Reactions, Transformations and Impacts of Sulfur Oxides during Oxy-fuel Combustion

A thesis submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

by

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Declaration

The thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University’s Digital Repository**, subject to the provisions of the Copyright Act 1968.

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Statement of Collaboration

I hereby certify that part of the work embodied in this thesis has been done in collaboration with other researchers, or carried out in other institutions. I have included below as part of the thesis, a statement clearly outlining the extent of collaboration, with whom and under what auspices the work was completed.

The University of Newcastle (Australia) and the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart (Germany) collaboration was funded by Xstrata Coal Low Emissions R&D Project CC08-71 on “Coal Impurity Impacts and Gas Quality Control in Oxy-fuel Technology for CCS” awarded to The University of Newcastle. Experiments and configurations focusing on impacts of coal quality and impurity injection on gas emissions and bag filter quality were carried out at the 20 kW Combustion Rig of IFK feeding three Australian commercial coals. The IFK experiments were supervised by Mr. Reinhold Spörl and Mr. Jörg Maier and involved technical staff at IFK. The experiments resulting from this collaboration are summarised and presented in Chapter 5 of this thesis. The author visited IFK in June to July 2012 as part of the collaboration to conduct preliminary gas measurements, observe the operation, collect coal and flue gas quality data, and collect fly ash samples that feed into the other sections (Chapters 6, 7 and 8) of the thesis. Joint publications detailing the IFK experiments reported and included in the thesis.

Signature: ________________ Date: 13 April 2015
FOR MY FAMILY:

Larry, Diana,

Lester, Lovely, Lyndon, Loverne,

J.L. & L.J.
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Abstract

Oxy-fuel combustion is one of the three main CO\textsubscript{2} capture and storage (CCS) technologies for coal-fired power generation; the other two being post-combustion and pre-combustion. Oxy-fuel combustion uses oxygen diluted with recycled flue gas as the oxidant rather than air to regulate temperature within the boiler. As a result, flue gas compositions are more concentrated in CO\textsubscript{2} and up to 4 times higher in impurities such as SO\textsubscript{x} and mercury. Emissions of SO\textsubscript{x} as well as condensation and deposition of corrosive sulfates are detrimental to processes utilised in oxy-fuel flow sheets and also to the plant efficiency. An understanding of the role and impacts of sulfur during coal combustion will benefit control of sulfur emissions and potential corrosion throughout the plant. It is vital for the Callide Oxy-fuel Project (COP) as no SO\textsubscript{x} and Hg removal is used at this plant due to the low sulfur coal used, as expected in all Australian plants. This study aims to establish an understanding of the reactions, transformations and impacts of SO\textsubscript{x} in oxy-fuel combustion by an experimental and theoretical study comparing oxy-fuel sulfur species with those in air firing for which plant impacts are known, including: (1) pilot scale coal combustion experiments to evaluate the overall impacts of coal quality on sulfur release and capture; (2) ash decomposition experiments to test the capture and retention of sulfur in the fly ash and the different sulfur species in fly ash; (3) conversion experiments to establish effects of different flue gas cleaning configurations on the pathways of SO\textsubscript{3} formation and the catalytic effect of fly ash on the conversion of SO\textsubscript{2} to SO\textsubscript{3}; and (4) mercury and SO\textsubscript{x} interaction experiments to investigate the speciation and competition between mercury and SO\textsubscript{x} species in the bag filter.

Ash produced during oxy-fuel combustion is expected to differ to ash produced during air combustion due to the higher CO\textsubscript{2} and SO\textsubscript{2} atmosphere in which it is generated. For a quantitative understanding of the sulfation behaviour of fly ash in oxy-fuel combustion, fly ash from three commercial Australian sub-bituminous coals were tested and decomposed under an inert atmosphere. Thermal evolved gas analysis was completed for ash produced in both air and oxy-fuel environments. Pure salts were also tested under the same conditions to allow identification of the species in the ash which potentially capture sulfur, along with thermodynamic modelling using FactSage 6.0. Sulfur evolved during the decomposition of air and oxy-fuel fly ash was compared with the total sulfur in the ash to close the sulfur...
balance. Both total sulfur captured by the ash and sulfur evolved during decomposition were higher for oxy-fuel fly ash than their air counterparts. The extent of sulfation resulting from thermal decomposition of oxy-fuel fly ash was 2 to 3 times greater than air fly ash. Correlations of capture with ash chemistry were attempted to show extent of sulfur capture and to identify active species in the fly ash responsible for the capture.

The reaction of SO$_2$ with fly ash in the presence of O$_2$ and H$_2$O may lead to the formation of SO$_3$ and eventually H$_2$SO$_4$. Homogeneous experiments were conducted to evaluate the effects of the procedural variables: temperature, gas concentrations and residence time on the post-combustion conversion of SO$_2$ to SO$_3$. Results were compared to those predicted by existing global kinetics and found to be dependent on SO$_2$, O$_2$, residence time and temperature and independent of H$_2$O content. For a residence time of 1 s, at least 900°C is needed to have an observable conversion of SO$_2$ to SO$_3$. Literature suggests that the conversion of SO$_2$ to SO$_3$ is dependent on the iron oxide content of the fly ash. Experiments using the same fly ash were used to investigate the catalytic effects of fly ash on SO$_2$ conversion to SO$_3$ at a temperature range of 400°C to 1000°C. It was observed that fly ash acts as a catalyst in the formation of SO$_3$, with the largest conversion occurring at 700°C. Homogeneous reaction at 700°C, without fly ash present, converted 0.10% of the available SO$_2$ to SO$_3$. When fly ash was present the conversion increased to 1.78%. The catalytic effect accounts for roughly 95% of the total conversion at 700°C. Average SO$_3$/SO$_2$ conversion values between fly ash derived from air and oxy-fuel firing and under different flue gas environments were found to be similar.

Increased mercury concentration is of concern because mercury is known to attack aluminium heat exchangers required in the compression of CO$_2$ during oxy-fuel combustion. A recent study has indicated that interaction of Hg and SO$_x$ may occur at oxy-fuel concentrations and so the competition between SO$_x$ and Hg was investigated in this study. The effect of Hg, SO$_x$, H$_2$O and temperature on the native capture of Hg by fly ash was assessed using a quartz flow reactor packed with fly ash to simulate a bag filter. Doubling Hg in the system from 5 to 10 µg/Nm$^3$ doubled the amount of Hg captured in the fly ash from 1.6 to 2.8% and increases the amount of Hg unaccounted from 5.8 to 18.1%. Increased SO$_2$ decreased the proportion of Hg$^0$ in the flue gas. Temperature in the bag filter was found to
have a huge impact on the mercury capture by fly ash. As temperature was increased from 90 to 200°C, Hg⁰ in the flue gas was found to increase from 77.9 to 98.3%, indicating better capture of Hg at lower temperatures.

The COP is the largest existing plant utilising oxy-fuel technology that combines retrofit options for existing power plants; electricity generation and CO₂ processing. As there is no dedicated SOₓ, NOₓ and Hg removal in place, removal is expected to occur at the fabric filter or during compression. With higher SO₂, SO₃ and H₂SO₄ during oxy-fuel combustion, sulfur capture by the ash is higher compared to oxy-fuel firing. Higher SO₂ forms sulfates responsible for fireside corrosion, SO₃ captured in the fabric filter causes corrosion in the metal components while H₂SO₄ causes fouling of the air pre-heater (APH) and low temperature corrosion due to condensation of H₂SO₄ on surfaces. Shifting from air to oxy-fuel with full flue gas recycling can easily increase the H₂SO₄ dew point by as much as 60°C. Apart from corrosion and fouling, maintaining the APH at high temperature results in efficiency losses. Native mercury capture by the bag filter is also decreased with increasing ADP since the BF must be operated at much higher temperatures. With these reductions in capture at the bag filters due to an increase in operating BF temperature, downstream impacts in the CO₂ processing requiring a need for secondary Hg removals could be created.
Acknowledgements

I would like to extend my deepest and sincerest gratitude to the following people for without them, this research would not have been possible:

- *Emeritus* Professor Terry F. Wall, my professor and supervisor, for his guidance and expertise in this field, and for believing in me and encouraging me to do my best. There had been times when I almost gave up but he restored my faith in myself. I could not have wished for a better supervisor.
- Mr. Reinhold Spörl and Mr. Jörg Maier of the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart for the research collaboration and the invaluable inputs and samples used in the experiments.
- Dr. Liza Elliott for her inputs, constant reminders, words of encouragement and all her guidance in my PhD journey.
- Dr. Rohan Stanger for challenging me in the lab and during the field campaigns and not giving direct answers all the time which helped me improve as a researcher.
- My brothers in our PhD journey Timothy Ting and Dunyu Liu for sharing with me their time and company through thick and thin.
- Other Oxy-fuel Working Group (Uni Newcastle) research associates and staff: Dr. Kalpit Shah, Dr. Wei Xie, Dr. Harold Rogers, Dr. Yinghui Liu, Dr. Xianchun Li, Ms. Jennifer Martin and Hongyu Li and Quang Anh Tran for they became my second family away from home and never failed to understand and encourage me.
- Dr. Stanley Santos for recommending me to my professor, it is because of him that I learnt about this scholarship.
- Chemical Engineering EB Staff of The University of Newcastle particularly Mr. Lonn Cooper and Mr. James Wilson for helping me with my setup; Mr. Stene Sanders from the School of Environmental and Life Sciences (Chemistry) for some of the reagents used in my experiments.
- Laureate Professor Graeme Jameson and Kit-yi Tang for allowing me access to the Mastersizer 2000 for the particle sizing of my fly ash samples.
- Prof. Behdad Moghtaderi, Prof. Bogdan Dlugogorski, Ms. Jane Hamson and the ATC staff for my Ion Chromatogram access.
- The EMX Unit of the University of Newcastle headed by Ms. Jennifer Zobec and Mr. David Phelan for the XRD Analyses of my fly ash samples.
- The University of Newcastle Security, especially Mr. Darren Kennedy and Ms. Fiona Byron for the late night pick-up service to my home.
• My parents, Larry and Diana; my siblings, Lester, Lovely, Lyndon and Loverne with the addition of my nephew John Lawrence and niece Liana Jazmine for always being my inspiration in life and for being the wind beneath my wings.
• My grandparents Erasmo & Felicitas Belo and Brigida D. Doolittle †, aunts, uncles and cousins especially Ely, Obet & Bellen Phoa, Gerald and Ann for being very supportive of my undertaking.
• Jan Zacchary Abad for always cheering me up during the times that I was really down.
• Francis D. Nazareno and his family for always believing in me and motivating me to aim high.
• Joshua James Hicks for being my best Aussie buddy especially when I needed to stay late and grab nourishment during the late nights writing the thesis.
• My family in Germany Aunt Melen Belo Bilger and cousins Christoph and Christina who welcomed me during my experiment campaign at IFK, Stuttgart.
• Joyeth Dorado together with her family Nikki and Matthew for welcoming me when I first arrived at the university and kept being very supportive of me in all my endeavours.
• Fremielle Lim for allowing me to stay late in her office in the course of my thesis writing.
• Edwin, Tess and Gelo Apawan for taking time out to make sure I keep my sanity intact.
• Noel and Vilma Sublay and family for being my shock absorber when I got depressed.
• Dr. Clovia Holdsworth for her inputs, together with her family for all their support.
• Raymond Tan, Kathleen Aviso, Pag-asas Gaspillo, Leonila Abella, Susan Gallardo, Nathan Dugos, Vergel Bungay, Jennifer Gutierrez, Rose Seva, Jo-anne Ballacillo, Valerie Ang, Delfin Mahinay, Cristina Pariña, Shirley Dita, Ariane Borlongan, Maan Gaerlan, Rommel Billena, Ruby Fortun †, Hope Tancinco, Uma Magluyan, Ching Ching, Dina Cruz, Jhona Camba, Grace Lebria, Michael Mercado, Paul Justine Go, Mark Abellanaeda, Job Gascon, Alex Stones, Joseph Thomas and PinAS@UoN members for checking up on me once in a while during my stay in Australia.
• The Robson family (Greg, Cherlene, Paul, James, Daniel & Grace) where I stayed with and treated me as their own family since I arrived in Australia.
• Andrian, Mercy and Andrea Derpo for giving me a place to stay in Sydney.
• The families in Australia who made it easier for me to adjust: The Halasan clan, Pedrita Spence, the Chehabs, the Viescas, the Marcoses, the Ponferradas and the Westaways.
• Family, friends, colleagues, technicians, staff, my students and others who, in one way or another, have contributed to the fulfilment of this thesis, I will be eternally grateful.
• Last but not the least, to God the Father, my refuge and provider, for giving me the strength and wisdom. I thank you also for surrounding me with wonderful people.
List of papers published and/or presented at conferences

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**List of Abbreviations**

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAEM</td>
<td>Alkali and Alkaline Earth Metal</td>
</tr>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>ACI</td>
<td>Activated Carbon Injection</td>
</tr>
<tr>
<td>ADP</td>
<td>Acid Dew Point</td>
</tr>
<tr>
<td>APCD</td>
<td>Air Pollution Control Device</td>
</tr>
<tr>
<td>APH</td>
<td>Air Pre Heater</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>ASU</td>
<td>Air Separation Unit</td>
</tr>
<tr>
<td>BF</td>
<td>Bag Filter</td>
</tr>
<tr>
<td>CCM</td>
<td>Controlled Condensation Method</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon Dioxide (CO₂) Capture and Storage</td>
</tr>
<tr>
<td>COP</td>
<td>Callide Oxy-fuel Project</td>
</tr>
<tr>
<td>CPU</td>
<td>CO₂ Purification Unit</td>
</tr>
<tr>
<td>DCCPS</td>
<td>Direct Contact Cooler and Polishing Scrubber</td>
</tr>
<tr>
<td>DTF</td>
<td>Drop Tube Furnace</td>
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<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
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<td>EOR</td>
<td>Enhanced Oil Recovery</td>
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<td>EPA</td>
<td>Environmental Protection Agency</td>
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<td>ESP</td>
<td>Electostatic Precipitators</td>
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<tr>
<td>FA</td>
<td>Fly Ash</td>
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<tr>
<td>FB</td>
<td>Fluidised Bed</td>
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<tr>
<td>FBC</td>
<td>Fluidised Bed Combustion</td>
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<tr>
<td>FF</td>
<td>Fabric Filter</td>
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<tr>
<td>FGD</td>
<td>Flue Gas Desulphurisation</td>
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<tr>
<td>FGR</td>
<td>Flue Gas Recycling / Recycle</td>
</tr>
<tr>
<td>ID</td>
<td>Inner / Internal Diameter</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency</td>
</tr>
<tr>
<td>IFK</td>
<td>Institut für Feuerungs- und Kraftwerkstechnik</td>
</tr>
<tr>
<td>IGCC</td>
<td>Institute of Combustion and Power Plant Technology</td>
</tr>
<tr>
<td>IHI</td>
<td>Ishikawajima-Harima Heavy Industries</td>
</tr>
<tr>
<td>IRCC</td>
<td>Integrated Reformer Combined Cycle</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
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<td>NPI</td>
<td>National Pollution Inventory</td>
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<tr>
<td>OD</td>
<td>Outer Diameter</td>
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<tr>
<td>PC</td>
<td>Pulverised Coal</td>
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<tr>
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<td>Post Combustion Capture</td>
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<td>PF</td>
<td>Pulverised Fuel</td>
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PFA  Perfluoroalkoxy alkane
PJFF  Pulse Jet Fabric Filter
PM  Particulate Matter
ppm  parts per million
PSD  Particle Size Distribution
RFG  Recycled / Recirculated Flue Gas
RT  Residence Time
SA  Surface Area
SCR  Selective Catalytic Reduction
SDA  Spray Dry Absorber
SEM  Scanning Electron Microscope
SI  Systeme Internationale de Unites
(ST)  (International System of Units)
STEL  Short Term Exposure Limit
STP  Standard Temperature Pressure
TGA  Thermogravimetric Analyser (Analysis)
TWA  Time Weighted Average
UBC  Unburned Carbon
UoN  University of Newcastle
US  United States (of America)
QW  Quartz Wool
WFGD  Wet Flue Gas Desulfurization
XRD  X-Ray Diffraction Analysis
XRF  X-Ray Fluorescence Analysis (X-Ray Fluoroscopy)
1 PROBLEM AND ITS BACKGROUND

1.1 INTRODUCTION

Alongside the world’s rapidly increasing industrialisation is the increasing demand for a stable and cheap energy source, primarily as electricity. Highly industrialised countries still rely on using fossil fuel as one of their main sources of energy [1]. Although other lower-carbon sources of energy are available, most of the renewable energy sources are restricted by geographic limitations [2]. Nuclear energy, on the other hand has received negative attention and raised worldwide environmental and safety concerns especially after major accidents like the 2011 Fukushima disaster in Japan [2]. As of 2011, the United States International Energy Agency (IEA) reported that fossil fuel comprised 82% of the world’s overall energy mix [3]. Among the fossil fuels (i.e. natural gas, oil, shale, peat), coal has always been the principal candidate for thermal power plants, being the cheapest and the most abundant fuel. In the 2013 key world energy statistics by the US-IEA [4], Australia is the second top coal exporting country contributing about 25.9% (302 Mt) of the world coal exports. About 64% [5] of Australia’s energy mix comes from coal as of 2012-2013 and it continues to be a major fuel source for electricity generation. With stable coal production it is unlikely that the coal boilers will be abandoned in the near future [6].

