.
Figure 9.40: Sulfur species composition when 60 ppmv COS was passed through a Fe treated (6.11 mass% Fe) primary alumina fluidised bed.

Figure 9.41: Sulfur species composition when 120 ppmv COS was passed through a Fe treated (6.11 mass% Fe) primary alumina fluidised bed.
Figure 9.42: Sulfur species composition when 60 ppmv COS was passed through a Ca treated (10.9 mass% Ca) primary alumina fluidised bed.

Figure 9.43: Sulfur species composition when 120 ppmv COS was passed through a Ca treated (10.9 mass% Ca) primary alumina fluidised bed.
Results from two fluidised experiments with Na treated alumina (at 80°C) are shown in Figure 9.38 for 60ppmv COS and Figure 9.39 for 120 ppmv COS gas. In the same manner as primary alumina, Na treated alumina experiments show that COS is hydrolysed into H\textsubscript{2}S. The rate of hydrolysis decreases over time, resulting in an increase in unreacted COS levels. No SO\textsubscript{2} forms during the experiments. There is perhaps a slightly lower amount of H\textsubscript{2}S formed at the maximum rate of hydrolysis compared to primary alumina experiments (Figure 9.3 and Figure 9.5), although this is not a significant change.

Fluidised bed experiments for Fe treated alumina are shown in Figure 9.40 for 60 ppmv COS and Figure 9.41 for 120 ppmv COS. The pressure levels appeared to drift slightly over time in the mass spectrometer for these experiments, resulting in an error of about 10%. While there is some H\textsubscript{2}S formation, it is significantly less than for the primary alumina experiments. Unreacted COS levels also increase sooner than for primary alumina, so the adsorption/reaction capacity of Fe treated alumina over primary alumina has been substantially decreased. These results are perhaps not surprising, given the very high level of Fe impurity present.

Fluidised bed results for 60 ppmv COS (Figure 9.42) and 120 ppmv COS (Figure 9.43) in the presence of Ca treated alumina show little COS adsorption, or reaction to H\textsubscript{2}S occurred, compared to primary alumina experiments.

### Table 9.3: Calculated mass percentages of COS adsorbed on alumina over the first 223 minutes of each experiment, with varying inlet gas compositions and alumina impurities.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>COS Inlet ppmv</th>
<th>Adsorbed COS mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
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<td>0.80</td>
</tr>
<tr>
<td>Undoped</td>
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<td>0.30</td>
</tr>
<tr>
<td>Na</td>
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<tr>
<td>Na</td>
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<td>0.75</td>
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<tr>
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<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>120</td>
<td>0.35</td>
</tr>
<tr>
<td>Ca</td>
<td>60</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>120</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Table 9.3 shows the calculated mass percentage of COS to adsorb on the different aluminas studied over the first 223 minutes of each experiment. Interestingly, more COS adsorbed (according to calculations) on Na doped alumina than on untreated alumina. Less COS adsorbed on Fe and Ca treated aluminas than on untreated alumina, as expected from the fluidised bed results. So impurities may either enhance or reduce COS conversion.

9.8.2 DRIFTS Studies of Alumina Impurities

Firstly, the interaction between COS (one 2 mL injection) and Na doped (0.78 wt%) primary alumina (50% in CaF$_2$) was studied. The DRIFTS results are shown in Figure 9.44. Although the band positions were similar compared to untreated alumina (see Figure 9.7), the increase in percentage transmittance of bands at 2068, 1600 and 1346 cm$^{-1}$ indicated that COS adsorbed more strongly on Na doped alumina than untreated alumina. As with untreated alumina, a band was detected at 1468 cm$^{-1}$, but an additional band has formed at 1383 cm$^{-1}$, which was also observed on calcined primary alumina (see Figure 9.16). As with untreated alumina (see Figure 9.9), adsorbed COS was stable at 200ºC, but removed after heat treatment at 500ºC on Na doped alumina.

When adsorption of COS was studied on freshly calcined Na doped alumina (500ºC for 30 minutes), the results in Figure 9.45 show that COS adsorption bands were narrower, reflecting interaction with more specific sites. These narrower bands allowed detection of a previously undetected band at 1281 cm$^{-1}$. As also observed in calcined untreated alumina (Figure 9.16), adsorbed COS in the 2000 cm$^{-1}$ region occurs only at the higher wavenumber of 2094 cm$^{-1}$. As a result of calcining, it can be seen that hydrogen carbonates (at 1655, 1433 and 1228 cm$^{-1}$) were more stable on the surface.

DRIFTS experiments with Na treated alumina showed a stronger interaction between COS and Na treated alumina, than that observed with primary alumina. However, the nature of the adsorbed species were the same with the two types of alumina. Fluidised bed studies confirm that Na treatment does not change the adsorption/reaction significantly, although the adsorption products may be more stable, resulting in a small decrease in H$_2$S formation.
Figure 9.44: Spectra following an injection of COS (2 mL) onto an Na doped primary alumina (50% in CaF$_2$, 0.78 mass% Na).

Figure 9.45: Spectra following an injection of COS (2 mL) onto freshly calcined Na doped primary alumina (50% in CaF$_2$, 0.78 mass% Na).
Similar experiments with Fe doped alumina (6.110 wt% Fe) were performed. Overall, the results in Figure 9.46 show that Fe doped alumina had a weaker interaction with COS than Na doped (Figure 9.44), but a stronger interaction than untreated alumina (based on %T, see Figure 9.7). The bands observed in DRIFTS spectra of Fe doped alumina on exposure to COS were different to those observed with other aluminas. Although adsorbed COS bands at 2085 and 2052 cm\(^{-1}\) were still present, the usual hydrogen carbonate or thiocarbonate bands were not observed in the 1700 to 1200 cm\(^{-1}\) region. Instead, a band formed at 1544 cm\(^{-1}\), with overlapping bands at 1611 and 1586 cm\(^{-1}\). Another possible band formed at 1261 cm\(^{-1}\) and there appeared to be a species lost at around 1640 cm\(^{-1}\) (most likely water) and 1300 cm\(^{-1}\). Adsorbed COS at 2085 cm\(^{-1}\) and the bands around 1550 cm\(^{-1}\) were stable after heat treatment at 200°C, but disappeared at 500°C.

The behaviour of COS adsorption onto Fe doped alumina was more similar to the equivalent untreated alumina experiment (see Figure 9.16) when the Fe doped alumina had been freshly calcined. Figure 9.47 shows that an adsorbed COS band formed at 2071 cm\(^{-1}\), along with small hydrogen thiocarbonate bands at 1583 and 1323 cm\(^{-1}\). As observed previously with freshly calcined undoped alumina, hydrogen carbonate formation dominated over hydrogen thiocarbonate formation.

![Figure 9.46: Spectra following an injection of COS (2 mL) onto Fe doped primary alumina (50% in CaF\(_2\), 6.11 mass% Fe).](image-url)
DRIFTS results determined that the COS adsorption species were different on Fe treated alumina than on primary alumina and that the adsorption species were more stable, which may explain the prompt increase in unreacted COS observed in fluidised bed experiments (see Figure 9.40 and Figure 9.41).

Very little adsorption of COS was observed on Ca doped alumina (10.9 wt% Ca), which could be a result of the very high Ca doping. The results of an experiment where COS was injected (2 mL) on a Ca doped primary alumina (50% in CaF$_2$) in Figure 9.48, showed only weak bands at 2059 (adsorbed COS), 1545 and 1389 cm$^{-1}$ (hydrogen thiocarbonates). The Ca doped alumina has the weakest interaction with COS when compared to untreated, Na doped and Fe doped aluminas. Adsorbed COS was stable after heat treatment at 200ºC, but not at 500ºC, as observed previously. DRIFTS experiment results confirm fluidised bed results, showing that there was little change in the Ca treated alumina surface in the presence of COS.
Figure 9.48: Spectra following an injection of COS (2 mL) onto Ca doped primary alumina (50% in CaF$_2$, 10.9 mass% Ca).

Although some of the impurity concentrations used for these experiments are unrealistically high, the results for Ca and Fe doped aluminas indicate that the presence of these impurities would be unfavourable in terms of maximising COS adsorption and reaction on smelter grade alumina. The results for Na doped alumina, particularly the DRIFTS results, seemed to suggest that the presence of Na may increase the stability of COS adsorbed species. This potential avenue for COS removal would require further investigation to be confirmed. However, the other problems with dry scrubbing COS gas, such as the presence of HF and SO$_2$ remain. Additionally, Na doping of smelter grade alumina for scrubbing has implications for the scrubbing of potentially more dangerous HF gas and the recycling of alumina back to the smelting cell as feed.
9.9 Effect of CO₂

CO₂ is the dominant anode gas under normal cell operation, but is diluted with large enough amounts of air in the cell hood that it is present at less than 1 vol% in the gas entering the dry scrubber. Thermodynamics showed that the presence of high concentrations of CO₂ stabilised COS at equilibrium at 80°C (see Chapter 7). CO₂ was also the reaction product from hydrolysis and oxidation reactions, so its presence in the dry scrubber may decrease the favourability of these reactions. DRIFTS experiments indicated that CO₂ existed on the alumina surface in the form of adsorbed hydrogen carbonates (see Section 9.2.2). All of these factors made it important to investigate the effect of CO₂ gas further.