On the other hand, combustion of coal results in greenhouse gas emissions, particularly CO₂. In 2010, energy generation alone contributed approximately 41% of the total 30 Gigatonnes CO₂ emissions [7]. Other than CO₂, combustion of coal also contributes emissions from the oxidation of several of coals impurities such as nitrogen, sulfur and mercury. The SOₓ, NOₓ and Hg emissions to the atmosphere are causing serious health and environmental concerns. Additionally, in chemical terms, coal is a complex composite material which contains inorganic species mainly as ash upon combustion alongside organic matter. In the coal matrix, these inorganics are present as free ions, salts and organically-bonded species as well as in the form of fine crystalline materials such as quartz, carbonates, oxalates, sulphides. Upon combustion, volatile minerals are released from the coal matrix
and forms gaseous and condensed ash components [8]. The gas phase inorganic elements may undergo numerous physical transformations such as nucleation, coagulation and homo- or heterogeneous condensation along with chemical transformations such as gas-gas, gas-solid and solid-solid reactions on a milliseconds timescale upon the onset of the combustion process. Ultimately the gas-to-particle transformations lead to the formation of homogeneous aerosol particles and/or heterogeneous fine ash particles. These gaseous SO\textsubscript{x} species as well as (super) fine condensed particles, may lead to numerous problems such as slagging, fouling, corrosion, erosion in power utilities and harmful emissions of gases and particulate matter to the atmosphere.

Due to the escalating emissions of CO\textsubscript{2} in the atmosphere, several technologies and strategies are being developed to reduce or sequester the carbon dioxide for coal based power plants which includes; efficiency improvements in existing power plants, introduction of advanced combined cycle power plants, use of alternative fuel sources, and CO\textsubscript{2} capture and storage (CCS) [9-12]. CCS is deemed the most suitable strategy to reduce if not totally remove CO\textsubscript{2} from flue gas emissions and will act as a complimentary technology to power plant and fuel efficiency improvement [7, 13]. Among all CCS technologies, oxy-fuel combustion offers a low risk step development for existing conventional coal based thermal power plants and therefore has received attention in the current years. It is often concluded/recommended in the literature that oxy-fuel, being a relatively new concept, needs more systematic scientific studies together with medium-large scale demonstrations that will make the technology more robust and acceptable to power generation companies. The main objective of this work is to investigate the fundamentals of the sulfur oxides (SO\textsubscript{x}) formation, interactions and impacts in oxy-fuel combustion.

It is essential to understand the fate of sulfur in oxy-fuel combustion as well as the differences with air-firing for the efficient design of flue gas cleaning and compression. Sulfur in coal is found in the form of sulfides, organic sulfur compounds, sulfates and traces of elemental sulfur. The sulfur content and its bonding within the coal matrix vary with the type of coal, its age and location. Most of the sulfur present in coal regardless of its parent form is released into the gas phase in the form of SO\textsubscript{2} at flame temperatures [14] for both air and oxy-firing modes. Under sub-stoichiometric conditions in the flame, hydrogen sulfide
(H₂S) is formed in the gas or released from organic sulfur compounds. Equilibrium favours SO₂ over H₂S at higher oxygen concentrations and temperatures. At lower temperatures, the equilibrium shifts towards sulfur trioxide (SO₃), but the reaction rate decreases with temperature and the concentration of SO₃ is normally several orders of magnitude lower than that of SO₂ in the emitted gas. The formation of SO₃ depends on a number of factors such as: concentration of SO₂, residence time, temperature profile, concentration of O₂, fly ash composition, concentration of NO₂ and the presence of iron catalysts [15]. At temperatures below 500°C, SO₃ reacts with H₂O in the flue gas to form gaseous H₂SO₄, which reaches complete transformation at about 200°C [11, 16]. H₂SO₄ can cause corrosion when it condenses on metal surfaces or particles below the acid dew point temperature (ADP). SO₃ promotes particle formation when condensed on the ash surface by lowering ash resistivity which is beneficial for improving the performance of electrostatic precipitators. However, it also increases plugging of air-preheater passages and emission of aerosols. Additionally in the fly ash, if present at sufficient levels as compared with chlorine, sulfur dioxide is prone to react with alkali chlorides to form alkali sulfates. Apart from this, SOₓ was found to also compete with mercury for active sites for adsorption on fly ash [6, 7]. As Hg concentration is higher in oxy-fuel, it is essential that competition of Hg and SOₓ be investigated since Hg corrodes the aluminium heat exchangers in the CPU [7, 17].

Wall [18] reported that sulfur may react with calcium and magnesium to form sulfates below 1450°C. Furthermore, Schurmann et al. [19] verified that sulfur and alumino-silicates compete for alkalis and the dominance of one or the other depends on the temperature as well as the actual flue gas chemical composition. Increased combustion temperature favours alkali-alumino-silicates over sulfates formation, even though both processes are thermodynamically less favourable at higher temperatures. Nonetheless, sufficiently high sulfur contents can support the formation of alkali sulfates even at high temperatures [20], despite the presence of the alumino-silicates.

Due to higher O₂ and impurity (e.g. SOₓ, Hg, and NOₓ) concentrations in the oxidant from flue gas recycling, higher sulfur capture in ash is expected in oxy-fuel firing compared to air-firing. These oxy-fuel configurations are also possible to have significant impacts on the reactions and interactions of these impurities [21]. Higher SO₂ concentration due to
higher oxygen partial pressure in flue gas may favour increased \( \text{SO}_3 \) formation. \( \text{SO}_3 \) at lower temperatures reacts with \( \text{H}_2\text{O} \) and converts to \( \text{H}_2\text{SO}_4 \) which if condenses on metal surface may enhance low-temperature corrosion problems. Also \( \text{SO}_x \) is said to compete with \( \text{Hg} \) capture on the active sites for adsorption in fly ash.

1.2 KEY FOCUS OF RESEARCH

The key focuses of this research were:

1. To investigate differences between the levels of sulfur species formed in air firing and firing conditions typical of oxy-fuel technology;
2. To develop a scientific understanding of the key issues associated with the differing \( \text{SO}_x \) levels such as impacts of \( \text{SO}_2 \) concentrations in the flue gas on \( \text{SO}_3 \) concentrations, \( \text{SO}_2/\text{SO}_3 \) capture by fly ash and its impact on acid dew point, and competition with \( \text{Hg} \) during capture by fly ash in the bag filter.

Therefore, a systematic experimental matrix was designed where three Australian coals A, B and C were fired and sulfur species compared in air and oxy-fuel combustion. The research work was subdivided into four parts as shown below:

I. **Coal combustion experiments** focusing on the impacts of coal quality and flue gas recycle impurities on the sulfur formation and capture by fly ash in air and oxy-fuel combustion conditions.

II. **Ash decomposition experiments** which utilised the bag filter fly ash coming from air and oxy-fuel combustion tests in Part I to determine the effect of differing \( \text{SO}_x \) levels on the capture behaviour of fly ash.

III. **Homogeneous and Catalytic \( \text{SO}_2 \) to \( \text{SO}_3 \) conversions experiments** with the use of fly ash obtained from different modes of firing in Part I and compare the extents of catalysis associated with flue gas and fly ash interaction.

IV. **\( \text{SO}_x \) and mercury competition experiments** which studies the effects of varying \( \text{SO}_x \) concentrations (based on Part III) simulating air and oxy-fuel conditions on the mercury capture by bag filter fly ash obtained in Part I.
Further details are given in Chapter 3. Chapter 2 will provide an overview on different CCS technologies, oxy-fuel combustion and sulfur and mercury in oxy-fuel. Finally, this chapter is concluded with the outline of report.

1.3 OUTLINE OF THE REPORT

Chapter 1 of this study has briefly outlined the background of CCS technologies and stated the motivation behind the research. Chapter 2 gives a summary of related literature to the study on the behaviour, interactions and reactions of sulfur during oxy-fuel combustion focusing on factors that affect the SO$_2$/SO$_3$ conversion, the controlled condensation techniques, the acid dew point temperature concept, and the interaction of SO$_x$ and mercury in a combustion system. Chapter 3 summarises the knowledge gap based on which hypothesis for the report is presented.

Chapter 4 provides the experimental design outlining the different parts of the experiments: (1) coal combustion experiments; (2) ash decomposition experiments; (3) homogeneous and catalytic SO$_2$ conversion experiments and (4) SO$_x$ and mercury competition experiments. The main experimental results are presented in Chapters 5 to 8.

Chapters 5 provides a discussion on the subcontracted experiments carried out at the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Germany focusing on the coal quality and recycled flue gas impurities impacts on the emissions quality and capture behaviour of fly ash.

Chapter 6 provides a detailed discussion of the results of the thermal decomposition experiments of fly ash obtained from air and oxy-fuel firing.

Chapter 7 presents the SO$_2$ to SO$_3$ conversion studies with and without the presence of fly ash.

Chapter 8 presents studies that focused on the competition between SO$_x$ species and Hg on the simulated bag filter fly ash.

Chapters 9 and 10 provide the summary, conclusions, practical implications and future directions for research.
2 RELATED LITERATURE

2.1 INTRODUCTION

Fossil fuels (coal, oil and natural gas) have been the primary source of energy for power generation and this is expected to continue in the distant future [22]. Coal is the cheapest among the fossil fuels which upon combustion emits CO₂, a greenhouse gas. In 2010 alone, 41% of the ~30 Gigatonnes CO₂ emissions was contributed by energy generation [7, 22]. Coal utility boilers also emit pollutants like SO₂ and mercury into the atmosphere [7]. Emissions of sulfur oxides (SOₓ) as well as the condensation and/or deposition of corrosive sulfates [23] pose major problems in coal-fired power plants. Apart from the problems caused to the components of the plants, substantial removal of sulfur must be done before being released to the atmosphere to meet environmental standards.

In order to address the growing concern of greenhouse gas and pollutant emissions, CO₂ capture and sequestration (CCS) technologies have been developed [17]. Oxy-fuel technology which burns coal in a mixture of oxygen and recycled flue gas (RFG) results in a high purity CO₂ which can then be processed and sequestered [6, 24]. Using the RFG in oxy-fuel combustion can be an issue as SO₂ concentrations can reach up to 4 times as high as that in conventional air firing [7, 11, 21]. Australian power plants do not utilise flue gas desulfurisation due to the innately low sulfur content of Australian coals [22]. It will therefore be challenging if high SOₓ is present in the flue gas; and even if sulfur removal processes are readily available for retrofitting existing plants, they are expensive. An understanding of the transformation, interactions, and impacts of sulfur is therefore imperative in order to help maximise plant efficiency and minimise damages to the components of the plant.
2.2 OXY-FUEL COMBUSTION AND CO$_2$ CAPTURE AND STORAGE (CCS) TECHNOLOGIES

Recent developments in CCS have established three technology options for power generation with CCS strategies; post-combustion, pre-combustion and oxy-fuel combustion [10, 12, 25-27]. Figures 2-1 to 2-3 show possible flowsheets for the three main CCS strategies and are summarised in Table 2-1.

1. Post Combustion Capture

In post-combustion capture (PCC), low concentration CO$_2$ (12-15%v/v) [28] coming from the flue gas of coal-fired power plants is captured by a scrubbing system to separate the CO$_2$ from the flue gas stream [6] (Figure 2-1). The system usually consists of a chemical absorption separation with the aid of either monoethanolamine (MEA) or a sterically hindered amine [12, 25, 26] to remove the CO$_2$ and a regenerator (or stripper) wherein the CO$_2$ is then released and the solvent is recovered [28]. One of the problems of this system is that the regenerative cost of the solvent is high [6].

![Figure 2-1. Flowsheet for post-combustion capture (PCC) with CO$_2$ ready for sequestration [12].](image)

This technology is sometimes employed in parallel with Integrated Gasification Combined Cycle (IGCC). On the other hand, using these absorbents is said to lower the net efficiency of the power plant by about 9 – 15% [25, 26] hence the need for alternative solvents or a more efficient process is imperative. One such
process utilising ammonia as the absorbent, known as the chilled ammonia process, showed promising reduction in the energy consumption of up to 50% as compared to the conventional MEA process. It should also be noted that chemical absorption requires special care when used in IGCC-CCS because any slippage of the solvent may have a detrimental impact on the gas turbine [26], and that the presence of sulfur (as SO₂) should first be removed from the flue gas prior to CO₂ capture because these can react irreversibly with the absorbent (MEA) and the hot carbonation process [29].

2. Pre-combustion Capture

Also termed as fuel decarbonisation where CO₂ is captured prior to combustion. Pre-combustion is used in conjunction with IGCC and termed as IGCC-CCS if it involved CCS (Figure 2-2). In IGCC-CCS coal gasification is first employed to obtain syngas (CO, CO₂ and H₂) then either the water-shift reaction is used in order to convert the CO into CO₂ to be separated from the H-containing gas before combusting in the turbine or H₂ is first separated from the syngas then the CO combusted under an O₂/CO₂ atmosphere and then captured [25, 26, 28].

![Figure 2-2. Flowsheet for pre-combustion capture (IGCC) with CO₂ ready for sequestration [12].](image)
One particular benefit of this IGCC-CCS is the H₂ produced from the process may be used as energy especially in steel-making and hydrocarbon manufacturing [6]. On the other hand, IGCC-CCS is capital cost intensive in terms of construction and that there is a limited availability of IGCC plants compared to the already mature coal-fired power plants hence making the operating experience limited [6, 25]. Although techno-economic calculations show that IGCC may have promising efficiency and economics, the disadvantages outweigh the advantages, making IGCC-CCS an unviable alternative for retrofitting existing power plants due to its high cost [25].

3. Oxy-Fuel Combustion

In oxy-fuel combustion, pulverised coal reacts in an atmosphere of O₂/CO₂ instead of the conventional air (O₂/N₂) to eliminate the bulk component N₂ from the flue gas [28] (Figure 2-3). In order to achieve this, the molecular nitrogen (N₂) is separated from air using an Air Separation Unit (ASU) giving rise to more than 95% purity oxygen [30]. Feeding O₂/CO₂ as the oxidant then leads to a high quality flue gas which consists mainly of CO₂ (80% to >95% vol. dry) [6, 16, 24, 26] and water vapour ready for processing, capture and storage [6]. More detailed discussion on oxy-fuel combustion is tackled in the succeeding sections.

Figure 2-3. Flowsheet for oxy-fuel combustion with CO₂ ready for sequestration [12].
In the CCS technologies summarised above, each has its own advantages and disadvantages. Before any choice of technology is made, several technological and economic factors should first be considered such as: capital costs and associated financing of the capture equipment; net output of plant; operation and maintenance costs; total and variable costs of electricity (COE); transport and storage site accessibility and availability; retrofit options; and physical size of the new equipment. **Table 2-1** presents the typical schemes recommended for power plants. Among the three CCS options, although the cost of producing oxygen and flue gas cleaning increases the COE [7] for oxy-fuel, it seems to have inherent advantages of efficiency, cleanliness and capacity to accommodate a step change as it shows options for retrofit.

**Table 2-1.** Typical schemes recommended for power plants for Post, Pre and Oxy-fuel Combustion (summarised from Wall [9], Rathnam [28], Dhungel [31], Shah, et al. [7] and Teir, et al. [14]).

<table>
<thead>
<tr>
<th>Feature</th>
<th>Post Combustion (PCC)</th>
<th>Pre Combustion (IGCC)</th>
<th>Oxy-Fuel Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>• Coal</td>
<td>• Coal, refinery residues via IGCC*</td>
<td>• Coal</td>
</tr>
<tr>
<td></td>
<td>• Natural Gas</td>
<td>• Natural gas via IRCC**</td>
<td>• Natural Gas</td>
</tr>
<tr>
<td>Combustion</td>
<td>Fuel with air (O2/N2) (conventional)</td>
<td>H₂ enriched flue gas with air</td>
<td>Fuel with O₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Recycling with CO₂</td>
</tr>
<tr>
<td>Oxygen supply</td>
<td>No</td>
<td>• Cryogenic ASU</td>
<td>• Cryogenic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• O₂ via membranes</td>
<td>• Membranes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Chemical looping</td>
</tr>
<tr>
<td>Separation</td>
<td>• Absorption (chemical)</td>
<td>• Absorption (physical / chemical)</td>
<td>• Condensation of H₂O from Flue Gas</td>
</tr>
<tr>
<td></td>
<td>• Adsorption Membranes</td>
<td>• H₂ via membranes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• CO₂ via membranes</td>
<td></td>
</tr>
<tr>
<td>CO₂ in the flue gas [%vol., dry]</td>
<td>3 – 18</td>
<td>15 – 60</td>
<td>80 – 95</td>
</tr>
<tr>
<td>CO₂ capture efficiency [%]</td>
<td>MEA: &gt;90</td>
<td>&gt;90</td>
<td>&gt;90</td>
</tr>
<tr>
<td>CO₂ conditioning, compression &amp; transport</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Potential for retrofit</td>
<td>Yes, High</td>
<td>Not Applicable</td>
<td>Yes, Good with modifications like recycle path and ASU</td>
</tr>
<tr>
<td>Commercial maturity</td>
<td>Partially Proven</td>
<td>Partially Proven</td>
<td>Not Yet Commercial</td>
</tr>
</tbody>
</table>

*IGCC – Integrated Gasification Combined Cycle, **IRCC – Integrated Reformer Combined Cycle*
2.2.1 The History and Development of Oxy-fuel Combustion

Oxy-fuel has long been applied in the glass, cement and steel processing industries however it was not until the 1980s that the concept of oxy-fuel combustion for the energy sector was first proposed for obtaining a CO₂-rich flue gas to be used for Enhanced Oil Recovery (EOR) [7, 28, 31]. In the late 1980s, due to concerns about rising atmospheric greenhouse gas emissions (particularly CO₂) that contribute to climate change, oxy-fuel technology received much attention [32]. It has been proposed as a viable CCS technology for newly built and for retrofitting existing coal-fired power plants [33] as it does not need any major new chemicals unlike post-combustion capture, nor is there any need for power plants to adopt a new process unlike pre-combustion capture (i.e. IGCC). The only major component that is added in oxy-fuel compared to conventional power plants is the Air Separation Unit (ASU) for separating N₂ from the air. The combustion is normally carried out in an O₂/CO₂ environment by eliminating N₂ and recycling the CO₂-rich flue gas. Just like the other CCS technologies, oxy-fuel technology’s purpose is to capture the flue gas that is highly enriched in CO₂ and then compress, transport and dispose of the CO₂ [32, 34]. Research, development and demonstrations of oxy-fuel combustion have been advancing in recent years; however, there are still fundamental issues and technological challenges that must be addressed before this technology can reach its full potential [33] and eventual full-scale demonstration and operation.

Figure 2-4 shows the timeline of the development of oxy-fuel combustion where the vertical axis shows energy output, and Table 2-2 presents some pilot oxy-fuel studies conducted and the areas covered. It can be noted that several pilot scale plants have been in operation since the early 90s however it was not until 2008 where Vattenfall’s 30 MWth (Schwarze Pumpe) demonstrated CCS. It can also be noted that most of the demonstrations were at small scale and to date no full-scale plants based on this technology have been built [31]. Because of this lack of demonstration, oxy-fuel combustion is still considered to be in a relatively early stage of development since its conceptualisation. The next major milestone for the technology is the Callide Oxy-fuel project (COP) which started its operation in 2012 [35] with FutureGen 2.0 to follow in
2015 and 300 MWe CFB plant in Compostilla which was supposed to follow but has been cancelled [7]. FutureGen 2.0 is expected to be the world’s first commercial scale oxy-fuel power plant with near-zero emission totalling $US 1.65 billion [7]. Although deemed to be efficient in terms of CO₂ capture and potential for retrofit, due to oxy-fuel’s air separation unit (ASU) and CO₂ compression processes, an efficiency penalty of 5 – 10% is imposed on power generation. And unless a significant carbon tax is legislated, the efficiency penalty could hinder full scale use of oxy-fuel technology (shown in Figure 2-5) [7].

![Figure 2-4. Historical Development of Oxy-fuel Combustion [35].](image)

<table>
<thead>
<tr>
<th>Pilot Plant</th>
<th>Size</th>
<th>Emissions</th>
<th>Sulfur</th>
<th>Fly Ash</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SO₂</td>
<td>Balance</td>
<td>Capture</td>
<td>Condensates</td>
</tr>
<tr>
<td>Chalmers, 2009</td>
<td>100 kW</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>IFK, 2008</td>
<td>20, 500 kW</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Callide/IHI, 2005</td>
<td>1.2 MW</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>CANMET, 2001</td>
<td>300 kW</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>IHI, 1993-1996</td>
<td>1.2 MW</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>IFRF, 1994</td>
<td>2.5 MW</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 2-2. Pilot Studies of Oxy-fuel Combustion with Recycle [6, 36].
Figure 2-5. Development of CO₂ Capture and Storage (CCS) Technologies Relative to CO₂ price [37].

2.2.2 The Callide Oxy-fuel Project (COP)

The Callide Oxy-fuel Project was launched in 2008 and is based in Biloela, Queensland, Australia, which began as a collaboration among Australian and Japanese industries; CS Energy, IHI and The University of Newcastle [35]. The COP is unique from the other oxy-fuel demonstrations throughout the world in that it is the first to evaluate a retrofit option for a 30-MWe with flue gas recycling, heat exchangers, ASU and CO₂ purification unit (CPU) as shown in Figure 2-6. It was the first with electrical generation in an open market using oxy-fuel and provided continuous operation under real electrical demand, and the first demonstration to evaluate a complete process with CO₂ capture, transport and storage [38]. It served as a critical step forward from pilot scale operation (e.g. Germany - 1 MWt Schwarze Pumpe) to a fully realised industrial scale demonstration (e.g. US – 200 MWe FutureGen 2.0) and eventually to commercialisation.
This study is significant, especially for the COP, in that most power utilities in Australia do not include emission controls which are commonly employed in the US and EU. The lack of SO$_x$ and NO$_x$ control units other than burner and furnace staging (e.g. Flue Gas Desulfurisation and Selective Catalytic Reduction) in Australian power plants apart from low-NO$_x$ burners makes this study relevant since power plants in Australia have relied on low-sulfur coals (< 1% S) and lenient Australian environmental regulations for their emissions [35]. Being able to quantify and predict SO$_x$ could potentially aid operating temperatures for the air preheaters, hence saving energy and minimising risk of corrosion.

### 2.3 OXY-FUEL AND AIR COMBUSTION: COMPARISON

Oxy-fuel combustion differs from conventional air firing from its oxidant composition to its flue gas composition (Table 2-3). Since oxygen is used for combustion instead of air, the flue gas volume from oxy-firing, after the recycle stream is removed, is one-fourth or one-fifth that of air combustion [32]. Recycling of the flue gas (RFG) is required to control the temperature of combustion and in retrofit situations make up the volume of the gas to
ensure heat transfer is still achieved in the boiler. As a consequence of this recycling, higher concentrations (ppm) of impurities but lower emission rates (mg/MJ) have been reported by several investigators [6, 16, 39-42].

**Table 2-3.** Comparison between Air and Oxy-fuel Oxidant gas composition and Flue Gas Composition (UoN - [37, 43], IEAGHG [44], IHI [38, 45], Callide [46] and IFK [11, 17, 21]).

<table>
<thead>
<tr>
<th>Location</th>
<th>Species</th>
<th>Air Combustion</th>
<th>Oxy-fuel Combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind box</td>
<td>O₂ (%v) [44]</td>
<td>21</td>
<td>21 - 30</td>
</tr>
<tr>
<td>Wind box</td>
<td>N₂ (%v) [44]</td>
<td>79</td>
<td>0 - 10</td>
</tr>
<tr>
<td>Wind box</td>
<td>CO₂ (%v) [44]</td>
<td>0</td>
<td>40 - 50</td>
</tr>
<tr>
<td>Wind box</td>
<td>H₂O (%v) [44]</td>
<td>small</td>
<td>10 - 20</td>
</tr>
<tr>
<td>Wind box</td>
<td>Others</td>
<td>-</td>
<td>NOₓ, SO₂</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>Gas flow rate (Nm³/s, wet) [37, 46]</td>
<td>3.5 – 5x</td>
<td>x</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>O₂ (%v) *</td>
<td>3 - 4</td>
<td>3 - 4</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>N₂ (%v) *</td>
<td>70 - 75</td>
<td>0 - 10</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>CO₂ (%v) *</td>
<td>12 - 14</td>
<td>60 - 70</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>CO (ppm) *</td>
<td>0 - 4</td>
<td>0 - 4</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>H₂O (%v) *</td>
<td>10 - 15</td>
<td>20 - 25</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>SO₂ (ppm) *</td>
<td>150 - 500</td>
<td>600 - 2800</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>SOₓ (ppm) *</td>
<td>2 - 10</td>
<td>7 - 50</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>NOₓ (ppm) *</td>
<td>470 - 950</td>
<td>950 - 1250</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>Hg (µg/Nm³) [17] before bag filter</td>
<td>2 - 8</td>
<td>10 - 32</td>
</tr>
<tr>
<td>Flue Gas</td>
<td>Total Solids loading (g/Nm³) [43]</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

Note: * Combination of investigators [11, 17, 21, 38, 43-45].

Flue gas components based on studies from IFK 20-kWth and IHI 0.5-MW oxy-fuel studies using the same 3 Australian coals used in this study.

Three approaches can be used when selecting the water content of the RFG depending on the location it was drawn from:

1. **Wet flue gas recycle** is when flue gas is extracted before it is cooled below its water dew point. This is when RFG is drawn downstream of the particulate removal devices but upstream of wet scrubbers or condensers.
(2) *Dry flue gas recycle* is when flue gas is extracted after allowing most moisture to condense. This is when RFG is drawn downstream of wet scrubbers or flue gas coolers/condensers.

(3) The practical situation is *partial flue gas drying*, with gas cooling/condensation in the primary burner flow to accommodate the drying function of coal milling, when RFG is drawn after particulate removal.

The accumulation of pollutants may have damaging effects on equipment and plant operation and thus these pollutants need to be minimised or removed before the flue gas can be recycled [32]. The level of sulfur (and its pollutants) coming from the coal combustion determine the flowsheet adapted to suit a power plant. These flowsheets are presented in Section 2.7. For these reasons, this research will focus on the sulfur compounds, specifically SOₓ, and their reactions, interactions and impacts during oxy-fuel combustion.

### 2.3.1 Sulfur Oxides (SOₓ) in Oxy-fuel Combustion

Sulfur is introduced by the coal, which generally ranges between 0.2%wt and 11%wt [1, 41, 47, 48]. Regardless of occurrence of sulfur in the parent coal, upon coal pyrolysis these sulfur forms are decomposed to form the gases H₂S, COS, SO₂ and CS₂. During combustion all the products of pyrolysis are oxidised to its main oxide: sulfur dioxide, SO₂ while a small percentage is further oxidised into sulfur trioxide (SO₃) as the gas cools [1]. Even if the amount of SO₃ present is very small when compared to SO₂, the former cannot be disregarded due to its negative effects on plant operations since SO₃ has a great affinity for water, producing sulfuric acid (H₂SO₄). This leads to low temperature corrosion of surfaces in the heat recovery zones, especially in the sections where temperatures are below the sulfuric acid dew point (ADP).

Several investigators [6, 40, 49] have indicated that oxy-fuel firing is associated with higher SO₂ and SO₃ concentrations throughout the process due to the elimination of N₂ in the oxidiser (and the flue gas) and the recirculation of the flue gas. This represents a significant issue in coal fired power plants, with the flue gas exhausted at temperatures above the ADP in order to prevent its condensation in the lines. ADP is dependent on the amounts of SO₃ and H₂O present, and in oxy-fuel is expected to be
around 10 – 30°C higher than those for air-firing of the same coal [6, 16, 50]. Stanger and Wall [6] gave a comprehensive review on the impacts of sulfur in an oxy-fuel process which will be discussed further in Section 2.6.

2.4 SULFUR IN COAL

Sulfur is a naturally occurring element in the environment and it is essential in the sustenance of plant and animal life. With this, it is not surprising to find sulfuric compounds in decayed matter, in coal deposits and in associated mineral matter strata [48]. It may be present in its pure elemental form, sulphides and sulphate minerals. In itself, elemental sulfur is nontoxic, however its derivatives i.e. sulfur dioxide, sulfur trioxide and hydrogen sulphide are. All coals contain sulfur and it is recognised as one of the major impurities in coal [51]. Sulfur in coal occurs in two general forms; organic and inorganic. Inorganic sulfur consists of sulfates and sulphides (pyritic) while organic sulfur consists of all sulfur bound to the hydrocarbon matrix [32, 47, 52-54].

Organic sulfur exists in the coal structure either in aromatic or in aliphatic functional groups and may vary from a small fraction of a percent of around 0.29% [55] to 8% [56]. Inorganic sulfur is predominantly present as iron pyrite (FeS₂) and exists as dispersed particles in coal present from 0% [56] to 3.97% [55], however interactions with the coal structure during pyrolysis is expected [30]. Sulphate sulfur is of minor importance in fresh coals as this is only a small portion of the total sulfur in most coals [30] generally less than 0.1% [51]. Elemental sulfur which may also be present in coal, is also small usually less than 0.2% [51]. Generally, coals may contain from 0.2% wt. to 11% wt. sulfur [1, 41, 47, 48, 57], but normally the sulfur content ranges between 0.2% wt. to 6% wt. [32, 41, 55, 58]. Upon coal combustion, typical pollutant emissions released into the atmosphere are presented in Table 2-4. This study will be focusing on the SOₓ, fly ash and the Hg components of the emissions.
Table 2-4. Emissions from Coal Combustion (adapted from Levy, et al. [59]).

<table>
<thead>
<tr>
<th>Particulates</th>
<th>Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon (coal, coke or soot)</td>
</tr>
<tr>
<td></td>
<td>Mineral matter</td>
</tr>
<tr>
<td>Gases</td>
<td>SO$_x$ (SO$_2$ and SO$_3$)</td>
</tr>
<tr>
<td></td>
<td>NO$_x$ (NO, NO$_2$, and N$_2$O)</td>
</tr>
<tr>
<td></td>
<td>CO$_2$ and CO</td>
</tr>
<tr>
<td>Organics</td>
<td>Hydrocarbons</td>
</tr>
<tr>
<td></td>
<td>Polycyclic organic matter (POM)</td>
</tr>
<tr>
<td>Trace Elements</td>
<td>Hg$^0$, Hg$^{2+}$</td>
</tr>
</tbody>
</table>

2.4.1 Behaviour of Sulfur during Oxy-fuel Combustion

Sulfur undergoes several chemical transformations during combustion and along the flue gas path. Figure 2-7 presents the main reaction routes of sulfur during coal combustion compiled from literature [11, 60, 61]. The two forms of sulfur (i.e. organic and inorganic) may not release at the same time during combustion, although the effect of this asynchronous release has no practical impact on the eventual SO$_x$ emissions [32]. During coal devolatilisation (under reducing conditions surrounding the burning coal particle), all forms of sulfur in the coal are decomposed into gas species which include H$_2$S (hydrogen sulphide – the major gas species), COS (carbonyl sulphide), SO$_2$ and CS$_2$, and mercaptans in the tar phase, whilst the rest remains trapped in solid char [62]. Nevertheless, as soon as the vapours (volatiles) diffuse from the burning particles, the oxidizing nature of the bulk gas stream would oxidise the sulfur species to their highest oxidation state [23]. However upon combustion, regardless of its occurrence in the parent coal, all forms of sulfur is transformed into either SO$_2$ at flame temperatures above 1200°C and secondary sulfur gas species SO$_3$, H$_2$SO$_4$ and inorganic solid sulfates in ash [14]; however not all of the SO$_x$ is emitted no matter how the coal is combusted [63].
Figure 2-7. The main reaction routes of sulfur during coal combustion [11].
2.4.2 Sulfur in Gaseous Phase during Oxy-fuel Combustion

As mentioned earlier, upon combustion the sulfur in coal devolatilises and may be present as SO\(_2\), SO\(_3\), H\(_2\)S, H\(_2\)SO\(_4\) and COS in gaseous form. SO\(_x\) is present as SO\(_2\) in the radiative and convective sections of the boiler and forms SO\(_3\) as flue gas cools [11, 16]. This SO\(_3\) reacts with water to produce sulfuric acid which is challenging since SO\(_3\)/H\(_2\)SO\(_4\) prevent the use of the selective catalytic reduction (SCR) process for NO\(_x\) control as it catalyses SO\(_2\) to form further SO\(_3\) [14]. The chemistry/interactions of sulfur with gaseous and solid species are described below. Moreover, review on acid dew point temperature and its measurement techniques are also presented in this section.

2.4.2.1 Sulfur Dioxide (SO\(_2\))

SO\(_2\) is formed from the decomposition and oxidation of pyrite (FeS\(_2\)), sulfates and organic sulfur associated in the coal matrix [11]. The sulfur oxides emissions are functions of the sulfur and ash composition of the coal [57, 59]. The main part of the fuel-bound sulfur is released to the gas phase during pyrolysis. Sulphides in the form of pyrite are usually a main fraction released according to the reactions [39, 41, 42, 48]:

\[
FeS\(_2\) (s) \rightarrow FeS (s) + \frac{1}{2} S\(_2\) (g) \quad \text{Reaction 2-1}
\]

\[
FeS (l) \rightarrow Fe + \frac{1}{2} S\(_2\) \quad \text{Reaction 2-2}
\]

\[
\frac{1}{2} S\(_2\) + O\(_2\) \rightarrow SO\(_2\) \quad \text{Reaction 2-3}
\]

Reaction 2-1 takes place during the heating phase of the fuel (under fuel-rich zones and reducing conditions [23]) and Reaction 2-2 takes place during the char combustion. On the other hand molten pyrite FeS (l), could also oxidise via the following reaction [48]:

\[
FeS + \frac{3}{2} O\(_2\) \rightarrow FeO + SO\(_2\) \quad \text{Reaction 2-4}
\]
Under oxidising conditions, some gas species formed during coal pyrolysis (reducing conditions) are oxidised via the following reactions [14]:

\[ H_2S + \frac{3}{2}O_2 \rightarrow H_2O + SO_2 \]  \hspace{1cm} \text{Reaction 2-5}

\[ CS_2 + 3O_2 \rightarrow 2SO_2 + CO_2 \]  \hspace{1cm} \text{Reaction 2-6}

2.4.2.2 Sulfur Trioxide (SO₃)

SO₂ is the thermodynamically favoured SOₓ at high temperatures (> 1200°C) and oxygen-rich conditions where H₂S can be deemed negligible [6, 16, 22, 41]. SO₂ is then converted to SO₃ via homogeneous gas phase or heterogeneous, catalytic reactions [11, 64]. The following reactions show the principal mechanisms for SO₃ production:

\[ SO_2 + O_2 \leftrightarrow SO_3 + O \]  \hspace{1cm} \text{Reaction 2-7}

Also, under high temperature and with oxygen radicals (O) present, SO₂ can further react with the oxygen radicals to form SO₃ [32, 65]:

\[ SO_2 + O(+M) \leftrightarrow SO_3(+M) \]  \hspace{1cm} \text{Reaction 2-8}

The above reaction proceeds rapidly near the flame zone (e.g. volatile flame), where oxygen atoms are present because of the high temperature. M indicates a third body usually a catalyst (e.g. Fe₂O₃). The catalyst works efficiently even at lower temperatures and found most efficient between 700 – 800°C [58, 66], and even at temperatures below ~400°C [64]. On the other hand Burdett, et al. [65] stated that if the oxygen atom concentration is not high enough, Reaction 2-8 will not occur. The following reactions are also important in the SO₃ formation [41]:

\[ SO_2 + OH \rightarrow HOSO_2 \]  \hspace{1cm} \text{Reaction 2-9}

\[ HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \]  \hspace{1cm} \text{Reaction 2-10}
While the equilibrium conversion of SO$_2$ to SO$_3$ is low under high temperatures, at lower temperatures, the equilibrium shifts towards SO$_3$ but the reaction rate slows as gas temperature cools; as a result, the reported conversion of SO$_2$ to SO$_3$ under typical combustion conditions ranges from 0.1 – 5% [15, 32, 41, 58, 59, 67, 68] which is several orders of magnitude lower than the SO$_2$ concentration in the emitted flue gas. The following reactions show SO$_3$ converting back to SO$_2$ [14]:

\[ \text{Reaction 2-11} \]

\[ SO_3 + O \rightarrow SO_2 + O_2 \]

\[ \text{Reaction 2-12} \]

\[ SO_3 + H \rightarrow SO_2 + OH \]

Annamalai and Puri [14] also stressed that whilst the formation of SO$_3$ is rapid near the flame zone, the conversion of SO$_3$ to SO$_2$, as shown in the reactions above, is relatively slow. Roughly 1.6% of the total SO$_2$ is converted to SO$_3$ in air-firing, 1.25% in an SCR-reactor with air-firing [58]. Whilst in oxy-fuel combustion, SO$_3$ production is more pronounced due to both higher SO$_2$ and O$_2$ concentration in the boiler, and is roughly a factor of 2–5 times greater than in conventional air-firing [58, 68-70].