9.9.1 Fluidised Bed Studies with CO₂

DRIFTS results indicated that when COS adsorbed on smelter-grade alumina, there was an initial unstable increase in bands assigned to adsorbed hydrogen carbonates (see Figure 9.7). Fluidised bed studies were performed to see whether saturating the alumina surface with CO₂ prior to COS adsorption would affect the extent of COS adsorption. It was of particular interest to determine if COS would displace CO₂ on the alumina surface or if a CO₂ saturated alumina would prevent COS adsorption. If CO₂ that formed from COS hydrolysis remained on alumina surface then that would poison the alumina surface, preventing further COS conversion. This experiment can be compared to the COS/primary alumina experiment shown in Figure 9.2.

A 0.5 g sample of primary alumina in the fluidised bed was saturated with 5% CO₂ in Ar. The saturation point was determined when reactor inlet CO₂ concentration equalled reactor outlet CO₂ concentration in the mass spectrometer. After saturation with CO₂, the CO₂ gas supply was turned off and a gas containing 60 ppmv COS was passed through the fluidised bed, tracking the outlet gas composition. The results, in Figure 9.49, show that CO₂ adsorbed and saturated the alumina surface very quickly (less than 1 minute), which was reasonable given the high concentration of CO₂ in the gas stream. When the gas stream was switched from CO₂ to COS, there was a large decrease in CO₂ levels and no unreacted COS was detected.
However, H$_2$S concentration was consistently about 10 ppmv less than when no CO$_2$ was present (see Figure 9.2). COS was not observed to displace CO$_2$ on the alumina surface. Although the presence of extra adsorbed CO$_2$ did not appear to reduce COS adsorption on the alumina surface, an overall decrease in the amount of COS hydrolysis into H$_2$S was observed.

![Figure 9.49: Sulfur species composition when 5% CO$_2$ and then 60 ppmv COS were successively passed through a primary alumina fluidised bed. The inlet gas composition for CO$_2$ is at –2 min, and for COS at 155 min. The gas stream was switched from CO$_2$ to COS after about 10 minutes.](image)

A similar experiment was performed to see whether SO$_2$ displaced CO$_2$ on the alumina surface, which was indicated in DRIFTS experiments (see Figure 9.29). Primary alumina (0.5 g) was saturated with 5% CO$_2$ before the flow was switched to 103 ppmv SO$_2$. The results of this experiment, Figure 9.50, show that again CO$_2$ saturated the alumina surface in less than one minute. SO$_2$ took about the same amount of time to saturate the alumina as observed when the alumina was not pre-exposed to CO$_2$ (see Figure 9.27). Although CO$_2$ was not fully calibrated (conversion from partial pressure to % is based only on the 5% CO$_2$ inlet concentration measurement), it did appear to take several minutes for CO$_2$ concentration to return to zero after SO$_2$ flow was turned on. Given the small amount of alumina present in the
fluidised bed and therefore a relatively limited adsorption capacity, it seems likely that SO$_2$ displaced adsorbed CO$_2$. This was confirmed with DRIFTS experiments (see Figure 9.29).

![Graph showing sulfur species composition](image)

**Figure 9.50:** Sulfur species composition when 5% CO$_2$ and then 103 ppmv SO$_2$ (after 5 min) were successively passed through a primary alumina fluidised bed. The inlet gas composition for CO$_2$ is at –2 min, and for SO$_2$ at 43 min.

### 9.10 Effect of H$_2$S

H$_2$S is the product of COS hydrolysis and could potentially poison the alumina towards further COS hydrolysis if it remained adsorbed. So several experiments were performed to determine the extent, if any, H$_2$S adsorption that would occur on primary alumina.

#### 9.10.1 Fluidised Bed Studies of H$_2$S on Alumina

The results of a fluidised bed experiment where 60 ppmv H$_2$S was passed through a fluidised bed containing primary alumina at 80°C are shown in Figure 9.52. Figure 9.51 shows 60
ppmv H$_2$S tracked over the same length of time in the mass spectrometer when no alumina was present in the fluidised bed.

**Figure 9.51:** 60 ppmv H$_2$S gas diluted in Ar, tracked over several hours in the mass spectrometer (no alumina is present).

**Figure 9.52:** Sulfur species composition when 60 ppmv H$_2$S was passed through a primary alumina fluidised bed.
The H$_2$S concentrations were the same at all times over the duration of both experiments, showing that H$_2$S did not adsorb to any significant extent on smelter-grade primary alumina. It was unclear why H$_2$S levels increased over time in the mass spectrometer with a constant inlet H$_2$S concentration. This effect may have been due to adsorption of H$_2$S on the walls of the mass spectrometer, resulting in a lengthy time before H$_2$S was pumped out of the vacuum system.

9.10.2 DRIFTS Studies of H$_2$S on Alumina

H$_2$S (50 mL injections of 2.5% H$_2$S in H$_2$) was injected into the DRIFTS cell, which contained primary alumina (50% on CaF$_2$ substrate), to determine if any bands due to adsorbed H$_2$S would appear. The spectra in Figure 9.53 show the alumina surface prior to H$_2$S injection (-05m26s), immediately following the first injection (00m00s) and the stable surface after two injections (18m32s).

Figure 9.53: DRIFTS spectra of primary alumina (50% in CaF$_2$) before and after injections of H$_2$S. (–05m26s: prior to H$_2$S injections, 00m00s: immediately following first injection of H$_2$S, 18m32s: spectrum of stable surface after 2 injections.)
The change in percentage transmittance was generally very small, suggesting that any interaction between H$_2$S and smelter-grade alumina was weak. A positive OH$^-$ band at 3746 cm$^{-1}$ (due to the liberation of hydroxyl groups on the surface) and the negative bands due to water loss (1640 and 3500 – 3000 cm$^{-1}$) show that the surface was being dried. Evidence of adsorbed H$_2$S was in an unstable band at 2580 cm$^{-1}$ (which has been previously observed in several studies [113, 114, 122]), appearing immediately following H$_2$S injection (00m00s), but disappearing over minutes. Calcining the alumina after injection of H$_2$S removed the adsorbed H$_2$S band.

![Figure 9.54: DRIFTS spectra following an injection of H$_2$S (50 mL of 2.5% H$_2$S in H$_2$) on calcined primary alumina (50% in CaF$_2$). (-02m02s = Surface prior to injection, 00m00s = surface immediately following injection, 27m04s = stable surface after injection.)](image)

Further information was obtained about the nature of H$_2$S adsorption on smelter-grade alumina by calcining the alumina first, removing hydrogen carbonates which were probably responsible for the bands observed in the 1530 – 1360 cm$^{-1}$ range (see Figure 9.53). Primary alumina (50% primary alumina in CaF$_2$) was calcined at 500ºC in-situ with argon flow for 30 minutes, then H$_2$S was injected (50 mL of 2.5% H$_2$S in H$_2$) at 80ºC. The results, in Figure
9.54, show DRIFTS spectra of the alumina surface prior to injection, immediately after H$_2$S injection and after the surface has stabilised.

The broad water band (3500 – 2500 cm$^{-1}$) indicated that the surface was rehydrating after calcining. Corresponding negative bands around 3700 cm$^{-1}$ were due to a decrease in free hydroxyl groups. Initially, bands were also present at 2585, 1596 and 1331 cm$^{-1}$. The band at 2585 cm$^{-1}$ was previously observed in uncalcined alumina and represents the SH stretching mode of adsorbed H$_2$S, while the 1331 cm$^{-1}$ band was the bending mode of adsorbed H$_2$S. In the final spectrum (27m04s), bands formed at 1621 and 1435 cm$^{-1}$. These indicated the presence of either adsorbed molecular CO$_2$, or dissociatively adsorbed H$_2$S, which was reported with bands at 1596 and 1435 cm$^{-1}$ by [123]. The latter explanation seemed most probable, where the band at 1621 cm$^{-1}$ was the presence of water which formed as H$_2$S dissociated on the alumina surface. The 1596 cm$^{-1}$ band observed initially may have been overshadowed in the 27m04s spectrum by the large 1621 cm$^{-1}$ water band.

These results showed that H$_2$S initially adsorbed directly with bands at 2580 and 1331 cm$^{-1}$, but this species was unstable over time. Eventually, H$_2$S dissociated into an adsorbed species with bands at 1621, 1596 and 1435 cm$^{-1}$. However, the interaction was weak and difficult to observe until the alumina had been freshly calcined.

If H$_2$S has only a weak interaction on smelter-grade alumina, then any COS hydrolysed into H$_2$S on the alumina surface in a commercial dry scrubber, will lead to an increase in H$_2$S gas emissions. So although, COS emissions are reduced, the net sulfur gas emissions would be relatively unchanged due to the emission of equally undesirable H$_2$S.