Fleig, et al. [39] stated that an SO$_3$/SO$_2$ formation ratio of 0.1% – 1% is often observed in air-fired PC combustion. On the other hand, the presence of even a small amount of SO$_3$ is significant because of the following:

1. SO$_3$ leads to increased formation of sulphate which is a known precursor for PM2.5 particulates [32] which could also cause increased plugging of air preheaters (APH) and aerosol emissions [41].
2. At temperatures below 500°C, SO$_3$ is highly reactive and readily reacts with water vapour and produces H$_2$SO$_4$ based on the reaction below [1, 58, 71]:

\[ \text{Reaction 2-13} \]

\[ SO_3 \left( g \right) + H_2O \left( g \right) \rightarrow H_2SO_4 \left( g \right) \]
2.4.2.3 Sulfuric Acid (H$_2$SO$_4$)

H$_2$SO$_4$ presents a major hazard to environment both as acidic vapour and mist, and that any contact (*i.e.* humans and animals) with this mist has serious effects, depending on the exposure, ranging from irritation of the airways to death [71]. The national pollution inventory (NPI) sulfuric acid 8-hour time weighted average (TWA) exposure limit is 1 mg/m$^3$, with a short term exposure limit (STEL) of 3 mg/m$^3$ [72].

In industrial plants, H$_2$SO$_4$ is strongly corrosive to various materials and boiler components (*i.e.* the air heater) upon deposition [13, 32, 41]. Equilibrium calculations using FactSage 6.0 showing typical conversions of SO$_2$ into SO$_3$ and then into H$_2$SO$_4$ as the temperature decreases is shown in Figure 2-8. From this figure, it can be noted that at higher temperatures (> 1000°C) the thermodynamically favoured product is SO$_2$. In the range of about 400 and 500°C, the equilibrium shifts towards SO$_3$ however the kinetics is slow [6, 16]. It is in this portion where SO$_3$ is said to have rapid formation enhanced by fly ash catalysis [15, 16, 36]. At temperatures below 200°C, it could be observed that all of the SO$_3$ would have already formed. This is a critical temperature region where all available SO$_3$ would react with the H$_2$O vapour available in the boiler to form H$_2$SO$_4$. The figure shows that at gaseous H$_2$SO$_4$ (dashed lines) condenses to form liquid H$_2$SO$_4$ (dotted lines - leftmost) at temperatures below 160°C.

It can also be seen in the figure above that at about 160°C, the H$_2$SO$_4$ vapour condenses and that this point where the sulfuric acid liquid starts forming is termed as the sulfuric acid dew point temperature or simply acid dew point (ADP) [15, 22, 73] which generally ranges from 95 – 150°C [16, 39, 41]. This agrees with equilibrium calculations completed by several researchers [16, 39, 41]. According to Spörl, *et al.* [58], in power plants there are no other flue gases condensing at 100 – 200°C.
Figure 2-8. Equilibrium Calculations for SO₂, SO₃ and H₂SO₄. Model Input: [SO₂] = 2000 ppm, [O₂] = 3% vol., [H₂O] = 30% vol. to simulate oxy-fuel combustion with full flue gas recycling (without cleaning).

2.4.2.4 Sulfuric Acid Dew Point (ADP) Temperature

Dew point is defined as the temperature at which the first liquid starts to condense from the gas phase. When the temperature drops below the dew point, H₂SO₄ will start condensing either as small fog droplets/mist or as a film onto the walls. Huijbregts and Leferink [73] stated that:

- **Condensation Droplets/Mist:** Will be formed very easily on particles in the flue gas, acting as condensation nuclei. For instance fly ash particles (coal fired boilers, waste incineration boilers) can cause the mist condensation.
- **Film Condensation:** In a clean gas, as in gas fired units, super-saturation will take place, resulting in film condensation on the cool walls or heat exchanger tubes.

Acid mist according to Liu, et al. [16] happens when the gas is cooled at high cooling rates. If a mist is formed, most of the droplets are carried away with the flue gas and, in case of acid droplets, the corrosion rate of steel will be low. However, in the case of super-saturation, film condensation will occur and a liquid film will be formed on the bundle tubes or on the flue gas line walls. Besides, in the case of mist
condensation, high gas velocities or local high flow disturbances will push the droplets onto the metal walls and a thin liquid film is formed as well by this mechanism [73].

Correlations show that concentrations of SO\textsubscript{3} and H\textsubscript{2}O are important factors in determining the acid dew point of the flue gas. The optimum operating temperature range at which SO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} ADP measurement should be taken is crucial as it causes boiler losses as shown in Figure 2-9. At temperatures below the acid dew point the liquid H\textsubscript{2}SO\textsubscript{4} begins to condense on component surfaces and potentially results in corrosion. During oxy-fuel combustion, as stated in the previous sections, SO\textsubscript{2} is expected to be higher due to the RFG and lower gas volumes resulting to higher SO\textsubscript{3} values which in turn give a higher acid dew point. This behaviour can be seen in Figure 2-9 where ADP temperatures can be 20 – 30\textdegree C higher during oxy-fuel when the recycled flue gas is partially cleaned, \textit{i.e.} practical oxy-fuel situation, and > 40\textdegree C higher during oxy-fuel when the flue gas is recycled without any cleaning compared to air-firing. This then increases the risks for corrosion in the cooler sections of the power plant and the requirement to operate at higher flue gas temperatures which results in boiler efficiency losses.

![Figure 2-9](www.landinst.com)

**Figure 2-9.** Exit Gas Temperature versus Boiler Losses indicating a small optimal window for operation (adapted from www.landinst.com).
Although correlations such as the ones by Verhoff and Banchero (VB) and the ones by Okkes exist and have previously been used in estimating acid dew points, the more recent correlation between $\text{SO}_3$ and $\text{H}_2\text{O}$ by ZareNezhad [50] were employed in this study. In ZareNezhad’s study, the VB correlation has shown over prediction of ADP which could lead to higher operating temperatures in the air pre-heaters (APH) and cause boiler efficiency losses whilst the Okkes correlation has shown under prediction of the ADP that the APH could potentially be at risk for cold end corrosion. The ZareNezhad correlation [50] estimates the ADP as presented in Equation (2-1):

$$T_{dew} = 150 + 11.664 \ln(p_{\text{SO}_3}) + 8.1328 \ln(p_{\text{H}_2\text{O}}) - 0.383226 \ln(p_{\text{SO}_3}) \ln(p_{\text{H}_2\text{O}}) \quad (2-1)$$

Where:
- $T_{dew}$ = sulfuric acid dew point temperature, °C
- $p_{\text{H}_2\text{O}}$ = partial pressure of $\text{H}_2\text{O}$ in the flue gas, mm Hg
- $p_{\text{SO}_3}$ = partial pressure of $\text{SO}_3$ in the flue gas, mm Hg

**A. Measurement of $\text{SO}_3$ and the $\text{H}_2\text{SO}_4$ Acid Dew Point: The Controlled Condensation Method**

The controlled condensation method (CCM) [16, 39, 70, 74, 75] is one of the most common techniques used to measure the amount of condensed $\text{SO}_3$. It is an American Society for Testing and Materials technique (ASTM D3226-73T) [1, 75, 76] employed by several facilities and investigators. Its basic aim is to take advantage of the differences between the sulfuric acid and water dew points to selectively collect $\text{H}_2\text{SO}_4$ [1]. The $\text{SO}_3$ is allowed to react with water in the gas stream and condense as sulfuric acid on cooled surfaces which according to Goksoyr [74] should be kept between 60 and 90°C because at these temperatures negligible amounts of $\text{H}_2\text{SO}_4$ exists in the gas phase. Also, water is not expected to condense between these temperatures, and that water in the flue gas generally condenses below 50°C [74].
The system used by the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Germany is shown in Figure 2-10. It shows the sampling and measurement train for SO$_3$ using the CCM technique, from a German standard VDI [77] based on the ASTM Method 8A [75, 76]. Flue gas enters the probe lined with quartz wool to prevent ash from entering the system however the catalysing potential of SO$_2$ to SO$_3$ is one of the greatest areas of uncertainty in this system. The glass coil condenser is kept between 85 and 95°C using a water bath to keep the system below the acid dew point but above the water dew point. Water vapour entering is then removed by silica gel and the collected SO$_3$ is measured by titration.

**Figure 2-10.** IFK Stuttgart SO$_3$ sampling and measurement (top left) SO$_3$ condenser (top right) and sampling probe (bottom) with quartz wool acting as ash filter (Liu, et al. [16]).

The total SO$_3$ is then collected with a known amount of water and titrated for H$_2$SO$_4$. Since SO$_3$ is highly reactive with water, it is accepted that all of SO$_3$ will react with water to form H$_2$SO$_4$. Then knowing the amount of sampled gas, this
amount of H₂SO₄ could then be calculated by basic stoichiometry as a concentration of SO₃ [16].

**Figure 2-11** shows the system used by the University of Utah based on ASTM D 3226-73T with the same concept of selectively condensing H₂SO₃. The heated quartz filter is used to separate the particulate matter, condensers maintained between 75 and 85°C for SO₃ condensation and the 3% peroxide for SO₂ capture. Then the collected condensed sulfuric acid and hydrogen peroxide solutions are titrated using barium perchlorate with thorin indicator (EPA Method 8A) for measurement. The gas then enters two columns of silica gel to remove the water prior to entering the pump and the gas meter.

![Diagram of CCM apparatus](image)

**Figure 2-11.** CCM apparatus used by the University of Utah for SO₃ measurement (Eddings, et al. [70, 78] Ahn, et al. [1]).

**B. Acid Dew Point Probe**

Direct online measurement of H₂SO₄ ADP was introduced by Land [16] where a conductive cell measurement is triggered by sulfuric acid condensing onto the tip of the probe itself thus closing the loop (**Figure 2-12**). In using this probe, cooling air (compressed air) is gradually increased to lower the
temperature of the probe where flue gas (containing SO₂, SO₃ and H₂SO₄) passes around it. When the tip is cool enough to cause the sulfuric acid to condense, the current will register on the ammeter and the temperature can be read with the thermocouple.

One of the main disadvantages of this ADP probe by Land is that the current signal is affected by fly ash build up on the probe. This means that measurements before particle removal at the Electrostatic Precipitators (ESP) or Fabric Filters (FF) are deemed impossible. Liu, et al. [16] also stressed that according to the equilibrium calculations between SO₂, SO₃ and H₂SO₄, above 200°C some SO₃ still presented as SO₃ and not as H₂SO₄ vapour. Therefore, an under-prediction of the amount of SO₃ present as SO₃ and H₂SO₄ would occur if ADP is measured at this temperature.

![Figure 2-12. Acid Dew Point (ADP) Probe used by Land as presented by Liu, et al. [16].](image)

2.4.3 Sulfur in Ash

Fly ash is a powdery substance, non-combustible residue which remains after combustion of coal [57, 79]. It is considered as the final form of mineral matter present
in coal and usually collected in dust collectors / bag filters [57]. All of the coal sulfur during coal devolatilisation and char combustion is released to form gas species. The gaseous sulfur species diffuse outwards through the char particle pores, during which a part of SO$_2$ may react with the base oxides forming sulfates that remain in the ash [80].

The formation of low-melting metal sulfates (Mg, Na, K, Ca, Fe) has been linked to corrosion by providing a surface for adhesion along the walls for other particulates as well [6]. The most important base oxide for sulfur self-retention (SSR) is CaO, which is formed as a result of CaCO$_3$ decomposition and combustion of the organic groups containing Ca [30]. Corrosion and damage to the radiative and convective sections of the furnace could also be attributed to molten slags and solid ash depositions. In oxy-fuel combustion conditions where there is higher dust loading [6, 81] as shown in Figure 2-13, investigators have noted higher SO$_2$ concentrations in the flue gas which could be captured in the fly ash (FA). Therefore, understanding on the amount of sulfur captured by the fly ash is essential in evaluating the fate of sulfur and closing its balance in oxy-fuel conditions where a lot more sulfur is said to be captured by the FA due to higher concentration of SO$_2$ in the RFG and in the oxidant.

![Graph showing differences between dust loading during air and oxy-fuel combustion](image)

**Figure 2-13.** Differences between the dust loading during air and oxy-fuel combustion [81].
2.4.3.1 Sulfur Capture and Retention in Fly Ash

Some of the SO\textsubscript{x} formed during combustion is captured and retained in ash whilst some coal-S still remains bound in the minerals without being released. Fleig, et al. [39, 41, 42] presented sulfur retention together with the calculated remaining SO\textsubscript{2} in flue gas under oxy-fuel conditions in their experiments with Lausitz lignite (Figure 2-14). It can be seen in the figure with the dashed line at 9% Ash Sulfur, the sulfur retention would be 60% and that nearly 2000 ppm SO\textsubscript{2} would still be measured in the flue gas. Levy, et al. [59] stated that in a typical coal with ~15% ash, ash would contain basic oxides: SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, CaO, MgO, K\textsubscript{2}O and Na\textsubscript{2}O of which the last four oxides, known in this thesis collectively as alkali and alkaline-earth metal oxides would comprise between 5 and 30% of the ash. The AAEM oxides can capture as much as 60% of the coal sulfur whilst the rest is emitted as SO\textsubscript{2} or SO\textsubscript{3} [59], similar to the capture determined by Fleig, et al. [39, 41, 42].

![Figure 2-14](image)

**Figure 2-14.** Sulfur retention versus sulfur content in ashes where Y\textsubscript{S} is the sulfur content of the fly ash based on a study conducted by Fleig et al. [41].

On the assumption that if SO\textsubscript{3}, H\textsubscript{2}S and the absorption of the sulfur compounds in condensing water is negligible, the retention of sulfur in ash was calculated by Fleig, et al. [41] as:
Fleig et al. [39] stated that the sulfur not found as SO\(_2\) is mainly captured by alkali and alkaline-earth metals (Na, K, Mg, Ca) in the ash and deposits as sulfates, or it is bound in the minerals without being released. Levy, et al. [59] even stressed that in coals, the oxides of Na, K, Mg and Ca which makes up about 5 to 30% of the fly ash will capture as much as 60% of the coal sulfur. The higher SO\(_2\) concentration in oxy-fuel combustion due to RFG may favour the formation of sulfates (capture of sulfur) [43]. Furthermore, the calcination and sulfation of CaCO\(_3\) is enhanced in an atmosphere with a high SO\(_2\), CO\(_2\) and partial pressure [79].

Schnurrer, et al. [43] conducted a modelling study on the influences of oxy-fuel environment on sulfur species that are captured in fly ash during pulverised fuel combustion. The FactSage model presented in Figure 2-15 shows temperature range as the flue gas cools from 1500 down to 100°C. The figure shows possible sulfur species present during combustion in gaseous, liquid and solid phases. Also, according to Schnurrer, et al. [43] due to the higher concentration of SO\(_2\) and CO\(_2\) during oxy-fuel combustion, the formation, condensation, solidification and decomposition of almost all the sulfates in oxy-fuel occur at temperatures of roughly 30 to 60°C higher than during air combustion. In the modelling studies, they have concluded that during oxy-fuel combustion higher capture was observed. With these it is essential that the amount of sulfur captured and the active species capturing sulfur be identified in order to address fouling and slagging issues that occur when dealing with higher impurity concentrations.
Figure 2-15. Sulfur species formation during gas cooling for air and oxy-fuel combustion conditions (Schnurrer, et al. [43]).
2.5 FACTORS AFFECTING SO₂ TO SO₃ CONVERSION

Several factors are said to impact the conversion of SO₂ to SO₃. This section presents and summarises the effects of these factors: composition of the combustion environment; temperature profile; residence time and fly ash composition.

2.5.1 The Effects of Combustion Environment

2.5.1.1 Concentration of SO₂

Several studies have shown that coal-S to SO₂ has a lower conversion (mg/MJ) but higher concentrations (ppm) under oxy-fuel than its air-fired counterpart [39–42]. Figure 2-16 shows different fuel-S to SO₂ conversions (mg/MJ) during oxy-firing and Figure 2-17 shows the conversion in concentration units (ppm). From Figure 2-17, it can clearly be seen that fuel-S levels dictate the amount of SO₂ emitted by the coals. However it may also be observed from the figure that for similar coals, e.g. IHI Air (shaded square marker) and Oxy (empty square marker), SO₂ concentrations in the flue gas are much higher. This higher SO₂ concentration in oxy-fuel could be attributed to the RFG which contains SO₂ and higher O₂ concentrations that make up the oxidiser in oxy-firing compared to conventional air-firing. Stanger and Wall [6] also stated that SO₂ emissions (mg/MJ), which are lower in oxy-fuel, may be due to higher sulfur retention in oxy-fuel ash.

Figure 2-16. Differences in SO₂ emissions (mg/MJ) during air and oxy-fuel combustion [36, 45].
Figure 2-17. Comparison of SO$_2$ emitted from air-fired with their corresponding oxy-fuel fired results for different fuel-S levels (Stanger and Wall [6]).

Typical conversions of SO$_2$ to SO$_3$ in coal-fired utility boilers were reported to be around 0.5 – 3% [68]. Roughly 1.6% of the total SO$_2$ is converted to SO$_3$ in air-firing, 1.25% in an SCR-reactor with air-firing [58]. Spörl, et al. [21] compiled pilot scale studies and plotted typical SO$_2$ to SO$_3$ conversions during air and oxy-fuel combustion (Figure 2-18). Further discussion on the results from this figure is discussed in Chapter 5. Whilst in oxy-fuel combustion, SO$_3$ production is more pronounced due to higher O$_2$ and SO$_2$ concentrations in the boiler (due to the RFG in the oxidiser). Concentration is roughly 2 – 5 times greater than in conventional air-firing [6, 21, 25, 41, 58, 68, 69] as shown in Figure 2-19 compiled by Stanger and Wall in their review on sulfur impacts during oxy-fuel combustion.

Homogeneous kinetic studies completed by Burdett, et al. [65] conducted at 900 – 1350 K concluded that SO$_3$ production is linearly related to SO$_2$ input concentration and that the SO$_3$ is first order with respect to SO$_2$. Svachula, et al.
[82], Schwaemmle, et al. [83] and Forzatti [84] among others confirmed that first order dependence with respect to SO$_2$ at concentrations 0 to 1000 ppm is reasonable but at low concentrations (< 200 ppm) apparent higher order exists.

Figure 2-18. Impact of different SO$_2$ concentrations on SO$_3$ production [39].
Figure 2-19. Comparison of SO$_2$ and SO$_3$ emissions from air and oxy-fuel combustions from different studies (Stanger and Wall, [6]). Change from Air to Oxy is denoted by the arrow directed to the right upwards.

2.5.1.2 Concentration of O$_2$

Reactions 2-7 and 2-8 presented the mechanisms of SO$_3$ formation by reacting SO$_2$ with either atomic or molecular oxygen. During oxy-fuel combustion where there is higher O$_2$ concentration and decreased volume flow through the furnace resulting to longer residence times, it is expected that SO$_3$ concentration in the flue gas increases [41]. Research work completed by Fleig, et al. [64] which involved feeding oxidant gases (SO$_2$, O$_2$, CO, H$_2$O, CO$_2$/N$_2$) through a vertical quartz reactor investigated the effects of varying amounts of O$_2$ in the system and the results revealed that O$_2$ concentration in the oxidant stream has a significant effect on the SO$_3$ output (Figure 2-20).
Figure 2-20. Effect of O$_2$ concentration on the output concentration of SO$_3$. Input concentrations: 1000 ppm SO$_2$, no CO (Fleig, et al. [64]).

Burdett, et al. [65] studied the kinetics of homogeneous SO$_3$ formation at 900 – 1350 K using a quartz tube reactor. Their results revealed that there is a linear relationship between O$_2$ concentration and SO$_3$ output indicating a first order relationship with respect to O$_2$ concentration in the oxidant. Svachula, et al. [82] and Forzatti [84] stated that a dependence of SO$_3$ production upon O$_2$ concentration manifests when their concentrations are comparable.

2.5.1.3 Concentrations of CO$_2$, CO and CH$_3$

A. Increased CO$_2$ during Oxy-fuel Combustion

Fleig et al. [41, 64] conducted modelling and noted that the change from N$_2$ to CO$_2$ increases the SO$_3$/SO$_2$ ratio, due to the increased CO$_2$ concentration during oxy-fuel combustion which affects the radical pool as it forms more OH. The elevated OH-radical concentration then enhances secondary formation of SO$_3$ (Reaction 2-12) [41]. This reaction between CO$_2$ and H is presented as follows:
\[ CO_2 + H \rightarrow CO + OH \]  

It was also noted by Fleig, et al. \[41\] that due to the RFG in oxy-fuel, the effects of having higher H\(_2\)O in the system increases SO\(_3\) in the flue gas. A latter experimental work by Fleig, et al. \[64\] proved the earlier modelling results where experiments in oxy-fuel resulted to slightly higher SO\(_3\) output concentrations than in N\(_2\); at 1300 K the effects of CO\(_2\) was most pronounced where SO\(_3\) produced was 30\% higher in oxy than in air.

**B. Combustibles CO and CH\(_4\) in the Oxidant**

Experiments were carried out by Fleig, et al. \[64\] involving combustibles CO and CH\(_4\) in the oxidant through a vertical quartz reactor to determine their effects on SO\(_3\) formation. Experimental and modelling results revealed higher SO\(_3\) formation during runs with the presence of CO and CH\(_4\). SO\(_3\) produced at 1200 K with 3\% vol. O\(_2\) and 1000 ppm CO produced SO\(_3\) threefold higher than without CO.

**2.5.1.4 Concentration of NO\(_x\)**

The effect of NO\(_x\) (as NO) on SO\(_3\) formation has also been studied by Fleig, et al. \[39\] and their modelling results showed that NO concentrations from 0 – 2000 ppm gave a slightly decreasing trend before reaching equilibrium. A smaller amount of NO favours SO\(_3\) production whilst a higher NO concentration decreases formation of SO\(_3\). Kinetic experiments conducted by Svachula, et al. \[82\] and Forzatti \[84\] confirmed that NO\(_x\) slightly enhances SO\(_3\) formation. Results from their experiments stated that from concentrations 0 to 1000 ppm NO\(_x\), only a slight increase in conversion from \(~2\) to 3\% was observed.
2.5.1.5 Concentration of $H_2O$ in the Recycled Flue Gas

Fleig et al. [39, 41] (Section 2.4.2.4) noted that for their three experimental conditions (air, oxy with RFG dry, oxy with RFG wet), the ADP increases with increasing $H_2O$ concentrations in the flue gas which agrees with the statements by ZareNezhad [50] on the influences of $SO_3$ and $H_2O$ on the ADP. They also stated that the influence of $H_2O$ content in the flue gas is considerable in the wet RFG. In this case, an increase in ADP by 20 – 30 K (°C) is expected due to higher $SO_3$ and $H_2O$ concentrations. Apart from increasing the ADP of the system, a more recent completed research by Fleig, et al. [64] provided experimental evidence that presence of $H_2O$ in the combustion system increases the amount of $SO_3$ produced. On the other hand, previous kinetic studies completed by Burdett, et al. [65], Schwaemmle, et al. [83], Svachula, et al. [82], and Forzatti [84] among others have stated that the $SO_3$ production is independent of the $H_2O$. With such varied claims, it is therefore quite interesting to see that in the absence of combustibles during flue gas cooling, will the presence of more water support higher $SO_3$ formation?

2.5.2 The Effects of Temperature Profile and Cooling Rate

Several investigators [1, 32, 40, 47] have presented evidence that at higher temperatures (>1000°C), $SO_2$ is the favoured $SOx$ and that equilibrium is shifted to $SO_3$ at lower temperatures as expected from thermodynamic considerations (Figure 2-8). Fleig et al. [41] stated that increase in $SO_3$ is primarily formed during the cooling of the flue gas in the temperature range 1300 to 900°C. Experiments were performed by Fleig et al. [41] to test the effect of cooling rate and stoichiometric ratio on the outlet $SO_3$ formation under oxy-fuel conditions (Figure 2-21). It can be seen that for all cooling rates, a higher stoichiometric ratio (oxidising conditions) results to higher $SO_3$ formation. Whilst for all stoichiometric ratios, it can be noted that as the cooling rate is increased (50 to 500°C/s) outlet $SO_3$ decreased.
Figure 2-21. Influence of cooling rate and stoichiometric ratio on SO$_3$ conversion under oxy-fuel with initial conditions: 2000 ppm SO$_2$, 1800°C cooled to 400°C (Fleig, et al. [39, 41]).

2.5.3 The Effects of Residence Time

Experiments conducted by Flint and Lindsay [85] involved air containing 0.14%vol. SO$_2$ and 8%vol. H$_2$O passing through an electrically heated quartz reactor to determine the effects of contact / residence time on SO$_3$ formation. Results plotted in Figure 2-22 show for homogeneous conversions of SO$_2$ to SO$_3$, temperatures of around 900°C should be maintained in the quartz reactor to have an observable conversion with a minimum residence time of ~1 seconds.

Figure 2-22. The effect of contact time in the quartz reactor on the conversion of SO$_2$ to SO$_3$ [85].
2.5.4 Fly Ash Composition

Fe\textsubscript{2}O\textsubscript{3} which is naturally occurring in fly ashes is known to catalyse the formation of SO\textsubscript{3} [39, 66, 70, 78, 86] in the convective zone [6, 70]. Experiments completed by Marier and Dibbs [66] involving 8\% SO\textsubscript{2} in N\textsubscript{2} showed that SO\textsubscript{3} production is linearly increasing with increasing iron oxide content. With 7 to 25\%w Fe\textsubscript{2}O\textsubscript{3} in fly ash enhances conversion of SO\textsubscript{2} from 10\% to about 30\%. Apart from iron oxides, Fleig et al. [39] stated that according to several authors, vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) was shown to favour the formation SO\textsubscript{3} however if the alkalinity of the fly ash is high (i.e. CaO and MgO), it might capture SO\textsubscript{3} instead (Discussion on sulfur in fly ash previously presented in Section 2.4.3).

2.6 IMPACTS OF SULFUR IN OXY-FUEL COMBUSTION

Increased SO\textsubscript{x} levels in oxy-fuel combustion have well been known to cause corrosion, slagging and particulate formation problems along the lines. Stanger and Wall [6] presented the impacts of sulfur in pulverised coal oxy-fuel combustion which will be further discussed in the succeeding sections. Figure 2-23 and Table 2-5 present and summarise the possible locations along the plant with their corresponding sulfur impacts.

![Figure 2-23](image)

**Figure 2-23.** The Callide Oxy-fuel Project (COP) schematic with markers showing sites for possible sulfur impacts during oxy-fuel operation and text in italics showing options for sulfur cleaning (Adapted from Stanger, et al. [6, 35]).
Table 2-5. Impacts of sulfur in a coal-fired power plant [6, 36].

<table>
<thead>
<tr>
<th>Location</th>
<th>Impacts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>Corrosion (High Temperature), slugging</td>
</tr>
<tr>
<td>Convective Pass</td>
<td>Corrosion (High Temperature), fouling</td>
</tr>
<tr>
<td>SCR</td>
<td>Fouling, catalytic formation of SO(_3) and ammonium sulfates</td>
</tr>
<tr>
<td>ESP</td>
<td>Increased performance</td>
</tr>
<tr>
<td>Heat Exchanger</td>
<td>Corrosion (Low Temperature) – H(_2)SO(_4) deposition and condensation below ADP</td>
</tr>
<tr>
<td>Compression Unit</td>
<td>Corrosion (Low Temperature) – H(_2)SO(_4)</td>
</tr>
<tr>
<td>CPU</td>
<td>SO(_2)</td>
</tr>
<tr>
<td>Transport</td>
<td>Corrosion</td>
</tr>
<tr>
<td>Storage</td>
<td>Corrosion</td>
</tr>
</tbody>
</table>

2.6.1 Corrosion

During combustion, sodium and potassium are likely to be released from coal as chlorides and hydroxides [23]. The formation of the low melting sulfates (Na, K, Ca, Mg, and Fe) [6, 39, 41] causes corrosion by providing a surface for adhesion for other solid particles that may react directly with the walls. A simple reaction was presented by Wen and Cowell [23] where at temperatures below 1800°F (< 1000°C), a significant portion of the vapour alkali will be converted to condensed sulphate according to the following:

$$2NaCl(g) + H_2O(g) + SO_2(g) + O_2(g) \leftrightarrow Na_2SO_4(c) + 2HCl(g) \quad \text{Reaction 2-15}$$

Wen and Cowell [23] estimated 2 seconds as the residence time for the evaporation of NaCl and its conversion to Na\(_2\)SO\(_4\) which could then condense onto entrained particulates or nucleate to form an aerosol. Corrosion is said to be initiated when the alkali sulfates condense on the metal surfaces due to temperature drops along the lines or due to an increased acidic component (SO\(_3\)) of the flue gas.

Stanger and Wall [6] reported that in oxy-fuel combustion the higher concentrations of SO\(_x\) can lead to increased corrosion potential from molten and solid ash
boiler deposits, or from acid gas corrosion by operating heat exchangers below the acid dew point. Liu, et al. [16] cited that other investigators completed studies at the University of Stuttgart exposing CaSO₄ in a CO₂-enriched atmosphere (oxy-fuel conditions) and found that CaSO₄ has a high tendency to form CaCO₃ at these conditions hence promoting corrosion potential across the lines as well. Liu, et al. [16] reviewed pilot scale oxy-fuel tests at the 40 MWt Doosan Babcock facility [87] where Figure 2-24 shows corrosion of the direct contact cooler (DCC) impeller used to remove water from the primary flue gas recycle. The water that is removed became acidic as SOₓ (particularly SO₂) was absorbed in the water.

Figure 2-24. Corrosion at the direct contact cooler from Doosan Babcock 40 MWt facility [16].

2.6.2 Particulate Formation

It can be noted from Table 2-5 that although the effects of SOₓ in the flue gas is generally negative, having a little SO₃ in the system is beneficial especially in the ESP section where SO₃ reacting with moisture (forming H₂SO₄) condenses to form a conductive layer on the surface of the fly ash that decreases its and in turn provides better ash and dust capture [6, 88]. This promotes the formation of particulate matter [6] which in turn provides a surface for sulfates to deposit which could cause corrosion on metal parts of the boiler.
2.6.3 Compression

In the review made by Stanger and Wall [6], it stated that that SO\textsubscript{x} impurities have the potential to interact unfavourably in the compression train, particularly through acidic corrosion. It was also mentioned that the energy requirements for the isothermal compression, distillation and purification of CO\textsubscript{2} are sensitive to SO\textsubscript{x} concentrations. Equilibrium modelling from the same review [6] shows that any moisture left in the supercritical CO\textsubscript{2}, during compression would react with the SO\textsubscript{x} to form H\textsubscript{2}SO\textsubscript{4} as opposed to H\textsubscript{2}CO\textsubscript{3}; this in turn is corrosive to the compression train. Also, as discussed in the previous section, NO\textsubscript{x} in the compression acts as a catalyst in SO\textsubscript{3} formation.

One of the main problems of having higher SO\textsubscript{2} and SO\textsubscript{3} in the system is that these SO\textsubscript{x} species readily react with water, hence with higher water during oxy-fuel combustion. The risk of low temperature corrosion by H\textsubscript{2}SO\textsubscript{4} is much higher.

2.6.4 Sulfur and Mercury Interaction during Oxy-fuel Combustion

Apart from typical corrosion impacts of SO\textsubscript{x} species in the combustion system. Several investigators [6, 68, 89, 90] stated that there is evidence of SO\textsubscript{x} levels inhibiting Hg oxidation within the SCR by competing for the same oxidation sites as well as for the unburned carbon (UBC) in fly ash. Sjostrom, et al. [89] have studied the effect of SO\textsubscript{3} on mercury removal using activated carbon and found that increasing SO\textsubscript{3} in the flue gas from 0 to 10.7 ppm, would cause a decrease in Hg removal by activated carbon from >95% down to 58%. This is an important consideration especially upstream of the CO\textsubscript{2} compressor as Hg must be removed prior to compression as it may cause corrosion. The following subsections will discuss coal in oxy-fuel combustion and the control options available for Hg removal.

2.6.4.1 Mercury in Coal

Mercury is a naturally occurring element found in air, water and soil. It is released by natural and anthropogenic sources. The US Environmental Protection Agency (EPA) considered mercury to be a hazardous pollutant for both humans and the environment [91]. Kostova, et al. [92] stated that with the concentrations of Hg\textsuperscript{0}
in the atmosphere at present, it is not considered harmful. However, it has received much attention due to its bio-accumulation tendency when converted into its toxic organic form (CH₃Hg⁺) within the aquatic system [92, 93], difficulty to control and persistence in the atmosphere (0.5 to 2 years residence time) [94]. Kong, *et al.* [93]

The single largest anthropogenic source of mercury is coal-fired utility boilers [91, 95, 96]. Coal contains trace amounts of mercury as contaminants depending on its rank, and is commonly associated with sulfur compounds in coals [17]. Due to the volatility of mercury and its compounds, when coal is combusted, Hg in the fuel completely evaporates and is converted to elemental mercury vapour with typical concentrations of 0.3 – 35 µg/Nm³. Some reported values have reached 70 µg/Nm³ [17, 94, 96, 97].

Mercury exists in three states; elemental mercury vapour (Hg⁰), oxidised mercury species (Hg²⁺) and particulate-bound mercury (Hgₚ). The speciation is said to be dependent on the concentration of sulfur and halogens in the coal [17, 91, 97], flue gas temperature and composition [7, 91, 97]. Galbreath and Zygarlicke, [94] and Monterroso, *et al.* [98] detailed the possible transformations of mercury in a combustion system, which are represented in Figure 2-25. Table 2-6 presents the appearance of different Hg species typically found in coal as summarised by Monterroso, *et al.* [98]. Monterroso, *et al.* [98] stated that in fly ash, the order of mercury appearance as per equilibrium calculations is HgCl₂ < HgS < HgO. Highlighted in the table are the Mercury-Sulfur compounds.