9.11 Effect of $\gamma$-Alumina

Smelter grade alumina has a much lower surface area (60 - 80 m$^2$g$^{-1}$), and therefore activity, than $\gamma$-alumina (typically >300 m$^2$g$^{-1}$), which is the catalyst used for COS hydrolysis in relation to Claus catalysis. It was expected that having $\gamma$-alumina present in the fluidised bed instead of smelter-grade alumina would enhance COS hydrolysis.
9.11.1 Fluidised Bed Studies of $\gamma$-Alumina Activity

The following $\gamma$-alumina experiments can be compared to smelter-grade experiments in Figure 9.2 and Figure 9.4. In a similar manner to previous experiments, a 0.5 g sample of $\gamma$-alumina beads (340 m$^2$ g$^{-1}$) was placed in the fluidised bed reactor at 80ºC, with an inlet gas composition of either 60 or 240 ppmv COS.

The results of the 60 ppmv inlet COS concentration experiment are shown in Figure 9.55. At this COS concentration, about 25 ppmv unreacted COS and 5 ppmv H$_2$S were detected in the outlet composition, with about 30 ppmv COS calculated to be adsorbed on the alumina. Unlike smelter-grade alumina experiments, little change was observed in the outlet composition over the duration (5 hours) of the experiment. 1.4 mass% COS was calculated to adsorb on the alumina over the first 223 minutes of the experiment, which was very similar to smelter-grade alumina results, despite the very different adsorption behaviour.

![Figure 9.55: Sulfur species composition when 60 ppmv COS was passed through a $\gamma$-alumina fluidised bed.](image-url)
Further fluidised bed experiments were performed at 240 ppmv COS to determine whether saturation of the alumina with COS could be achieved and to determine whether adsorbed S could be detected using available characterisation techniques, including XPS, SEM with EDS and XRF. A gas stream containing 240 ppmv COS in N₂ at 80°C was passed through a γ-alumina (0.5 g) fluidised bed for 5 hours.

The results, in Figure 9.56 show that maximum conversion of COS into H₂S was achieved in the first hour of the experiment. Initially about 160 ppmv COS was adsorbed or hydrolysed on the alumina surface, with the remaining 80 ppmv passing through unreacted. However, conversion of COS decreased over the last hours of the experiment, with nearly 190 ppmv COS passing through the reactor unreacted after 5 hours. This suggested that COS was saturating the surface of the γ-alumina over time, due to limited adsorbed water available for hydrolysis, as was observed with smelter-grade alumina. Proportionately higher COS conversion was observed initially in the 240 ppmv COS experiment compared to 60 ppmv COS, but conversion in the former case was reduced significantly over time. In total, 1.8 mass% COS was calculated to adsorb on γ-alumina in the first 223 minutes of experiment.

Figure 9.56: Sulfur species composition when 240 ppmv COS was passed through a γ-alumina fluidised bed.
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After the experiment, the $\gamma$-alumina from the fluidised bed was visibly yellow, suggesting the presence of elemental sulfur. $H_2S$ gas was smelt when the alumina was removed from the reactor. It was found that the alumina decolourised over several days after the experiment, so reacted $\gamma$-alumina samples were frozen after removal from the reactor, and characterised using XPS, SEM with EDS and XRF with the minimum lag time. Details of the analysis techniques are included in Chapter 8.

No sulfur was detected on $\gamma$-alumina using XPS after 240 ppmv COS adsorption, probably because adsorbed COS was not stable in the vacuum system of the XPS. No visible changes to the $\gamma$-alumina surface were observed after COS adsorption using SEM, and very little (if any) sulfur was detected in EDS spot scans of the alumina surface. However, an increase in sulfur after COS exposure was detected using XRF fused bead analysis, shown in Table 9.4. Generally, the in-situ DRIFTS experiments were more successful at detecting potentially unstable adsorbed COS species.

Table 9.4: XRF fused bead analysis of unreacted and COS exposed (240 ppmv COS for 5 hours) $\gamma$-alumina.

<table>
<thead>
<tr>
<th>Species</th>
<th>Unreacted $\gamma$-alumina mass %</th>
<th>COS exposed $\gamma$-alumina mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Al_2O_3$</td>
<td>99.00</td>
<td>98.00</td>
</tr>
<tr>
<td>$Na_2O$</td>
<td>0.62</td>
<td>0.59</td>
</tr>
<tr>
<td>$SiO_2$</td>
<td>0.25</td>
<td>0.20</td>
</tr>
<tr>
<td>$CaO$</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>$SO_3$</td>
<td>0.06</td>
<td>1.10</td>
</tr>
<tr>
<td>$NiO$</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

9.11.2 DRIFTS Studies with $\gamma$-Alumina

COS (2 injections of 2 mL) was injected into the DRIFTS cell, containing $\gamma$-alumina (50% ground in $CaF_2$) at 80°C. On $\gamma$-alumina, the results in Figure 9.57 show that adsorption of COS occurred with bands at 2100 and 2057 cm$^{-1}$, representing “linear” COS. The shape and position of these bands was similar to that observed in smelter-grade alumina experiments.
Hydrogen thiocarbonates also formed, with bands at 1588 and 1356 cm\(^{-1}\). Despite the large surface area difference between γ-alumina and smelter grade, the two aluminas appear to behave similarly in the presence of COS.

![Successive DRIFTS spectra after COS injection (2 mL injections, 00m00s and 16m46s) on γ-alumina (50% in CaF\(_2\)).](image)

**Figure 9.57:** Successive DRIFTS spectra after COS injection (2 mL injections, 00m00s and 16m46s) on γ-alumina (50% in CaF\(_2\)).

### 9.12 Discussion

Two sets of experiments were performed to determine the behaviour of COS gas on smelter-grade alumina. The first set modelled the dry scrubber in a laboratory scale fluidised bed reactor containing smelter-grade alumina and a mass spectrometer to measure the reactor inlet and outlet gas composition. The second set of experiments investigated the adsorbed COS species that formed on the alumina surface using DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy).

Thermodynamic calculations of the stability of COS at equilibrium in the presence of humidity or gibbsite (Al(OH)\(_3\)) showed that COS would hydrolyse into H\(_2\)S and CO\(_2\). Studies
relating to Claus catalysis, where the objective is to hydrolyse COS into H$_2$S on catalyst grade alumina, seem to confirm that this is the expected reaction arising from this system.

Table 9.5: A summary of experimental results, compared to thermodynamic predictions from Chapter 7 to determine the behaviour of COS in dry scrubbing conditions.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Thermodynamically</th>
<th>Effect on COS Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>COS in isolation</td>
<td>Unstable; disproportionates to S</td>
<td>COS &gt; 90 % stable</td>
</tr>
<tr>
<td>Smelter Grade Primary Alumina</td>
<td>Unstable; hydrolyses to H$_2$S (assuming Al(OH)$_3$)</td>
<td>COS hydrolysed into H$_2$S, activity decreased with time</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Unstable; hydrolyses to H$_2$S</td>
<td>COS &gt; 80 % stable</td>
</tr>
<tr>
<td>H$_2$O and Primary Alumina</td>
<td>Unstable; hydrolyses to H$_2$S</td>
<td>COS hydrolysed into H$_2$S</td>
</tr>
<tr>
<td>O$_2$</td>
<td>Unstable; oxidises to SO$_2$, SO$_3$</td>
<td>Little effect</td>
</tr>
<tr>
<td>O$_2$ and Primary Alumina</td>
<td>Unstable; oxidises to Al$_2$(SO$_4$)$_3$</td>
<td>COS hydrolysed into H$_2$S, activity decreased with time</td>
</tr>
<tr>
<td>Secondary Alumina</td>
<td></td>
<td>Little effect</td>
</tr>
<tr>
<td>HF</td>
<td>No effect; disproportionates to S</td>
<td>Little effect</td>
</tr>
<tr>
<td>Fluorinated Primary Alumina</td>
<td></td>
<td>COS hydrolysed to H$_2$S, alumina activity significantly reduced</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>No effect; disproportionates to S</td>
<td>Little effect</td>
</tr>
<tr>
<td>SO$_2$ and Primary Alumina</td>
<td>Unstable; mix of SO$_2$, S and Al$_2$(SO$_4$)$_3$</td>
<td>COS hydrolysed to H$_2$S, alumina activity significantly reduced</td>
</tr>
<tr>
<td>SO$_2$ and Fluorinated Primary Alumina</td>
<td></td>
<td>COS hydrolysed to H$_2$S, alumina activity further reduced</td>
</tr>
<tr>
<td>Na doped Primary Alumina</td>
<td></td>
<td>COS hydrolysed into H$_2$S, activity decreased with time</td>
</tr>
<tr>
<td>Fe doped Primary Alumina</td>
<td></td>
<td>COS hydrolysed to H$_2$S, alumina activity significantly reduced</td>
</tr>
<tr>
<td>Ca doped Primary Alumina</td>
<td></td>
<td>COS hydrolysed to H$_2$S, alumina activity significantly reduced</td>
</tr>
<tr>
<td>$\gamma$-Alumina</td>
<td>Unstable; disproportionates to S</td>
<td>COS hydrolysed into H$_2$S, activity decreased with time</td>
</tr>
</tbody>
</table>

Initial experiments, simulating dry scrubbing conditions in an aluminium smelter with COS, humidity and smelter grade alumina, also found that COS would be hydrolysed into H$_2$S, although the activity of the alumina was found to decrease over time, relative to the amount
of available adsorbed water or humidity present. Prior to hydrolysis, COS was found to adsorb on the smelter-grade alumina surface, forming adsorbed molecular COS and hydrogen thiocarbonates. Following initial experiments, the effect of different gas compositions and aluminas were investigated. The results from these experiments are summarised in Table 9.5 and compared to predictions from thermodynamic calculations in Chapter 7.

Experiments studying the effect of humidity addition to or loss from the alumina surface (see Section 9.3), show how important the concentration of humidity or adsorbed water is in determining the extent of COS hydrolysis, confirming thermodynamic predictions.

Some smelters have suggested seasonal variations in COS and SO₂ emission levels, with a report by one group that COS emission levels were inversely related to SO₂ levels [38]. One study indicates that H₂S is present in the gas entering the scrubbing system [5]. This indicates that changing humidity levels and temperatures between summer and winter may be affecting the stability of COS in the gas ducting and scrubbing equipment, especially given the strong effect humidity was found to have on COS experimentally.

In a commercial dry scrubber, the hydrolysis of COS into H₂S however, could create undesirable H₂S emissions instead of COS emissions, especially since H₂S does not have a strong affinity for the surface of smelter grade alumina. Unfortunately, humidity levels were not reported in studies of COS emissions from aluminium smelters, but if hydrolysis is the dominant COS decomposition reaction in the scrubber, this may partly explain the large variation in measured COS emission levels, as the humidity at the time of measurement may be significant in determining the final COS concentration leaving the scrubber.

Smelter emission measurements, summarised in Section 2.4, show that there is only a very small decrease in COS emission levels before and after dry scrubbing. This suggests that the overall extent of hydrolysis in a commercial dry scrubber must be quite small. Alumina that has been used in a commercial dry scrubber, known as secondary alumina, was found to be inactive in laboratory experiments towards COS adsorption and hydrolysis (see Section 9.5). This was the first indicator that interactions are occurring in addition to the hydrolysis of COS into H₂S.
Two likely species to affect the adsorption and hydrolysis of COS are \( \text{SO}_2 \) and HF gas. A previous study found that HF gas displaced \( \text{SO}_2 \) on smelter grade alumina [21], so it is feasible that HF will also affect COS adsorption and hydrolysis. In the laboratory, fluorination of the smelter grade alumina surface was found to reduce the number of sites available for COS adsorption on alumina and to inhibit the hydrolysis reaction (see Section 9.6). However, while fluorinated alumina is less active than untreated primary smelter-grade alumina, it is still more active than secondary alumina with respect to COS, suggesting that other compositional changes on the secondary alumina surface are also affecting COS adsorption and reaction.

Despite thermodynamic calculations predicting that \( \text{SO}_2 \) would form a sulfate species on alumina at equilibrium, Claus catalysis studies suggest temperature (greater than 400\(^\circ\)C) and the presence of \( \text{O}_2 \) are required in order for sulfate formation to occur [112]. The dry scrubber is much closer to ambient temperature and sulfate species were not observed experimentally with DRIFTS when \( \text{SO}_2 \) adsorbed on smelter grade alumina. However, \( \text{SO}_2 \) did adsorb in the form of predominantly hydrogen sulfite species, in line with the behaviour of COS and \( \text{CO}_2 \) (see Section 9.9) on smelter grade alumina. Some adsorbed \( \text{SO}_2 \) species were found to be quite stable, indicating fairly strong adsorption. Therefore, smelter grade alumina does have some limited capacity to reduce \( \text{SO}_2 \) emissions, provided no HF is present. This has implications for recycling the secondary alumina back to the cell as alumina feed, since any stable adsorbed \( \text{SO}_2 \) would also be recycled, potentially increasing the sulfur impurity in the cell.

Further experiments showed that COS and \( \text{SO}_2 \) share some of the same adsorption sites, but \( \text{SO}_2 \) can adsorb on more sites than COS, maybe because \( \text{SO}_2 \) can displace hydrogen carbonates, but COS cannot. Based on DRIFTS results, the adsorbed species from COS and \( \text{SO}_2 \) gas did not appear to displace each other on the alumina surface.

The \( \text{SO}_2 \) experiments show that in addition to the effect of adsorbed HF, adsorbed \( \text{SO}_2 \) dramatically reduces the adsorption and hydrolysis of COS, helping to explain why secondary alumina was so inactive towards COS. Importantly, these results show that COS hydrolysis would occur in a commercial dry scrubber to only a limited extent and that the majority of COS surviving through the cell ducting will pass through the scrubbing system.
and stack of a smelter unreacted. Therefore, conventional dry scrubbing in aluminium smelters is not an effective way to reduce COS emissions.

Unlike a catalyst grade alumina, smelter grade alumina cannot be specifically designed for scrubbing alone and as a result, can contain other impurities, which affect its scrubbing ability. Although quite high impurity concentrations were used in laboratory experiments (see Section 9.8), the results for Ca and Fe doped aluminas indicate that the presence of these impurities would reduce COS adsorption and reaction on smelter grade alumina. The results for Na doped alumina, particularly the DRIFTS results, seemed to suggest that the presence of Na may increase the stability of COS adsorbed species. This potential avenue for COS removal would require further investigation to be confirmed. However, this doesn’t change the fact that preferential adsorption of HF and SO₂ would still occur in the scrubber. Na doping of smelter grade alumina for scrubbing would also have implications for the scrubbing of other gases and recycling of impurities to the smelting cell.

Overall, the presence of HF, SO₂ and impurities in a commercial dry scrubber make the adsorption and hydrolysis of COS unlikely.
Chapter 10  CONCLUSIONS

10.1 Introduction

Few studies of carbonyl sulfide (COS) in aluminium smelting have been published, and the significance of this gas has only recently been noted. The source of COS and other sulfur gases is in the petroleum cokes used to make anodes, which are consumed during aluminium smelting, but the exact form of sulfur in the anode has not been confirmed [3].

The presence of COS in anode gas was first noted and published in 1957 [37], but it wasn’t until publications in 1995 indicated that aluminium smelters contributed significantly to anthropogenic COS emissions in the global atmospheric budget that interest in these emissions was renewed [6, 7]. Smelter measurements indicate that COS is the dominant sulfur gas to form at the anode face, but most is subsequently oxidised into SO\textsubscript{2} in the cell hood. Despite this, some COS does survive in the cell ducting leading to the dry scrubber and there appears to be very little reduction in COS levels through the scrubbing systems [4, 5, 38].

The following sections describe the major conclusions of this thesis, from the exact nature of the source of sulfur in aluminium smelting, through to mechanistic studies on the effectiveness of COS capture in the dry scrubbing system.

10.2 Sulfur Speciation in Anodes Using XANES

XANES (X-Ray Adsorption Near Edge Structure) was used successfully to determine the nature of sulfur species present in anodes and cokes, which are the major source of sulfur in aluminium smelting.
A detailed analysis of sulfur reference compounds using XANES determined that all major classes of inorganic S species could be distinguished from each other, based on oxidation state edge shifts at the K-edge. For the organic sulfur species, the XANES K-edge of C-S-C species was similar, but the fine structure at the L-edge for these sulfur species was quite distinctive. Measurement of small and larger polymeric organic structures, found that the size of the sulfur containing structure did not affect the XANES spectra, validating the use of small-molecule reference spectra to identify the sulfur species in much larger-molecule coke and anode materials.

Petroleum coke is the major component and the major source of sulfur in anodes. A study of eight petroleum cokes from different sources, representing the dominant suppliers to the aluminium industry, was carried out using XANES. Some variation in sulfur speciation occurred from cokes of different origins, although the dominant species were usually sulfur containing organic ring structures. From comparison of peak shape and position in reference and coke spectra, thiophenic sulfur (sulfur in a 5-membered ring) was the major sulfur species for one coke studied, but sulfur in a 6-membered ring or a mixture of 5- and 6-membered ring sulfur were usually the major sulfur species. Lesser amounts of S-S sulfide (e.g. pyrite or elemental sulfur) and sulfate bonding were observed in the most of the petroleum cokes studied.

Peak modelling was performed, where various reference sulfur species spectra were summed to fit coke spectra, using a difference of least squares fit. Peak modelling often favoured thiophenic sulfur over sulfur in a 6-membered ring. However, peak modelling was necessarily performed with K-edge spectra, which were very similar for sulfur ring structures. Previous XANES studies of fossil fuel materials such as coal support the conclusion that cyclic sulfur structures are the dominant sulfur species in petroleum cokes [62].

A suite of anodes were studied using XANES, along with their source coke. The anodes studied consisted of:

- Four anode samples, that had been baked at a different temperatures between 940ºC and 1280ºC,
- An anode butt from a smelting cell,
Two anode samples, initially baked at 940°C, which were rebaked at 1400°C and 1500°C.