Hg⁰ is released upon volatilisation at about 200°C and continues throughout coal combustion. Hg⁰ can then be oxidised to Hg²⁺ via homogeneous (gas phase) and/or heterogeneous (gas-solid) oxidation reactions as the flue gas cools [7, 17, 98]. Galbreath, *et al.* [94] stated that the oxidised mercury are usually found either as gaseous (g) or solid (s) inorganic mercuric compounds, Hg²⁺X (where X are anions, e.g. Cl₂(g), SO₄(s), O(g,s), S(s)). The gaseous Hg²⁺ species may either stay in the gas phase or be captured by the fly ash together with any solid Hg²⁺ as Hgₚ. The gaseous Hg²⁺ is soluble in water and can also associate with particulate matter [99] and get captured as Hgₚ. Hence, Hg²⁺ and Hgₚ can easily be captured and removed
through conventional air pollution control devices (APCDs) like electrostatic precipitators (ESP), fabric filter (FF) or bag houses, scrubbers, flue gas desulfurisers (FGDs) and selective catalytic reducers (SCR) [98, 99].

Table 2-6. Typical mercury species found in coal showing initial and final temperatures of appearance including the temperature at which maximum concentrations were obtained [98].

<table>
<thead>
<tr>
<th>Mercury compound</th>
<th>Temperature at maximum concentration (°C)</th>
<th>Initial temperature of appearance (°C)</th>
<th>Final temperature of appearance (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl₂</td>
<td>120 ± 10</td>
<td>70</td>
<td>220</td>
</tr>
<tr>
<td>Hg₂Cl₂</td>
<td>80 ± 5 and 130 ± 10</td>
<td>60</td>
<td>220</td>
</tr>
<tr>
<td>HgBr₂</td>
<td>110 ± 5</td>
<td>60</td>
<td>220</td>
</tr>
<tr>
<td>HgS (black) (metacinnabar)</td>
<td>205 ± 5 and 245 ± 5</td>
<td>170</td>
<td>290</td>
</tr>
<tr>
<td>HgS (red) (cinnabar)</td>
<td>310 ± 10</td>
<td>240</td>
<td>350</td>
</tr>
<tr>
<td>HgSO₄</td>
<td>540 ± 20</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>Hg₂SO₄</td>
<td>280 ± 10</td>
<td>120</td>
<td>480</td>
</tr>
<tr>
<td>HgO</td>
<td>505 ± 5</td>
<td>430</td>
<td>560</td>
</tr>
</tbody>
</table>
Figure 2-25. Routes of Hg transformation during combustion of coal [94, 98].
2.6.4.1 Mercury in Oxy-fuel Combustion

Due to the recycling of the flue gas, concentrations of the oxy-fuel impurities (e.g. CO₂, SO₂ and H₂O) are increased by up to 4 times [6, 7, 11, 15, 17, 21]. Together with this, higher mercury concentrations are also expected. Although it has been established that mercury still represents an environmental problem, higher Hg concentrations pose an additional operational / technological problem; Hg⁰ vapour in the flue gas can accumulate in the CO₂ compression and processing units and corrode the aluminium heat exchangers used in cryogenic liquefaction [17, 100]. Liu, et al [101] reported that typically for low temperatures, aluminium alloys Al 3003, Al 5083 or Al 6061 are used. Alloys such as Al 5083 is said to be an Al-Mg alloy where it is susceptible to attacks by mercury when allowed to condense and in the presence of moisture. Attack on aluminium heat exchangers could happen in several ways, namely [101]:

- *Amalgamation*, where Hg forms liquid solution with metal surfaces;
- *Amalgam corrosion*, where Hg attacks the metal and causes pits;
- *Liquid metal embrittlement* (LME), usually at around – 40°C
- *Galvanic corrosion*.

Figure 2-26 presents a photo of heat exchanger corroded by mercury attack as reported by Liu, et al. [101]. Presented in Figure 2-27 is a mechanistic diagram showing mercury attack on aluminium [102].
Figure 2-26. Al-Mg alloy used in heat exchangers showing mercury attack [101].

Figure 2-27. Amalgamation and amalgamation corrosion of aluminum showing pitting caused by mercury attack [102].

Due to the RFG, amalgamation would be more challenging since according to Wilhelm [102], spontaneous amalgam corrosion occurs when water comes in contact with the amalgam (condensed mercury-metal species) and that the rate is proportional with humidity. Amalgamation and amalgam corrosion occur via the following reactions as presented by Wilhelm [102]:

\[ Hg + Al \rightarrow Hg(Al) \] \hspace{1cm} \text{amalgamation} \hspace{1cm} \text{Reaction 2-16}

\[ Hg(Al) + H_2O \rightarrow Al_2O_3 \cdot 3H_2O + H_2 + Hg \] \hspace{1cm} \text{Reaction 2-17}

\[ Hg + Al \rightarrow Hg(Al) \] \hspace{1cm} \text{Reaction 2-18}
2.6.4.2 Mercury and SO\textsubscript{x} Competition

An extensive review by Stanger and Wall [6] which focused on sulfur impacts in oxy-fuel noted that apart from SO\textsubscript{x} inhibiting mercury oxidation within the SCR, SO\textsubscript{x} was also said to compete with Hg for the active sites on the activated carbon. A study by Wang, et al. [99] also presented evidence of increasing mercury removal with increasing sulfur content in the coal. They stated that presence of sulfur and chlorine could oxidise Hg\textsuperscript{0} (g) into Hg\textsuperscript{2+} by the following reactions [99]:

\[
SO_2(g) + O_2(g) + Hg^0(g) \rightarrow HgSO_4(g, s) \quad \text{Reaction 2-19}
\]

\[
HgCl_2(g) + SO_2(g) + O_2(g) \rightarrow HgSO_4(s) + Cl_2(g) \quad \text{Reaction 2-20}
\]

SO\textsubscript{2} in the flue gas has been shown by several researchers [99, 103, 104] to be an important factor in the oxidation of Hg\textsuperscript{0} and can overshadow the effects of Cl in the oxidation. At temperatures > 700 K, the major oxidised species is HgCl\textsubscript{2} but at temperatures < 590 K, the major species is HgSO\textsubscript{4} (s) [99] and as SO\textsubscript{2} in the flue gas increased, Hg\textsuperscript{2+} increased and Hg\textsuperscript{0} [99] decreased. Wilcox, et al. [97] stated that iron oxides which comprise a significant proportion in fly ashes are commonly used as adsorbents for trace metals like Hg. Their experiments revealed that at bag filter temperatures of 122 and 171°C, Hg oxidation increased with increasing magnetite for magnetite concentrations up to 13%w (Figure 2-28) with slightly higher oxidations observed at lower bag filter temperatures.
Figure 2-28. Effect of magnetite on the oxidation of Hg in bituminous ash samples [97].

Activated carbon injection has always been the primary control used for mercury removal [98]. Several studies have focused on mercury removal by activated carbon injection [89, 98]. Studies conducted by Sjostrom, et al. [89] where ~ 3 lb/MMacf of AC sorbents were used showed Hg removal rates of up to 85%. However, just as stated in the previous sections SO$_3$ competes with Hg removal and removal rates decreased to about 17% when SO$_3$ was present (Figure 2-29).
Other sorbents are also being used like Ca-based sorbent and fly ash injection. Ren, et al. [103] noted that injecting fly ash in bag filters showed removal from 13% ~ 80% of mercury at temperatures of 135°C ~ 160°C. In studies by Ren, et al. [103] relating Ca-based sorbents and mercury capture revealed that the presence of SO$_2$ positively influenced the active sites increasing the capture by 15% ~ 20%.

### 2.6.4.3 Mercury Control in Combustion Systems

Understanding mercury speciation and factors affecting its distribution in the flue gas is important to be able to properly address and appropriate the cleaning options suitable for its removal. Amongst the three forms of mercury, Hg$^0$ has been found to be the most difficult to handle due to its abundance [92], chemical inertness [7, 92], insolubility in water [7], high volatility [7] and lower bonding energy on sorbent surfaces [7] and the one that has the longest residence time in the atmosphere [92]. Sorbent injection using activated carbon (AC) has been viewed as one of the most effective methods for Hg$^0$ removal [99]. The presence of unburnt carbon (UBC), *i.e.* coal chars or carbon in combustion fly ash (FA), is favourable in mercury capture.
Conventional air pollution control devices (APCD) can to some extent control and remove mercury from combustion systems. Table 2-7 presents existing options for mercury removal with their respective removal efficiencies. Although removal efficiencies might seem low, Monterroso, et al. [98] stated that once Hg has oxidised better capture especially by fly ash can be achieved.

**Table 2-7.** Hg removal efficiency of conventional APCDs [98].

<table>
<thead>
<tr>
<th>Technology</th>
<th>Hg removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Cleaning</td>
<td>21</td>
</tr>
<tr>
<td>ESPs</td>
<td>24</td>
</tr>
<tr>
<td>Baghouses</td>
<td>28</td>
</tr>
<tr>
<td>FGDs</td>
<td>34</td>
</tr>
<tr>
<td>SCR combined with scrubber</td>
<td>61</td>
</tr>
</tbody>
</table>

2.7 SULFUR CONTROL OPTIONS DURING OXY-FUEL COMBUSTION

As previously noted, coal is a highly heterogeneous solid containing impurities such as sulfur and Hg. According to Levy, et al. [59], fly ash, sulfur oxides and trace elements (e.g. Hg) are emissions originating from the coal’s inorganic components. As previously discussed SO$_2$, apart from being a health concern (eye, nose, throat irritant causing respiratory illness) and an environmental concern (acid rain) is also an operational concern (slagging, fouling, corrosion, competition with Hg sorption and ADP increase) and therefore requires particular attention. Technologies have been presented in the Pollution Prevention and Abatement Handbook [105] to address SO$_x$ emissions in coal-fired power plants (Table 2-8). It has been discussed in the previous sections that the amount of SO$_x$ emissions is proportional to the amount of sulfur in the fuel hence the use of low-sulfur fossil fuel (e.g. natural gas, low-sulfur oil) would drastically decrease the SO$_x$ emissions into the atmosphere.
2.7.1 Sulfur Control and Removal

One of the options for sulfur removal is coal benefaction where the fuel is cleaned prior to feeding. This can remove about 50% of the pyritic sulfur and 20-30% of the total sulfur in coal [105]. Although it has been stressed in the previous chapter that in the Australian scenario, there is a lack of SO\textsubscript{x} and NO\textsubscript{x} control units and that apart from low-NO\textsubscript{x} burners, Australian power plants relied on lenient Australian environmental regulations [6, 35] and low sulfur content of Australian coals [35, 57]. During oxy-fuel combustion where there is a recycle stream (RFG) to make up the volume in the boiler, higher concentrations of impurities pose environmental [57], health [13, 106] and technical problems [57].

<table>
<thead>
<tr>
<th>Option</th>
<th>SO\textsubscript{x} reduction (%)</th>
<th>Capital Cost ($/kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent Injection</td>
<td>30-70</td>
<td>50-100</td>
</tr>
<tr>
<td>Dry Flue Gas Desulfurisation</td>
<td>70-90</td>
<td>80-170</td>
</tr>
<tr>
<td>Wet Flue Gas Desulfurisation</td>
<td>&gt;90</td>
<td>80-150</td>
</tr>
</tbody>
</table>

Sorbent injection involves adding alkali sorbents (usually lime) to coal combustion gases to react with SO\textsubscript{2} [105]. Flue gas desulphurisation (FGD), whose concept is physical absorption of SO\textsubscript{2} in water, is still the most widely used technique in removing the sulfur species in flue gases. The solubility of SO\textsubscript{2} in water is low; so increasing the pH (alkalinity) of the scrubbing media increases the solubility of SO\textsubscript{2}, hence increasing the removal of SO\textsubscript{2} from the flue gas [51]. In pulverised coal (PC) / pulverised fuel (PF) power plants, wet FGD using limestone as the agent is often employed to remove the sulfur species from the plant. Zheng [32] stated that modern wet lime-based FGDs can achieve sulfur removal rates >90% with the more advanced
amine scrubbers reaching 100% removal of sulfur. Dry FGDs are also being used in sulfur removal however a lower rate of about 80% is achieved.

Reducing sulfur (and SO$_3$) in a power plant is not only beneficial in reducing corrosion potential, it could also reduce boiler losses and increase fuel savings. In a study by Moser in 2006 [107], using a 500 MW power plant with heat rate 9500 BTU/kWh utilising coal which costs $1.80/MM Btu, and operating at 80% capacity factor, the following heat rate improvement analysis is presented (Figure 2-30). His assumption is that for every APH temperature reduced is a corresponding ADP suppression, for every 35°F reduction is equivalent to 1% change unit heat rate [107].

![Figure 2-30. Heat Rate Improvement Analysis showing varying SO$_3$ removal rates (Moser [107]).](image)

So that with an expected SO$_3$ output of roughly 30 ppm for air-fired power plants using med-high sulfur coals, even an 80% reduction in SO$_3$ could save the plant roughly $432,000/year of fuel. However in oxy-fuel scenarios where SO$_3$ concentrations can reach to even 80 ppm, even an SO$_3$ concentration of 60 ppm reduced by 95% could save the plant roughly $1 M/year in fuel cost.
2.7.2 Flowsheet Options for differing coal-S levels

Since oxy-fuel needs to recycle portion of the flue gas to regulate temperature and volume lost when changing from O2/N2 to O2/CO2, three major ways of recycling are currently being employed as previously discussed in Section 2.3. The three options wet flue gas recycling, dry flue gas recycling and partial flue gas recycling depend on the amount of sulfur in the system. As discussed in the previous section, Australia relied on its low Sulfur coals and lenient government emissions regulations hence the absence of SOx removal devices. On the other hand, the presence of even small amounts of SO3 hydrates to form H2SO4 attacks boiler components operated below the ADP as previously noted. The amount of sulfur species (e.g. SO2, SO3 and H2SO4) determine the flow sheets that can be adapted by coal-fired power plants to accommodate differing sulfur levels. The following sub-sections present the different oxy-fuel flowsheets currently employed in demonstrations to address different cleaning options.

2.7.2.1 Callide Oxy-fuel Project Low Sulfur (< 0.5% S) Flowsheet

As discussed in Section 2.2.2, the COP flowsheet presented in Figure 2-6 is a retrofit option for existing power plants. The flowsheet is per IHI design and allowed changing an existing air-fired coal power plant with no CO2 recovery system to an oxy-fuel power plant [7]. This flowsheet is suitable for the Australian scenario as there is no dedicated SOx, NOx and Hg removal, hence this design by IHI avoided the need for such pollution control devices. In the COP flowsheet, the gas cooler was proposed to cool gas at the outlet to 150°C [7] prior to entering the fabric filters. The recycle stream is then divided into primary and secondary streams. The primary stream goes into the coal mills and the secondary stream flows into the windbox prior to the boiler. According to a report by Shah, et al. [7], roughly 70% of the flue gas is recycled causing SOx and impurity levels in the oxy-fuel system to triple that of its air counterpart. However, they also stated that this amount of sulfur is roughly equivalent to bituminous coals with moderate sulfur levels combusted in air.
2.7.2.2 Babcock & Wilcox Low Sulfur (< 1%) Flowsheet

Figure 2-31 presents B&W’s flowsheet for FutureGen 2.0 low sulfur coals. The system uses a warm recycling process. Since the system uses low sulfur coals, cleaning of the recycle streams is not employed. The recycle stream is divided into two parts; the cold primary recycle stream for the coal mills and a warm recycle where the temperatures are cooled to approximately 150°C before passing thru the fabric filters (PJFF) and draft fans which returns the recycle stream to the windbox of the boiler. The flue gas which is not recycled then goes thru the spray dry absorber (SDA), the fan then the direct contact cooler and polishing scrubber (DCCPS) to remove remaining SO₂ while Hg is removed in SDA and PJFF prior to compression.

Figure 2-31. Babcock & Wilcox and Air Liquide’s 100 MWe oxy-fuel flowsheet option for low sulfur (< 1% S) coal [7].

2.7.2.3 Babcock and Wilcox Medium Sulfur (1% < %S < 3%) Flowsheet

For coals with medium sulfur content ranging from 1 to 3% sulfur, two flowsheets were designed by B&W for oxy-fuel scenarios as shown in Figures 2-32 (a) and (b). Figure 2-32 (a) may be likened to B&W’s flowsheet for low sulfur coals except instead of recycling prior to the SDA, the SDA is used as a desulfurisation unit. The temperature of the flue gas coming off the recycle heater is cooled to
between 150 and 180°C [7] prior to entering the SDA where a 30°C temperature difference is maintained across the SDA.

![Diagram](image)

**Figure 2-32.** Babcock & Wilcox and Air Liquide’s 100 MWe oxy-fuel flowsheets option for medium sulfur (> 1% S, < 3% S) coals utilising (a) Dry Scrubber and (b) Wet Scrubber [7].

Flue gas coming from the SDA then enters the PJFF to remove the fly ash together with some of the SO$_x$. The recycle stream is then drawn by the fans to the windbox while the remaining goes to the DCCPS to remove some of the moisture. The dewatered flue gas from the DCCPS is then divided into two streams; roughly
half going to compression and processing while the remaining is drawn by a fan to the recycle heater heating the primary stream prior to the coal mills.

**Figure 2-32 (b)** on the other hand uses flue a wet flue gas desulfurisation (WFGD) unit which is maintained at around 50 – 60°C. The flue gas leaving the recycle heater then enters the PJFF to remove fly ash and some SO$_x$ prior to entering the gas cooler and WFGD. Dry sorbent injection prior to PJFF to remove SO$_3$ which would potentially cause corrosion downstream is suggested. The recycle stream saturated with liquid coming from the WFGD is then heated to remove any water in order to prevent water condensing causing low temperature corrosion. This recycle stream then goes to recycle heater and into the windbox as the secondary stream whereas the remainder of the flue gas coming from the WFGD goes to the DCCPS where liquid water is removed. Similar to the Dry Scrubbing option for medium sulfur flowsheet, about half of the stream goes to compression and the other half heated prior to going to primary recycle to coal mills.