The dominant sulfur species in the source coke was sulfur in a 6-membered ring, or a similar ring structure. XANES analysis of the anodes indicated that speciation did not change significantly in this regard after anode baking or usage in the cell. A small increase in sulfate species with increasing baking temperature was observed, along with evidence of graphitisation and desulfurisation occurring during anode baking and soak time (following anode usage in the cell). However, quantification of sulfur species did not result in any trend in the amount of sulfate present with baking temperature or usage. Significant desulfurisation did not occur until temperatures exceeded 1400°C in agreement with the observations of [151], however this is not accompanied by significant changes in speciation. High levels of desulfurisation occurred in the anode sample rebaked at 1500°C, but even this failed to reduce the stability of the dominant organic sulfur ring structures present.

Overall, it appears that the nature of the source coke predominantly determines the sulfur speciation of the resulting anode regardless of baking temperature. In both petroleum cokes and anodes, sulfur in organic ring structures were the dominant sulfur species present.

### 10.3 Thermodynamic Calculations for the Formation of COS

A thermodynamic study to predict COS formation at the anode at equilibrium was performed, starting with various sulfur species in the anode, including thiophenic sulfur. Only very minor changes in the equilibrium composition at 970°C were observed when the source sulfur species in the anode was changed. However, anode sulfur gas compositions similar to those measured in commercial smelting cells, where COS was the dominant sulfur gas, were predicted at equilibrium [36]. COS gas was the stable sulfur species at equilibrium up to CO₂/CO ratios of 90:1, beyond that SO₂ gas was favoured.

When modelling the equilibrium composition of sulfur gases leaving the cell, COS is stable with temperature from 970°C down to about 300°C, at which point elemental S is favoured. However, when atmospheric air is added, as is the case in the cell hooding, SO₂ is the stable species down to 500°C, then H₂SO₄ is favoured down to 0°C. The oxidation of the majority of
COS into SO$_2$ in the cell hooding has previously been observed in smelting cells [36]. However, since 100% conversion of COS is not achieved in smelters, it is clear that thermodynamics alone do not determine sulfur gas speciation. This leads to the conclusion that the kinetics of COS decomposition must also play an important role in determining the sulfur gases which enter the dry scrubber.

**10.4 Thermodynamic Calculations of COS Stability in Dry Scrubbing**

COS is not stable at equilibrium at 80ºC (dry scrubbing temperature), even in isolation, where it disproportionates into elemental sulfur and carbon, and CO$_2$ gas. The presence of alumina, if it contains water, as modelled by the gibbsite Al(OH)$_3$ surface, reduces the stability of COS further at equilibrium, leading to hydrolysis into H$_2$S. Hydrolysis also occurs in the gas phase in the presence of humidity.

The presence of O$_2$ gas leads to the oxidation of COS into either SO$_2$ or SO$_3$ gas. If alumina is also present, COS stability is further reduced, forming Al$_2$(SO$_4$)$_3$ at equilibrium. The presence of high levels of CO$_2$ gas however, increases the stability of COS. The effect of other dry scrubbing gases, such as CO, HF, SO$_2$ and H$_2$S were investigated, but these gases have less impact on COS stability at equilibrium. In thermodynamic modelling of the dry scrubber as a complete system, the most favoured path for COS destruction is to form Al$_2$(SO$_4$)$_3$•6H$_2$O at equilibrium.

**10.5 COS Hydrolysis on Smelter-Grade Alumina**

Contrary to thermodynamic predictions, mass spectrometer measurements showed that in experimental studies, COS was stable in the absence of alumina through the experimental apparatus. COS, H$_2$S and SO$_2$ gases were all successfully measured using both mass spectrometry and FT-IR, which were the two major methods used for studies of COS adsorption and reaction on smelter-grade alumina.

In the presence of smelter-grade alumina in a fluidised bed reactor, COS adsorbed on the alumina surface and was then hydrolysed producing H$_2$S gas, which was detected using mass
spectrometry. The activity of the alumina decreased with time, which is attributed to adsorbed water being the limiting reactant available for hydrolysis, resulting in a decrease in H₂S formed and COS saturating the alumina surface. Eventually COS largely passes through the fluidised bed unreacted.

A high level of COS adsorption and hydrolysis could be maintained over a number of hours, if a low level of humidity (4 %RH) was added in the gas stream passing through the fluidised bed. However, excessive humidity (16 %RH) reduced the overall amount of COS conversion, probably due to H₂O competing with COS for adsorption sites on the alumina surface.

It was suspected that COS was adsorbed on smelter-grade alumina, based on calculation of a sulfur mass balance across the fluidised bed. However, the adsorbed species did not seem to be stable outside of the fluidised bed reactor. FT-IR studies, using a DRIFTS cell containing smelter-grade alumina, confirmed the presence of this adsorbed species. Based on previous studies of COS adsorption on γ-alumina [96, 101], the adsorption bands in the DRIFTS spectra were assigned to adsorbed molecular COS and adsorbed hydrogen thiocarbonates (HCO₂S⁻). The former species was stable to 500ºC when heated in the DRIFTS cell. The latter species was removed at 200ºC and is likely to be an intermediate in the hydrolysis of COS, producing H₂S.

The addition of O₂ gas in COS/smelter-grade alumina fluidised bed studies had little effect on COS hydrolysis, despite thermodynamic predictions of oxidation to SO₂. Of the other gases of interest, HF is known to adsorb strongly on alumina [134], and fluorination of smelter-grade alumina in the fluidised bed was found to reduce adsorption of COS and resulting hydrolysis, possibly due to a reduction in available water and surface sites on the alumina after HF adsorption.

Using the fluidised bed and DRIFTS analysis, SO₂ was found to also adsorb strongly and saturate the alumina surface relatively quickly compared to COS. Although SO₂ was not observed to adsorb in preference to COS, its presence did result in a significant reduction in the amount of COS adsorbed in fluidised bed studies. DRIFTS studies showed that the nature of adsorbed species due to SO₂ and COS were similar and fluidised bed studies showed that
COS did not adsorb after saturation of the alumina by SO$_2$, so it is concluded that COS and SO$_2$ share the same adsorption sites.

A combination of adsorbed SO$_2$ and HF lead to almost no COS adsorption in the fluidised bed. This explained why secondary alumina, which is smelter-grade alumina that has been used for dry scrubbing, was also inactive towards COS, based on both fluidised bed and DRIFTS results.

DRIFTS studies showed that there is always some adsorbed CO$_2$, in the form of hydrogen carbonates, present on the alumina surface. Despite this, CO$_2$, one of the two products of COS hydrolysis, did not appear to have a strong effect on the overall rate of COS conversion. H$_2$S, the second hydrolysis product, was found to have very little affinity for the alumina surface in DRIFTS and fluidised bed experiments.

The effect of impurities on the reactivity of the alumina surface was also investigated. The presence of 0.8 mass% Na, had little effect on COS adsorption and hydrolysis in the fluidised bed. DRIFTS studies indicated that the presence of Na may have made adsorbed COS species more stable. The presence of 6 mass% Fe or 11 mass% Ca (based on XRF analysis), both appeared to significantly reduce COS adsorption and therefore hydrolysis in the fluidised bed. Using DRIFTS, very little COS adsorption was observed on Ca treated alumina. Some adsorption occurred on the Fe treated alumina, but it was of a slightly different nature to COS adsorption on untreated smelter-grade alumina.

When $\gamma$-alumina was substituted for smelter-grade alumina in the fluidised bed reactor, the rate of COS conversion did not decrease as much with time, which is probably due to the significantly larger surface area (and therefore greater capacity for adsorbed water) on the surface of $\gamma$-alumina. The adsorbed species observed in DRIFTS studies on $\gamma$-alumina are the same as those on the smelter-grade material. While hydrolysis producing H$_2$S in the fluidised bed was still detected, the high initial rate of COS conversion achieved on smelter-grade alumina was in fact not achieved on $\gamma$-alumina. So smelter-grade alumina, despite its relatively low surface area, is the better alumina of the two for high initial rates of COS conversion. However, over time the COS conversion rate on $\gamma$-alumina surpasses that of smelter-grade when no humidity is added into the system.
10.6 Industrial Implications

Removing COS from the duct gas using smelter grade alumina in the dry scrubber is an attractive proposition, since the existing commercial dry scrubbers in aluminium smelters could be used, requiring no further investment and using materials (such as alumina) already required for the process. This must be considered with the caveat that the adsorbed/reacted S species would subsequently be returned to the cell with the secondary alumina. However, this study has shown that while smelter-grade alumina is active towards COS adsorption and hydrolysis, this reaction does not proceed in the presence of HF and SO₂. Therefore, while this reaction is useful in Claus catalysis, where the levels of SO₂ can be controlled and HF is not present, it makes COS hydrolysis on the alumina surface of limited use in the dry scrubbers at aluminium smelters.

Using existing plant technologies to remove COS, the cell gases would first have to pass through dry scrubbers to remove HF, then wet scrubbers to remove SO₂, before passing again through another dry scrubber to remove COS. The resulting formation of H₂S would need to be dealt with separately. Of course, any extra equipment would be limited by the space available at the site and must be obtained for the least cost, with minimum possible pressure drop. Given the huge volumes of gas to be processed, the low concentrations of COS present and the relative slowness of the adsorption/reaction, this process seems unfeasible.

Any process that consumes fossil fuels has a potential sulfur gas emission problem. There may be an existing process that could be modified for the aluminium industry that could remove COS and other sulfur gases downstream from where they are formed. The difficulty is finding one of these processes that is both effective and feasible in terms of capital investment to install the necessary equipment. The trend of increasing sulfur impurities in petroleum cokes and the inevitability of more stringent emissions regulations in the future, may force aluminium smelters to consider a new process in this manner.

The advent of inert anode technology, if and when it becomes feasible, will overcome the need for sulfur containing anodes. In the meantime, another option for removing the sulfur at its source, but one which is dependant on coke suppliers, is by desulphurising the coker feed.
Desulfurisation is of course essential to the rest of the refinery operation but can lead to higher S in the effectively waste product coker feed. Desulfurisation of coker feed can be made profitable by the refining and selling of its byproducts, elemental sulfur and light hydrocarbons. As the sulfur content of cokes increases, as lower quality crude oils are used, perhaps advances in this desulfurisation process will become necessary.

Understanding the formation mechanism of COS better at the anode may lead to a solution to the problem of COS emissions in aluminium smelting. Knowing both the type of sulfur species present in the anode, and the conditions which optimise conversion to \( \text{SO}_2 \) and \( \text{CO}_2 \) is a start in this respect. The simplest solution for removing COS emissions from aluminium smelters is to ensure that all the COS formed at the anode is oxidised into \( \text{SO}_2 \) on leaving the cell and entering the ducting to the dry scrubber. COS levels are already significantly reduced on leaving the cell and being mixed with the induced air draft in the cell hood. There is some suggestion from smelters that there is seasonal variation in the COS/\( \text{SO}_2 \) balance, suggesting that atmospheric and temperature changes can influence the final sulfur gas composition. Thermodynamic calculations show also that COS is completely oxidised into \( \text{SO}_2 \) at equilibrium. It may be possible to control this oxidation reaction:

- Using insulation, or perhaps heating, of gas ducts to control temperature
- Altering gas flow rate or adding a gas holding tank to allow the duct gases to be held for a longer period of time at high temperatures, ensuring more complete oxidation.
- Altering air flow in the cell hooding. Increased oxygen levels in the induced air draft may influence the extent of COS oxidation into \( \text{SO}_2 \).
Chapter 11  REFERENCES


APPENDICES

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APPENDIX A: Glossary for XANES Theory

Atomic Absorption Coefficient

The atomic absorption coefficient, \( \alpha \), is related to the atomic cross section for absorption (the likelihood of absorption depends largely on the cross section of the atom being bombarded), \( \sigma \):

\[
\alpha = n \sigma \tag{A.1}
\]

- \( n \) = Atomic density \((10^{24} \text{ atoms cm}^{-3})\)
- \( \alpha \) = Atomic absorption coefficient \((\text{cm}^{-1})\)
- \( \sigma \) = Cross section of absorption atom \((\text{barn/atom, where 1 barn} = 10^{-24} \text{ cm}^2\))

Atomic absorption can be considered in terms of a one electron excitation from the deep 1s and 2p shells or the shallow 3p, 3d and 4d shells and multielectron excitations [73].

The total electron yield, fluorescence yield and Auger electron yield are proportional to absorption, and so these yields are often measured in experiments to represent absorption. As atomic number \( Z \) decreases, the fluorescence yield decreases and Auger electron yield increases. For S L-edge, the fluorescence yield is 0.03%, while Auger electron yield is 99.97%. For S K-edge, the fluorescence contribution increases to 8% [62].

Hamiltonian (H)

The Hamiltonian is an expression for the total energy of a mechanical system in terms of momenta and positions of constituent particles [130]. In quantum mechanics, the Hamiltonian operator appears in the eigenvalue equation:
\[ H\Psi = E\Psi \]  \hspace{2cm} (A.2)

\( E \) = Energy eigenvalue
\( \Psi \) = Corresponding eigenfunction

**Schrödinger Equation**

The Schrödinger equation is the basic equation of wave mechanics [130]. For time independent systems, this equation takes the form:

\[-\left( \frac{\hbar}{2m} \right) \nabla^2 \Psi + V\Psi = E\Psi \]  \hspace{2cm} (A.3)

\( \Psi \) = Wavefunction
\( V \) = Potential energy, expressed as a function of spatial co-ordinates
\( E \) = Energy eigenvalue
\( \nabla^2 \) = Laplacian operator
\( \hbar \) = Planck’s constant divided by \( 2\pi \)
\( m \) = Mass

**Work Function (\( \phi \))**

The energy difference between an electron at rest at infinity and an electron at the Fermi level in the interior of a substance is the work function [130]. It is thus the minimum energy required to remove an electron from the interior of a solid to a point just outside the surface.
### APPENDIX B: Sulfur Speciation Nomenclature

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-C-S-H</td>
<td>Thiol</td>
</tr>
<tr>
<td>R-C-S-C-R</td>
<td>Sulfide</td>
</tr>
<tr>
<td>R-C-S-S-C-R</td>
<td>Disulfide</td>
</tr>
<tr>
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<td>Thiophene</td>
</tr>
<tr>
<td><img src="image" alt="6-membered heterocyclic S" /></td>
<td>6-membered heterocyclic S</td>
</tr>
<tr>
<td>R-S-R</td>
<td>Sulfoxide</td>
</tr>
<tr>
<td>R-S-O-R</td>
<td>Sulfone</td>
</tr>
<tr>
<td>R-S-O-O-R</td>
<td>Sulfonate</td>
</tr>
</tbody>
</table>
APPENDIX C: Peak Models for Cokes and Anodes

Two examples of the model fitting used in Chapter 5 to calculate sulfur compositions in cokes and anodes are included here in Figure C.1 (for a coke) and Figure C.2 (for an anode). In both figures, the actual sample (coke or anode) spectra is in dark blue and the model for that spectra (sum of reference spectra) is in pink. At the bottom of the key, “TOTAL” indicates the total of the different proportions of reference spectra (1 is ideal) and “least squares” is the sum of the difference between the sample and model spectra squared at each data point. This latter value gives an indication of the model fit (0 is ideal) – however, it is only a relative term to compare to other model spectra. The number beside each reference spectrum in the key is the proportion of that reference spectrum used in the model – this indicates the %S present in that form in the sample.
Figure C.1: An example of model fitting using reference spectra for a coke sample containing 2.73%S.

Figure C.2: An example of model fitting using reference spectra for an anode sample baked at 944°C.
APPENDIX D: Humidity and HF Solution Calculations

Humidity Calculations

4, 16 and 20% RH (relative humidity) were initially specified for fluidised bed humidity experiments. Using a psychometric chart[152] these values were converted to a mass of water per mass of air value at a temperature of 80ºC as follows:

4% RH = 0.115 lb water/lb dry air
20% RH = 0.0635 lb water/lb dry air.

Using the relationship 1 pound mass = 453.5924g [152], these values were converted into g/g units:

4% RH = 11.36 g water/g air
20% RH = 62.71 g water/g air.

Then they were converted to pumping flow rates as follows:

Density (water, 80ºC) = 972 kgm$^{-3}$
Density (air, 80ºC) = 0.29016 kgm$^{-3}$

4% RH = 0.28 mLhr$^{-1}$
20% RH = 1.55 mLhr$^{-1}$ [153].

These pumping rates were then corrected for due to the syringe pump that was used using the pump calibration in Figure 8.6:

4% RH = 0.2 mLhr$^{-1}$
20% RH = 1.2 mLhr$^{-1}$.

These values agreed with Gillespie’s work [154].
HF Solution Calculations

The HF concentration in the experiments was specified to be 80 – 100 mgNm\(^{-3}\), with a RH of 4% and a gas flow rate of 0.4 Lmin\(^{-1}\). The humidity requirements meant that the syringe pump needed a flow rate of 0.2 mLhr\(^{-1}\). Using the gas flow rate of 0.4 Lmin\(^{-1}\) and 90mgNm\(^{-3}\) HF, the amount of HF per hour was calculated to be 2.16 mghr\(^{-1}\). Knowing that the water pump rate was 0.2 mLhr\(^{-1}\), the HF solution concentration was calculated to be 10.8 mg HF / mL H\(_2\)O. This was checked and agreed with Gillespie’s work, which had calculated a flow rate of 10.9 mg HF / mL H\(_2\)O.

The HF solution was supplied at 40% HF, and the following information was obtained:

- Molar mass (HF) = 20 g mol\(^{-1}\)
- Molar mass (H\(_2\)O) = 18 g mol\(^{-1}\)
- Density (HF) = 0.991 g mL\(^{-1}\) (HSC Chemistry©)
- Density (H\(_2\)O) = 1.000 g mL\(^{-1}\) (HSC Chemistry©).