**2.7.2.4 Babcock & Wilcox High Sulfur (> 3%) Flowsheet**

For higher sulfur content coals, B&W designed a flowsheet for FutureGen 2.0 which unlike COP and Low Sulfur B&W flowsheets uses cold recycling, slightly similar to medium sulfur coals. In **Figure 2-33**, it can be observed that similar to **Figure 2-32 (b)**, sorbent injection is employed to remove SO$_3$ prior to the PJFF and a WFGD to strip out SO$_2$/SO$_3$/H$_2$SO$_4$ and HCl from the system. However, instead of the secondary recycle stream being drawn from WFGD, it is drawn after the DCCPS to further remove some SO$_x$ together with the liquid. The flue gas exiting the DCCPS is then heated to avoid liquid condensation in the lines and prevent low temperature corrosion in the system. The stream is then split into three: (1) a secondary stream that is drawn by a fan which is then heated prior to entering the windbox; (2) a primary recycle stream drawn by a fan that is heated prior to going into the coal mills; and (3) the flue gas stream remaining that goes to the compression system for processing and storage. Similar to the other B&W designs, no dedicated NO$_x$ and Hg removal is in place.
Figure 2-33. Babcock & Wilcox and Air Liquide’s 100 MWe oxy-fuel flowsheet option for high sulfur (> 3% S) coal [7].
### 2.8 SUMMARY OF LITERATURE FOCUSED ON SULFUR PRODUCTS, ITS REACTIONS AND INTERACTIONS IN OXY-FUEL COMBUSTION

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title/Focus</th>
<th>Findings / Conclusions</th>
<th>Gaps in Knowledge / Future work</th>
</tr>
</thead>
</table>
| Spörl, R. et al. (2011) [58] | SO$_3$ measurement in Oxy-fuel using in-filter stack gas dust removal (IFK oxy-fuel pilot plant) | • Higher SO$_3$ in oxy-fuel  
• ADP air: 130-140°C  
  Oxy: approximately 160°C  
• Coil Temp air: 75-80°C  
  Oxy: 85-95°C  
• Influence of SCR catalyst on ADP is less pronounced in oxy-fuel | • Test and evaluation of continuous SO$_3$ analysers  
• Influence of FA in gas sampling probe on SO$_3$ measurement  
• Evaluation of SO$_3$ evolution over flue gas path  
  * SO$_3$ capture in ESP  
  * SO$_3$ formation in the boiler  
  * Possibility of SO$_3$ enrichment due to FGR |
| Dhungel et al. (2011) [69] | SO$_3$ control in oxy-fuel applications (Doosan 160 kW power system) | • Water vapour content is 3 times ↑ during oxy-fuel wet FGR  
• Most of the missing sulfur in balance is in the furnace:  
  * air: from 5-20% discrepancy w/ sorbent  
  * oxy: ~20% discrepancy constant  
• When SO$_2$ capture potential is high, discrepancy in S balance increases  
• Discrepancy in C balance <5% both  
• SO$_3$ reduction up to 95% using sorbent injection during oxy and air.  
• FG duct (post combustion) sorbent injection for max SO$_3$ reduction  
• Discrepancies in sulfur balance was seen higher in Oxy-fuel than air | • Detailed investigation on SO$_3$ formation during oxy-fuel comb  
• Means to reduce SO$_3$ formation |
| Ahn, Ji et al. (2011) [1] | SO$_3$ formation in oxy-fuel | • PC-fired:  
  • [SO$_3$] 4-6 times higher in oxy at a sampling temp of 800K but at higher sampling temp (~1200K), levels are the same for air and oxy  
  • mg/MJ SO$_3$ higher in air than oxy  
• For low-S Utah coals, [SO$_3$] levels are same for air and oxy  
• CFB:  
  • For low-S Utah coals, [SO$_3$] is higher for oxy than air  
  • mg/MJ is same for air and oxy | • Not many studies on SO$_3$ formation in oxy-fuel combustion  
• Varying conclusions on the SO$_2$/SO$_3$ concentration and emissions in oxy-fuel  
• Formation of SO$_3$ under oxy-fuel conditions merits additional info |
| Yan, J. et al. (2011) [108] | Sulfur behaviour in Oxy-fuel combustion of Lignite | • Higher [SO$_3$] in the convective pass which may indicate formation or conversion of SO$_3$  
• Sulfur behaviour in oxy affect flue gas cleaning mainly for PM removal and FGD i.e. wet FGD | • Deposit potential seems higher under oxy but needed to be proven  
• Retention mechanism of FA in oxy and air firing should be investigated |
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title/Focus</th>
<th>Findings / Conclusions</th>
<th>Gaps in Knowledge / Future work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stanger R. and Wall, T. (2011) [6]</td>
<td>Sulfur impacts during pulverised coal combustion in oxy-fuel tech</td>
<td>• Oxygen content shows to have a large impact on [SO$_2$] through dilution effects and not fuel-S conversion.</td>
<td>• SO$_3$/SO$_2$ conversion rates needed to be investigated</td>
</tr>
<tr>
<td>Eddings, E. et al. (2011) [70]</td>
<td>SO$_3$ measurements under oxy-coal (1.5MW furnace / 0.33MW CFB)</td>
<td>• Used CCM (ASTM D 3226-73T)</td>
<td>• No clear trends in SO$_3$ with Ca:S ratio</td>
</tr>
<tr>
<td>Eddings, E. et al. (2011) [78]</td>
<td>Fluid Bed experiments of SO$_2$/SO$_3$ formation and S-capture in air/oxy</td>
<td>• CCM to measure SO$_3$</td>
<td>• Difficulty in addressing mechanism (variable S release) direct sulphation or indirect sulphation  <strong>Possible experiments:</strong></td>
</tr>
<tr>
<td></td>
<td>Evaluation of sulphation behaviour of CaCO$_3$</td>
<td>• Higher [SO$_2$] but similar mass emission rate for both pilot scale and w/o FGR</td>
<td>• Sintering of CaCO$_3$ to check for decomposition</td>
</tr>
<tr>
<td>Author(s)</td>
<td>Title/Focus</td>
<td>Findings / Conclusions</td>
<td>Gaps in Knowledge / Future work</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
</tbody>
</table>
| Fleig, D et al. (2009) [41]      | Fate of sulfur during oxy-fuel combustion of lignite (modelling) | - Release of SO$_2$ is strongly dependent on combustion temperature  
- In oxy, furnace temperature is closely related to RFG  
- Modelling shows [SO$_3$] is 4 times greater in oxy than in air  
- Changing from N$_2$ to CO$_2$ increases [SO$_3$]                                                                                                                                                                                             | - Measurements of SO$_3$ and ADP in oxy-fuel combustion are needed as inputs for the models                                                                                                                                                              |
| Fleig, D. et al. (2011) [39]     | SO$_3$ formation under oxy-fuel (modelling)     | - An increase in SO$_2$, O$_2$, H$_2$O & residence time strongly enhance SO$_3$ formation  
- Combustion atmosphere influences amount of SO$_3$ formed  
- Lower SO$_2$ is observed in FGR wet than dry  
- SO$_3$ content in the recycling loop will not affect the SO$_3$ outlet conc. in oxy-fuel combustion since SO$_3$ is reduced at high temp and under substoichiometric conditions                                                                 | - Uncertainties in measurement accuracy of measured SO$_3$ values                                                                                                                                                                                     |
| Wilcox, J. et al. (2012) [97]    | Mercury adsorption and oxidation in coal combustion and gasification | - Increase in Hg oxidation with increasing magnetite on UBC  
- Temperature affects adsorption of Hg on UBC by affecting surface area ($\uparrow$ SA, $\uparrow$ adsorptive capacity)  
- Acid sites are responsible for Hg$_0$ capture on AC because Hg$_0$ acts as a base  
- $\uparrow$ Hg capture on sulfur treated AC sites  
- SO$_3$ (H$_2$SO$_4$) displaces Hg in AC sites and released as HgCl$_2$                                                                                                                          | - Understanding the mechanism of Hg capture and interaction with flue gas components for sorbent / catalyst injection  
- Further investigations of Hg stability on fly ash  
- Little is known on Hg interaction with inorganic portions of fly ash                                                                                                                                                                  |
- Hg$_{\text{tot}}$/Hg$_{\text{tot}}$ is positively correlated with changing from air to oxy-fuel (increasing SO$_2$)  
- Decrease in Hg capture with increasing SO$_2$ + SO$_3$  
- However with low UBC in the fly ash tested, Hg$_{\text{tot}}$ capture on ash may profit from the improved Hg oxidation at higher SO$_3$/H$_2$SO$_4$ concentration and acidification of the ash                                                                 | - Unclear competition between purely SO$_3$ and Hg capture  
- A better understanding on capture in bag filter is crucial  
- Investigation on different flue gas temperature-residence time profiles is needed                                                                                                                                                        |
| Hower, J. et al. (2010) [109]    | Mercury capture by native fly ash carbon in coal-fired power plants | - Hg capture is negatively proportional to Temperature  
- Higher Carbon, greater Hg capture  
- Calcium can enhance Hg oxidation  
- Hg oxidation is promoted by presence of HCl and other acids                                                                                                                                                                                    | - Most of studies involved organic portion of FA, inorganics in FA should be studied                                                                                                                                                                  |

The summary of the chosen gaps in knowledge that the thesis aims to answer is presented in Chapter 3.
3 HYPOTHESIS AND CONCEPTUAL FRAMEWORK

3.1 INTRODUCTION

Understanding the fate of sulfur is critical in the design and operation of the oxy-fuel fired power plant with CO₂ capture [40]. Oxy-fuel is of particular interest since impurity level concentrations (ppm) are much greater, roughly around 2 – 5 times [6, 11, 40], compared to conventional air-fired combustion. Therefore, it is anticipated that oxy-fuel combustion may have higher sulfur capture in ash compare to air-firing due to higher O₂ and SO₂ concentration in the recycling flue gas. The need to address and properly account for the SOₓ (SO₂, SO₃ and H₂SO₄) species in combustion (i.e. gas, ash, coal) is imperative since higher SO₂ concentration with higher oxygen partial pressure in flue gas may favour increased SO₃ formation which is a key component in plume opacity and acid deposition (H₂SO₄) in boiler tubes and other components (i.e. air heaters) [13], hence imposing higher corrosion potential [6, 13, 58] even in small quantities.

It is also suggested in the literature that accurately measuring the ADP temperature allows optimum level of heat extraction thus improving overall efficiency [16]. Because in oxy-fuel flue gas must be cooled below the ADP temperature prior to compression in order to remove the H₂O. To date, problems in closing the sulfur balance during oxy-fuel combustion has also been reported by several investigators [40]. In 2006, Moser [107], reported that potential savings for effective SO₃ control (with output SO₃ ranging from 30-60 ppm with removal of 95%) could reach close to $1M/year of fuel savings for a 500 MW unit power plant. An understanding of the role and impacts of sulfur during coal combustion will benefit control of sulfur emissions and potential corrosion throughout the plant.
3.2 KNOWLEDGE GAPS FROM INVESTIGATORS

The chemistry/reactions between different forms of sulfur with several gaseous and mineral species need to be understood and compared more comprehensively for oxy- and air-firing. With increased concern over SO\textsubscript{x} emissions together with expected larger SO\textsubscript{3} formation in oxy-firing, the current research work also intends to develop/test appropriate techniques for the measurement of SO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} and acid dew point temperature in an ash-laden environment (Oxy-fuel conditions). This research aims to be able to address the gaps in knowledge as presented in Table 3-1.

Table 3-1. Summary of Knowledge Gaps from Literature Review in Chapter 2.

<table>
<thead>
<tr>
<th>Focus</th>
<th>Knowledge Gaps / Author Comments</th>
<th>Investigators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly Ash</td>
<td>• Capture mechanism of SO\textsubscript{x} on Fly Ash</td>
<td>[70, 78, 108, 110]</td>
</tr>
<tr>
<td></td>
<td>• Catalytic effect of FA in oxy-fuel on the SO\textsubscript{2} to SO\textsubscript{3} conversion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Deposition potential seems higher under oxy-fuel but is needed to be proven</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No clear trends in SO\textsubscript{3} with Ca:S ratio of coal during oxy-fuel combustion</td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{x}(SO\textsubscript{2}/SO\textsubscript{3})</td>
<td>• Establishing SO\textsubscript{2} to SO\textsubscript{3} conversion at different oxy-fuel configurations</td>
<td>[1, 6, 58, 69]</td>
</tr>
<tr>
<td></td>
<td>• Need to evaluate SO\textsubscript{3} evolution over flue gas path on the following:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>o SO\textsubscript{3} capture in ESP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>o SO\textsubscript{3} formation in the boiler and</td>
<td></td>
</tr>
<tr>
<td></td>
<td>o possibility of SO\textsubscript{3} enrichment due to FGR</td>
<td></td>
</tr>
<tr>
<td>SO\textsubscript{x} and Hg</td>
<td>• Understanding the mechanism of Hg capture and interaction with flue gas components</td>
<td>[17, 97, 109]</td>
</tr>
<tr>
<td></td>
<td>• Further investigations of Hg stability on fly ash</td>
<td></td>
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<tr>
<td></td>
<td>• Further investigations on Hg interaction with inorganic portions of fly ash</td>
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</tr>
<tr>
<td></td>
<td>• A better understanding on capture in bag filter is crucial</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Investigation on different flue gas temperature-residence time profiles is needed</td>
<td></td>
</tr>
</tbody>
</table>

3.3 HYPOTHESIS

The hypothesis for this study is:

*There are differences in sulfur levels between conventional air firing and oxy-fuel firing in terms of the SO\textsubscript{x} conversion and retention in fly ash.*
3.4 FOCUSING QUESTIONS

In line with the hypothesis, the study will address the following focusing questions:

1. Does higher partial pressure of SO$_2$ in oxy-fuel flue gas favour higher sulfur capture in ash?
2. What is the catalytic effect of fly ash on SO$_2$ to SO$_3$ conversion in oxy-fuel combustion conditions?
3. How does oxy-fuel configuration affect SO$_3$ formation and sulfur capture?
4. How does sulfur distribution in ash vary between air-firing and oxy-fuel firing?
5. How does the presence of SO$_x$ affect Hg capture by fly ash?

3.5 OBJECTIVES OF THE STUDY

3.5.1 General Objective

This study primarily aims to establish an understanding of the reactions, transformations and impacts of sulfur oxides (SO$_x$) in oxy-fuel combustion

3.5.2 Specific Objectives

In order to address the general aim of this study, the following specific objectives were established:

1. To investigate the impacts of coal quality on sulfur levels during air and oxy-fuel combustion using the 20-kW combustion rig at IFK Stuttgart, Germany;
2. To establish the effects of oxy-fuel conditions on the pathways of SO$_3$ formation;
3. To perform ash decomposition experiments for analysing different forms of sulfur in air and oxy-fuel combustion conditions;
4. To analyse the effect of fly ash on the SO$_3$ formation in oxy-fuel combustion;
5. To investigate the SO$_x$–mercury interaction in fly ash during oxy-fuel combustion.
4 EXPERIMENTAL

This section provides the experimental description of the study outlining the materials and setup utilised and the analytical methods employed in the conduct of the study. In order to achieve the research goal of understanding the impacts of elevated SO\(_x\) concentrations in the flue gas on the sulfur impurity formation, reactions and interactions during oxy-fuel combustion, four major experiments are presented. Following the descriptions of each of the experiments, an outline of the equipment and analytical methods and techniques used are discussed.

4.1 MATERIALS

Coals A, B and C and their properties, the ash composition and particle sizing are provided in specific chapters depending on their significance to the discussion.

Reagents used in the experiments included magnesium oxide (MgO, > 99%), sodium carbonate (Na\(_2\)CO\(_3\)), sodium sulfate (Na\(_2\)SO\(_4\), >99%), potassium sulfate (K\(_2\)SO\(_4\)), tin (II) chloride (SnCl\(_2\), 98%), barium chloride (BaCl\(_2\)), silver nitrate (AgNO\(_3\)), sodium hydroxide pellets (NaOH, > 97%), hydrochloric acid (HCl, 36%w), HgNO\(_3\) standard solution (1000 mg/L), purchased from Sigma Aldrich Chemicals; ammonium hydroxide solution (NH\(_4\)OH, 28-30% NH\(_3\)) from Chem Supply. Gases include O\(_2\), CO\(_2\) (min 99.5%), SO\(_2\) (1% in 99% N\(_2\)), N\(_2\) (min. 99.99%) purchased from Coregas. Apart from the reactors and standard glasswares used, quartz wool (from Alpha, Australian Scientific), and high alumina crucibles (from Ceramic Oxide Fabricators) were utilised in the conduct of parts of the experiments.

4.2 EXPERIMENTAL DESCRIPTION AND METHODOLOGY

The experimental section was divided into four major experiments which are detailed in the following sections: I. Coal Combustion Experiments; II. Ash Decomposition
Experiments; III. SO\textsubscript{2} to SO\textsubscript{3} Conversion Experiments; and IV. Hg and SO\textsubscript{x} Competition Experiments.

Coal combustion experiments were conducted to understand impacts of impurity injection levels in oxy-fuel and air combustions on the flue gas quality in a pilot scale using IFK’s 20-kW\textsubscript{th} once-through furnace. The experiment also aimed to obtain the fly ash samples required for parts II, III and IV of the experiments. Ash decomposition experiments were designed to understand differences in sulfur capture behaviour between air and oxy-fuel derived fly ash. Conversion experiments were designed to study the difference between post flame homogeneous and fly ash-catalysed SO\textsubscript{2} oxidation at different flue gas conditions. Competition experiments were specifically designed to understand the speciation, interaction of Hg and its competition with SO\textsubscript{x} in fly ash during air and oxy-fuel conditions. Overall, these four experiments would be able to investigate the effects of differing sulfur levels during air and oxy-fuel combustion and its associated impacts on SO\textsubscript{2} to SO\textsubscript{3} conversion; mercury speciation, competition and capture by fly ash.