Assuming that the solution was 40% HF on a molar basis, the relative amounts of HF and H\(_2\)O were converted to masses and then volumes. Then the proportion of HF could be determined (HF volume divided by total volume) and the concentration was calculated to be:

\[
\text{Concentration of supplied HF solution} = 21.2 \text{ mol L}^{-1} = 424 \text{ g L}^{-1}.
\]

5mL of this solution was then measured using a plastic pipette and then diluted with 100mL using a volumetric flask. The resulting solution was diluted by a further 100mL in a volumetric flask to give a solution of 10.6 g L\(^{-1}\). This resulted in a calculated HF gas concentration of 88.3 mgNm\(^{-3}\).
APPENDIX E: Al₂O₃, CaF₂ and KBr Reference DRIFTS Spectra

Alumina absorbs infrared strongly below 1000 cm⁻¹ (Figure E.3), so a substrate material is chosen to dilute the alumina and therefore improve the signal in this region. The substrate must be inert to sulfur gases and temperature changes. Mixtures of alumina, CaF₂ and KBr were studied to optimise the spectra for COS, SO₂ and H₂S adsorption – too much alumina and the results are too noisy in the 1000 cm⁻¹ region, too little results in weak adsorption bands. Once a 30% Al₂O₃ – 70% CaF₂ mixture was chosen for SO₂ experiments, and 50% Al₂O₃ – 50% CaF₂ for COS and H₂S experiments. Although KBr appeared to be more inert towards sulfur gases, it was believed that it might exchange ions with alumina at the temperatures required for calcining. All spectra were recorded at room temperature in a closed cell with argon gas flowing.

![Graph of Al₂O₃-CaF₂ absorbance](image)

**Figure E.3: Absorbance of various mixtures of primary alumina and CaF₂.**

While COS clearly has no effect on CaF₂ (Figure E.4), SO₂ does alter the DRIFTS spectra of CaF₂ (Figure E.5). As a result, SO₂ was also injected on pure alumina (Figure E.6) to check...
that its affect on alumina was stronger. H₂S has very little interaction with alumina or CaF₂ (See results in Chapter 9).

When SO₂ gas (6 mL, 1372, 1360 and 1345 cm⁻¹) is injected onto CaF₂ (Figure E.5), the DRIFTS spectra show hydrogen carbonate loss (1512 and 1409 cm⁻¹) and positive bands at 1164, 1135, 1013, 942 and 910 cm⁻¹. Although CaF₂ appears to react with SO₂ to a certain extent, SO₂ has a significantly larger effect on primary alumina (Figure E.5). Although introducing CaF₂ in experiments is not ideal, Figure E.5 results, show that it is necessary in order to observe the bands around 1000 cm⁻¹, which are completely obliterated by the high absorbance of alumina in this region.

To check that it is the change in the alumina surface that is observed when SO₂ is injected into a cell containing a mixture of alumina and CaF₂, the effects of SO₂ on various mixtures was compared (Figure E.7). A 30 wt% alumina – CaF₂ mixture was chosen as optimal, based on the resolution in the 1000 cm⁻¹ region and the absence of any CaF₂ peaks at this composition. Based on the weaker affect observed between COS and alumina, a slightly higher alumina concentration was chosen for these experiments (50%) and likewise for H₂S experiments.

![Figure E.4: DRIFTS spectra following an injection of COS onto CaF₂.](image-url)
Figure E.5: DRIFTS spectra following an injection of SO\textsubscript{2} onto CaF\textsubscript{2}.

Figure E.6: DRIFTS spectra following a 6 mL SO\textsubscript{2} injection onto primary alumina.
Figure E.7: DRIFTS spectra of SO$_2$ injections on various primary alumina – CaF$_2$ mixtures.
APPENDIX F: FT-IR Spectra of COS, SO₂ and H₂S Gases

For DRIFTS studies, the FT-IR spectrum of each sulfur gas, COS, H₂S and SO₂, were measured using a gas cell. Figure F.8 shows the FT-IR spectrum for the COS gas used in DRIFTS experiments (5mL COS injected into an N₂ containing gas cell) ratioed to an N₂ background. The strongest absorption band for COS gas occurred around 2060 cm⁻¹ and this was usually the only gas band strong enough to observe during DRIFTS experiments with COS on alumina.

The FT-IR spectrum for H₂S gas (2.5% H₂S in H₂ gas) is shown in Figure F.9 ratioed to a dry air background. H₂S gas did not have strong IR bands, but there were regions of noisy bands (4000 – 3500 and 1700 – 1400 cm⁻¹). The positive band at 2360 cm⁻¹ was in fact due to a small reduction in atmospheric CO₂ levels and was not related to the FT-IR spectrum of H₂S. The FT-IR spectrum for SO₂ gas, shown in Figure F.10, was for pure SO₂ gas injected into a dry air background. The major SO₂ gas band to be observed in DRIFTS was a doublet centred at 1368 cm⁻¹.

![Graph showing FT-IR spectrum of COS gas.](image)

Figure F.8 : COS gas (ratioed to an N₂ background) FT-IR spectrum.
Figure F.9: FT-IR spectrum of H$_2$S gas (2.5% in H$_2$, ratioed to dry air).

Figure F.10: FT-IR spectrum of SO$_2$ gas in dry air (ratioed to dry air).
APPENDIX G: Gas Phase Fluidised Bed Experiments and Mass Spectrometer Calibration

G.1 Mass Spectrometric COS, H₂S and SO₂ Calibrations

The sulfur gases of interest for this study were COS, H₂S and SO₂, and all were readily detected using mass spectrometry. The precise partial pressure measured in the mass spectrometer for each of these gases did vary gradually over time, so calibration was checked at regular intervals, usually every few months. This variation in partial pressure occurs because measurement depends on applied voltage, therefore different filament characteristics give slightly different calibrations. Calibration involved tracking the partial pressure of selected gases with increasing sulfur gas (COS or H₂S or SO₂) concentration.

![Figure G.11: Partial pressure of selected gases in mass spectrometer as inlet COS gas concentration increases (Dilutant = Ar, T = 80°C, no other gases or alumina present).](image)

The mass spectrometer measurements for a typical experiment, where the inlet concentration of COS was increasing, is shown in Figure G.11. COS was diluted in Argon and was passed
through the fluidised bed apparatus at 80°C and 0.4 L min⁻¹ with no alumina present. This experiment was also used to calibrate for COS gas, allowing conversion of COS concentration from partial pressure into parts per million by volume (ppmv). The other two sulfur gases of interest were H₂S and SO₂, because they are the products of COS hydrolysis and oxidation reactions (see Chapter 7) and they were calibrated in the same manner.

The conversion factor, I, from partial pressure into ppmv is a measure of the sensitivity to ionisation in the mass spectrometer for a particular gas and the mass transmission of the mass spectrometer (see Chapter 8). It took approximately 4 seconds for a gas to pass through the apparatus and be detected in the mass spectrometer after it had been turned on and about 6 seconds to detect that the gas had disappeared after being turned off. In some cases, this residence time before detection was sufficient time for a small amount of gas phase reaction to occur. A sulfur mass balance of the COS gas phase experiment (shown in Figure G.11) showed that small amounts of COS were converted into H₂S, therefore calculations to determine I were done iteratively on COS, H₂S and SO₂ calibration results simultaneously. The calculated COS conversion factor for this particular calibration was \( I = 2.22 \times 10^{-12} \text{ torr/ppmv} \), as shown in Table G.1. An earlier calibration, prior to filament replacement in September 2001 had a calculated COS conversion factor of \( I = 3.78 \times 10^{-12} \text{ torr/ppmv} \). Within each of these periods (prior to or after September 2001), the ionisation factors for COS, H₂S and SO₂ were reasonably stable. To allow for smaller changes a daily correction factor was also incorporated into calculations, based on measured background pressures (see Chapter 8).

<table>
<thead>
<tr>
<th>Species</th>
<th>Ionisation Factor ( \text{torr/ppmv} )</th>
<th>Prior to Sep 2001</th>
<th>After Sep 2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>COS</td>
<td>3.78E-12</td>
<td>2.22E-12</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>1.42E-12</td>
<td>4.60E-12</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>3.38E-11</td>
<td>2.30E-11</td>
<td></td>
</tr>
</tbody>
</table>

Partial pressures were measured for all fluidised bed experiments in the manner shown in Figure G.11, but most subsequent results in this appendix will be presented as a mass balance in ppmv, based on COS, H₂S and SO₂ calibrations. The mass balance (in ppmv) from this COS gas phase experiment, in Figure G.12, shows that the extent of hydrolysis of COS in the
gas phase with increasing COS concentration was a linear relationship. In this case, when the maximum COS supply was 187 ppm, the COS outlet concentration was about 171 ppmv, with less than 1 ppm SO$_2$ and approximately 12 ppm H$_2$S forming. The hydrolysis of COS in the gas phase is thermodynamically favourable (see Chapter 7) and occurs according to the reaction:

$$\text{COS}_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{S}_{(g)} + \text{CO}_2_{(g)} \quad \text{(G.4)}$$

It was concluded that residual water present in the apparatus was sufficient to allow this small amount of gas phase COS hydrolysis to occur.

![Sulfur mass balance with increasing COS concentration in isolation](image)

**Figure G.12: Sulfur mass balance with increasing COS concentration in isolation (also see Figure G.11).**

The sulfur mass balances for H$_2$S and SO$_2$ calibrations are shown in Figure G.13 and Figure G.14 respectively. H$_2$S was quite stable up to 200 ppmv, however the SO$_2$ calibration showed a significant amount of H$_2$S was present. This may have been bottle contamination or gas phase reaction and with an inlet concentration of 206 ppmv SO$_2$, there was 165 ppmv SO$_2$ and 30 ppmv H$_2$S calculated to enter the mass spectrometer.
Figure G.13: Sulfur mass balance for increasing H$_2$S concentration in isolation.

Figure G.14: Sulfur mass balance for increasing SO$_2$ concentration in isolation.
The ionisation factors calculated for each gas are summarised in Table G.1. Prior to the mass spectrometer filament replacement, H$_2$S was unusual, in that its ionisation factor increased with increasing inlet H$_2$S concentration. The number given in Table G.1 is the average ionisation factor, but the factor at each inlet H$_2$S concentration is given in Table G.2 and these were used for subsequent mass balance calculations.

Table G.2: Changing ionisation factor with inlet H$_2$S concentration prior to filament replacement in September 2001.

<table>
<thead>
<tr>
<th>Inlet H$_2$S Concentration ppmv</th>
<th>Ionisation Factor torr/ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.90</td>
<td>9.00E-13</td>
</tr>
<tr>
<td>29.85</td>
<td>1.10E-12</td>
</tr>
<tr>
<td>39.80</td>
<td>1.15E-12</td>
</tr>
<tr>
<td>49.75</td>
<td>1.19E-12</td>
</tr>
<tr>
<td>99.50</td>
<td>1.68E-12</td>
</tr>
<tr>
<td>149.25</td>
<td>1.93E-12</td>
</tr>
<tr>
<td>199.00</td>
<td>2.01E-12</td>
</tr>
</tbody>
</table>

G.2 Gas Phase Experiments with Humidity

Gas phase experiments were used to check the measurement of water in isolation in the mass spectrometer. Further gas phase experiments determined the extent of any gas phase reactions between water and COS, H$_2$S or SO$_2$. Additionally, the results of these experiments were used in calculations to check that no change in the ionisation efficiency of the sulfur gases occurred in the presence of water.

Figure G.15 shows the change in partial pressure of selected m/z ratios as relative humidity increases 0 – 20 RH% diluted in Ar in the mass spectrometer with no other species present at 80°C. As humidity increased, an increase in background noise was observed in the mass spectrometer, but humidity did not have a strong effect on the partial pressure measurement of relevant m/z ratios for sulfur gases.
Figure G.15: Partial pressure of selected gases in the mass spectrometer as relative humidity increases (Dilutant = Ar, T = 80°C).

Figure G.16: Sulfur gas composition with 60 ppm inlet COS and increasing relative humidity (0 – 20 RH%).
Figure G.17: Sulfur gas composition with 50 ppm inlet H$_2$S and increasing relative humidity (0 – 20 RH%).

Figure G.18: Sulfur gas composition with 100 ppm inlet SO$_2$ and increasing relative humidity (0 – 20 RH%).
Gas phase experiment results for increasing humidity with 60 ppmv COS (Figure G.16), 50 ppmv H$_2$S (Figure G.17) and 100 ppmv SO$_2$ (Figure G.18) are shown. Increasing humidity levels did not have a great effect on COS stability (Figure G.16), with H$_2$S formed from hydrolysis constant with increasing humidity. Inlet H$_2$S was also stable with increasing humidity (Figure G.17), although the results are noisy, which is probably due to the relatively low sensitivity to ionisation of H$_2$S. Likewise, SO$_2$ was stable with increasing humidity (Figure G.18). The presence of added humidity, although adding considerable background noise to partial pressure measurements, did not change the stability or ionisation efficiency of COS, SO$_2$ or H$_2$S.

G.3 Gas Phase Experiments with O$_2$

Gas phase experiments were conducted to check the measurement of O$_2$ gas in isolation in the mass spectrometer and to determine how the presence of O$_2$ gas affected the measurement and stability of COS, H$_2$S and SO$_2$. Figure G.19 tracks various m/z ratios in the mass spectrometer with increasing O$_2$ concentration (diluted in Ar). It is clear from these results that the measurement of H$_2$S (m/z 34) and CO$_2$ (m/z 44) were increasingly affected as O$_2$ concentration increased. The measurement of COS (m/z 60) and SO$_2$ (m/z 64) seemed relatively stable however.

Gas phase experiments with a known concentration of a sulfur gas and increasing O$_2$ showed that the presence of O$_2$ affected the ionisation factors of COS, H$_2$S and SO$_2$. Table G.3 shows that the ionisation factors for COS and SO$_2$ decreased with increasing O$_2$ concentration, while the opposite was true for H$_2$S ionisation factors. The measurement of COS and SO$_2$ in the presence of O$_2$ was reliable. However, the high partial pressures of O$_2$ that were present swamped the H$_2$S signal at m/z 34, so its ionisation factors were estimated using O$_2$/Ar background levels and COS/O$_2$/Ar and SO$_2$/O$_2$/Ar sulfur mass balances. H$_2$S partial pressures proved difficult to calibrate with respect to concentration if more than 1% O$_2$ was present.
Figure G.19: Partial pressure of selected gases (m/z ratio) in mass spectrometer as O₂ gas concentration increases (Dilutant = Ar, T = 80°C).

Table G.3: Ionisation factors for COS, H₂S and SO₂ with varying O₂ concentration.

<table>
<thead>
<tr>
<th>O₂ %</th>
<th>60 ppmv COS</th>
<th>120 ppmv COS</th>
<th>65 ppmv H₂S</th>
<th>67 ppmv SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>torr/ppm</td>
<td>torr/ppm</td>
<td>torr/ppm</td>
<td>torr/ppm</td>
</tr>
<tr>
<td>0</td>
<td>2.9E-12</td>
<td>2.7E-12</td>
<td>3.8E-13</td>
<td>4E-11</td>
</tr>
<tr>
<td>0.5</td>
<td>2.8E-12</td>
<td>3.03E-12</td>
<td>2E-12</td>
<td>3.4E-11</td>
</tr>
<tr>
<td>1</td>
<td>2.25E-12</td>
<td>2.75E-12</td>
<td>4.5E-12</td>
<td>3.25E-11</td>
</tr>
<tr>
<td>1.75</td>
<td>1.95E-12</td>
<td>2.07E-12</td>
<td>7E-12</td>
<td>3.55E-11</td>
</tr>
<tr>
<td>2.5</td>
<td>1.75E-12</td>
<td></td>
<td>9.5E-12</td>
<td>3.3E-11</td>
</tr>
<tr>
<td>3.375</td>
<td>1.6E-12</td>
<td></td>
<td>1.2E-11</td>
<td>3.1E-11</td>
</tr>
</tbody>
</table>

Figure G.20 shows the results of a gas phase experiment with 60 ppmv COS and increasing O₂ concentration. COS concentration was stable with increasing O₂ concentration, although there may have been a small drop in the amount of hydrolysis to H₂S beyond 1% O₂ and small increase in SO₂ concentration by several ppmv up to 3.4% O₂. At a higher COS concentration of 120 ppmv (see Figure G.21), COS was increasingly stable, but the level of H₂S was observed to slowly decrease, while SO₂ levels correspondingly increased to about 3 ppmv at 1.75% O₂.
Figure G.20: Sulfur mass balance with increasing O$_2$ concentration and 60 ppmv COS entering the mass spectrometer.

Figure G.21: Sulfur mass balance with increasing O$_2$ concentration and 120 ppmv COS entering the mass spectrometer.
The results for a gas phase experiment with 65 ppmv H$_2$S and increasing O$_2$ concentration are shown in Figure G.22. As previously mentioned, H$_2$S partial pressure in the mass spectrometer was increasingly affected by O$_2$ concentration in the mass spectrometer. So the measurement of H$_2$S concentration beyond 0.5% O$_2$ was difficult.

Figure G.22: Sulfur mass balance with increasing O$_2$ concentration and 60 ppm H$_2$S entering the mass spectrometer.
Figure G.23 shows the results of a gas phase experiment with 67 ppmv SO$_2$ and increasing O$_2$ concentration. From SO$_2$ partial pressure measurements, it was observed that predictably, SO$_2$ became increasingly stable with increasing O$_2$ concentration.

![Graph showing sulfur mass balance](image)

**Figure G.23**: Sulfur mass balance with increasing O$_2$ concentration and 60 ppmv SO$_2$ entering the mass spectrometer.
G.4 Gas Phase Experiments with SO$_2$

The effect of varying concentrations of SO$_2$ on the stability of COS in the gas phase was tested using mass spectrometry. Figure G.24 shows that COS is stable in the gas phase within the range of SO$_2$ concentrations (0 – 150 ppmv) studied in the gas phase.

![Figure G.24: Sulfur mass balance for 60 ppmv inlet COS concentration and increasing inlet SO$_2$ concentration.](image-url)