4.2.1 Combustion Experiments: The 20 kW\textsubscript{th} Once-through Furnace, IFK Stuttgart, Germany

This set of experiments were carried out at the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Germany whose main focus were on the impacts of the coal quality and impurities of the recycled flue gas on the flue gas emissions and fly ash capture. Since this part of the experiment were a result of a collaboration between the University of Newcastle, Australia and University of Stuttgart, Germany, a separate chapter (Chapter 5) was dedicated solely for all the work completed at IFK including objectives, experimental description, results and discussion.

4.2.2 Ash Decomposition Experiments: Description of the Carbolite Horizontal Furnace for Ash Decomposition

The bag filter fly ash collected from IFK, Stuttgart were then characterised by thermal decomposition. Figure 4-1 shows the schematic diagram of the setup used for the thermal decomposition of fly ash to determine the differences in the amount of sulfur captured in the fly ash during air and oxy-fuel combustion of the 20-kW\textsubscript{th} IFK rig. The
reactor used for the experiments is made of high-grade 1” O.D, 1.5 mm thickness high grade alumina tube from Ceramic Oxide Fabricators in an electrically heated horizontal Carbolite furnace fitted with 1” I.D. Swagelok stainless steel fittings and graphite ferrules and connected with ¼” Perfluoroalkoxy alkane (PFA) lines to the analysers. Nitrogen gas was used as the carrier gas. In all experimental runs, a flow rate of 1.5 L/min was maintained using a calibrated Dwyer rotameter and a heating rate of 5°C/min was used based on previous experiments to obtain the optimum operating conditions. All experiments were completed at atmospheric pressure.

Two 3 mL alumina crucibles containing a combined mass of ~1.0 gram samples were placed in the reactor tube. The samples filled the crucibles to roughly half the crucible height and contained ~0.5 grams per crucible. Sample temperature was measured by a Type R thermocouple and recorded using PicoLog data logging software. Experiments were held at a nominal furnace temperature of 1400°C ± 20 K for about 2 hours to ensure that all sulfur species have been evolved and liberated. Decomposition gases were then sent to a Vaisala CO₂ infrared analyser and Testo 350XL gas analyser to continuously measure the concentration of the different gases (CO₂, SO₂, and O₂). Table 4-1 presents a summary of the operational parameters used in the conduct of the experiment.

Table 4-1 presents a summary of the operational parameters used in the conduct of the experiment.

Figure 4-1. Schematic diagram of the Carbolite Horizontal Furnace used for the fly ash deomposition experiments.
Table 4.1. Experimental Design used in the Ash Decomposition Experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values / Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Fly Ash Source</td>
<td>From coals A, B and C</td>
</tr>
<tr>
<td>Mass of Fly Ash</td>
<td>~ 1 gram (contact time ~41 ms)</td>
</tr>
<tr>
<td>Heating Rate</td>
<td>5°C/min</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>1.5 L/min (295 K, 1 atm)</td>
</tr>
<tr>
<td>Sample Temperature</td>
<td>1400 °C ± 20 K</td>
</tr>
<tr>
<td>Output Gas Quality</td>
<td>SO$_2$, O$_2$ (Testo 350 XL)</td>
</tr>
<tr>
<td></td>
<td>CO$_2$ (Vaisala CO$_2$ analyser)</td>
</tr>
</tbody>
</table>

4.2.3 Conversion Experiments: Description of the SO$_2$ to SO$_3$ Conversion Rig

The setup (Figure 4.2) consisted of a 12 mm I.D. (S/V ratio = 3.33 cm$^{-1}$) quartz tube flow reactor placed in an electrically heated horizontal furnace; the reactor has an isothermal length of 25 cm (Figure 4.3) Quartz was chosen as the reactor material and packing material as previous researchers [85, 86] verified quartz’s inert properties to SO$_2$ oxidation. Reactant gases (SO$_2$, O$_2$, N$_2$/CO$_2$) were supplied through ¼” PFA lines by gas cylinders and controlled by Brooks mass flow controllers with a combined flow rate of 0.5 L/min at 298 K and 1 atm. Water vapour was introduced to the system using a water saturator: where gas (N$_2$ or CO$_2$) flowing at 1 L/min bubbles through 100 mL of DDI water placed in a 150 mL conical flask (roughly 90 mm height) maintained at a controlled temperature. The amount of water present was measured by a Testo 350XL Relative Humidity Probe prior to the actual experiments. Testo 350XL was also used initially in the experiments in order to calibrate the gases (i.e. SO$_2$, O$_2$) flowing through the reactor. Reactant gases were heated with heating tapes to approximately 80°C before entering the reactor (Figure 4.4). The experiment consisted of two parts; homogeneous conversion reaction with gases only and heterogeneous conversion: the reaction of gases in the presence of fly ash.

In the homogeneous experiments, the quartz tube was empty except for the oxidant gases flowing through the reactor. In the heterogeneous (catalysed) experiments, the quartz tube reactor held ~0.5 g of fly ash with a thickness of ~1 cm supported by
quartz wool placed in the centre of the isothermal region (Figure 4-5). Blank tests for water dew point were conducted as well as shown in Figure 4-6 while doing the profile.

Figure 4-2. Schematic of the Rig used for High Temperature SO₂ to SO₃ Conversion Experiments.

Figure 4-3. Temperature profile of the horizontal furnace used for the conversion experiments. Approximately 25-cm isothermal regions from 10 to 35 cm mark.
To determine the conversion of SO₂ to SO₃, the concept of controlled condensation method [16, 39, 74, 75] (CCM) was employed. CCM assumes that if an excess partial pressure of water vapour is maintained in the reaction zone [66] all SO₃ is converted to H₂SO₄ as SO₃ readily reacts with water vapour to form H₂SO₄ [1, 58, 71], which can then be separated from the gas stream by condensation. Passing the gas stream through a condenser at temperatures below the sulfuric acid dew point (90°C) [16, 66, 74, 75, 77] and above the water dew point [76] (generally below 60°C [74, 77]) allowed collection of the H₂SO₄. The condenser was maintained at temperature using heated water being recirculated by Iwaki Magnetic Drive recirculating pump that can handle temperatures around 80°C (water). Quartz wool was placed inside the quartz condenser to provide more surface area for condensation. The surface of the quartz wool was calculated based on the assumption that the wool is made up of a cylindrical thread [86] of average diameter 8 µm and a density of 2.65 g/cm³ (Sigma Aldrich). Conversion of SO₂ to SO₃ in the gas mixture was determined by the amount of H₂SO₄ produced during each experiment, completed after 60 minutes. A known quantity of distilled deionised (DDI) water was used to flush out the condenser to collect the H₂SO₄. The H₂SO₄ concentration was then determined using a Dionex Dx-100 ion chromatogram (IC).

Figure 4-4. Actual setup used to feed gas mixture saturated with H₂O vapour showing heated lines controlled by a temperature controller left; right end of the furnace where the Testo 350XL H₂O dew point probe and gas analyser is placed to determine working temperature.
Figure 4-5. Packed bed of fly ash supported by quartz wool for heterogeneous experiments.

Figure 4-6. Temperature Profile Testing and Water Dew Point for the reactor. Hazy end of the quartz reactor (right side) showing water condensing on the wall of the tube.

In order to determine the amount of quartz wool needed to fully capture the acid condensate, different amounts (0.25 g, 0.50 g, 0.75 g, 1.0 g, 1.5 g and 2 g) of quartz wool were placed in the condenser to collect prepared concentrations of H$_2$SO$_4$ vaporised within the furnace. The prepared concentrations of H$_2$SO$_4$ were approximately 1 (0.1 M) and 2 (1.0 M) magnitudes higher than the equivalent amount of SO$_3$ generated in power plants. **Figure 4-7** shows the graph relating the amount of quartz wool and the recovery (%) of the H$_2$SO$_4$ used. **Table 4-2** shows the surface area provided by the quartz wool with its corresponding mass and capture rate. From the test, it was observed that an average 92% to 99.98% capture was achieved with greater than 1.0 g of quartz wool for both high and low H$_2$SO$_4$ concentrations. Hence this amount of quartz wool (~1.0 g) in the condenser was used throughout the experiments.
$0.1 \text{ M } H_2SO_4$

<table>
<thead>
<tr>
<th>Quartz Wool mass, g</th>
<th>Surface Area m$^2$</th>
<th>Capture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.00</td>
<td>5%</td>
</tr>
<tr>
<td>0.01</td>
<td>0.00</td>
<td>6%</td>
</tr>
<tr>
<td>0.50</td>
<td>0.09</td>
<td>86%</td>
</tr>
<tr>
<td>0.52</td>
<td>0.10</td>
<td>85%</td>
</tr>
<tr>
<td>1.04</td>
<td>0.20</td>
<td>104%</td>
</tr>
<tr>
<td>1.02</td>
<td>0.19</td>
<td>100%</td>
</tr>
<tr>
<td>1.53</td>
<td>0.29</td>
<td>96%</td>
</tr>
<tr>
<td>1.47</td>
<td>0.28</td>
<td>93%</td>
</tr>
</tbody>
</table>

$1.0 \text{ M } H_2SO_4$

<table>
<thead>
<tr>
<th>Quartz Wool mass, g</th>
<th>Surface Area m$^2$</th>
<th>Capture %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.00</td>
<td>25%</td>
</tr>
<tr>
<td>0.26</td>
<td>0.05</td>
<td>81%</td>
</tr>
<tr>
<td>0.50</td>
<td>0.09</td>
<td>90%</td>
</tr>
<tr>
<td>1.00</td>
<td>0.19</td>
<td>92%</td>
</tr>
<tr>
<td>1.90</td>
<td>0.36</td>
<td>99%</td>
</tr>
</tbody>
</table>

Table 4-2. Quartz Wool Capture Test using Controlled Condensation Method for $H_2SO_4$ capture.

In order to investigate the individual kinetic effects of $SO_2$, $O_2$ and $H_2O$ in the post-flame conversion of $SO_2$ to $SO_3$ at temperatures between 400 and 1000°C, the following experimental design was used in this study (Table 4-3). Homogeneous conversions investigating the effects of gas concentrations $O_2$, $SO_2$ and $H_2O$ were set. Heterogeneous conversions were carried out in the presence of fly ash heated to the reaction temperature, $i.e.$ 400°C, 500°C, 700°C, 900°C and 1000°C. Investigations were also completed that determined if the mode of firing would affect the formation of $SO_3$. This was completed by replacing the $N_2$ gas stream with 85% $CO_2$. $N_2$ could not be completely replaced as the $SO_2$ source used contained $N_2$, which limited the replacement of $N_2$ to 85%.
Figure 4-7. \( \text{H}_2\text{SO}_4 \) capture test with quartz wool using 1.0 M and 0.1 M \( \text{H}_2\text{SO}_4 \).

Table 4-3. Experimental Design used for the \( \text{SO}_2 \) to \( \text{SO}_3 \) Conversion Experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Control</th>
<th>Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. SO(_2) effect</td>
<td>([\text{O}_2] = 5% \text{ vol.}, \ [\text{H}_2\text{O}] = 3% \text{ vol.})</td>
<td>([\text{SO}_2] \text{ (ppm)} = 500, 1000, 1500, 2000)</td>
</tr>
<tr>
<td>2. O(_2) effect</td>
<td>([\text{SO}_2] = 1000 \text{ ppm}, \ [\text{H}_2\text{O}] = 3% \text{ vol})</td>
<td>([\text{O}_2] \text{ (% vol.)} = 3, 5, 10)</td>
</tr>
<tr>
<td>3. H(_2\text{O}) effect</td>
<td>([\text{SO}_2] = 1000 \text{ ppm}, \ [\text{O}_2] = 5% \text{ vol})</td>
<td>([\text{H}_2\text{O}] \text{ (% vol.)} = 3, 4, 7, 9)</td>
</tr>
</tbody>
</table>

The \( \text{H}_2\text{SO}_4 \) ADP was also solved to compare differing ADPs at different \( \text{SO}_3 \) levels. In estimating the acid dew point temperatures, the \( \text{SO}_2 \), \( \text{SO}_3 \) and \( \text{H}_2\text{O} \) values from literature [6, 17, 39, 41, 45] were used as a guide for the inputs (Table 4-4). Air combustion which used cleaned air as the oxidant, termed in this study as Air, practical oxy-fuel combustion with partial flue gas cleaning (with simulated removal of nominal 20% \( \text{H}_2\text{O} \), 20% \( \text{SO}_2 \) and 50% \( \text{Hg}^{\text{tot}} \) from flue gas based on theoretical maximum conversion [17]) termed here as Oxy. The oxy-fuel combustion with full flue gas recycling without cleaning is termed in this section as Oxy Full.
Table 4-4. Parameters used in the estimation of the sulfuric acid dew point temperature.

<table>
<thead>
<tr>
<th>Mode</th>
<th>[SO\textsubscript{2}] ppm</th>
<th>[SO\textsubscript{3}] ppm</th>
<th>[H\textsubscript{2}O] % vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>500</td>
<td>0 - 100</td>
<td>3</td>
</tr>
<tr>
<td>Oxy (practical)</td>
<td>1000</td>
<td>0 - 100</td>
<td>10</td>
</tr>
<tr>
<td>Oxy Full (no cleaning)</td>
<td>2000</td>
<td>0 - 100</td>
<td>30</td>
</tr>
</tbody>
</table>

4.2.4 Competition Experiments: Description of the Rig used to measure interaction between SO\textsubscript{x} and Hg

A schematic diagram of the experimental setup is shown in Figure 4-8. In order to investigate the competition between SO\textsubscript{x} and Mercury, the setup is divided into five major parts:

1. The SO\textsubscript{3} generator where the gas mixture SO\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O vapour and N\textsubscript{2}/CO\textsubscript{2} are fed using Brooks mass flow controllers. The 2 L/min (298 K, 1 atm) gas mixture is then preheated at 80°C (±10 K) using a heating tape and then fed into a 1” I.D. quartz tube flow reactor controlled by a 45 cm electrically heated furnace. The reactor contains ~2 g of fly ash acting as a solid catalyst supported by quartz wool and operated at a wall temperature of 700°C (±10 K) for SO\textsubscript{3} production basing on the results obtained from the conversion of SO\textsubscript{2} to SO\textsubscript{3} in Chapter 7;

2. A mercury (as Hg\textsuperscript{0}) feeding system which consists of a mercury permeation tube (produced by Valco Instruments Co., Inc. - VICI) containing liquid mercury with 1 L/min (298 K, 1 atm) N\textsubscript{2} as the carrier gas. The permeation rate of Hg\textsuperscript{0} was regulated by controlling the vapour pressure of Hg\textsuperscript{0} in the tube which was achieved by controlling the temperature using a Labec NBCT7S water bath. The Hg\textsuperscript{0}-laden gas is then fed after the 700°C SO\textsubscript{3} generator to avoid any reaction/conversion of Hg\textsuperscript{0} before the gases were mixed and entered the simulated Bag Filter;
(3) The Simulated Bag Filter consisting of a 1” I.D. quartz tube with ~2 g of fly ash supported by quartz wool and controlled by a HTS/Amptek Heavy Amox Insulated Duo heating tape maintained at temperature (90°C to 200°C);

(4) The 3 L/min (298 K, 1 atm) gas mixture then passes through an insulated PFA line directly into an impinger system in an ice bath. The exhaust gas passing through route ①, a SnCl₂–NaOH–Coil–Blank system, was used in this study for the total Hg (Hg²⁺) measurement, whilst the gas passing through route ②, a NaOH–Coil–Blank system, was used in this study for the elemental Hg (Hg⁰) measurement; and

(5) The gas mixture then goes through Ohio Lumex RA-915+ Mercury analyser that measures online Hg⁰ measurement based on cold-vapour atomic adsorption at 254 nm. The exhaust gases then passed through an activated carbon bed before venting to atmosphere.

**Figure 4-8.** Schematic diagram of the SO₃ and Hg competition rig.
Since the Ohio Lumex RA-915+ only measures Hg\(^0\), gas conditioning was employed such that all oxidised Hg (Hg\(^{2+}\)) would be reduced to Hg\(^0\) by contacting with a freshly prepared, aqueous 0.05 M SnCl\(_2\)/0.1M HCl reduction solution; a modified concentration of the solution used by Spörl, et al.[17]. The gas which still contained high concentrations of SO\(_2\) was then scrubbed using a NaOH solution before passing through a coil and a blank impinger to capture any carry-over liquid from the solutions, all of which are kept in an ice bath. Scrubbing was completed to remove SO\(_2\) which can interfere with the Hg measurement [111]. Experiments were conducted using fly ash obtained from experiments described in Section 4.2.1 conducted in IFK, Stuttgart, Germany.

The experimental design for the study to test the competition between SOx and Hg in fly ash is presented in Table 4-5. Hg\(^0\) injections at 5 and 10 µg/m\(^3\) were selected to simulate typical concentrations found in practical oxy-fuel combustion [17]. The Hg\(^0\) permeation rate was calculated using the Wagner equation with coefficients given by the supplier of the Hg permeation tubes with permeation rates quoted at 25°C and corrected for any temperature increase. The concentration produced by the mercury permeation tube was measured by the mercury analyser prior to starting the experiments. The Wagner equation used in the calculation of the Hg\(^0\) permeation rate is given by Equation (4-1) and the coefficients provided by the supplier VICI are presented in Table 4-6:

\[
\ln\left(\frac{p}{p_c}\right) = \left(\frac{T_c}{T}\right)\left(a_1\tau + a_2\tau^{1.89} + a_3\tau^2 + a_4\tau^8 + a_5\tau^{8.5} + a_6\tau^9\right)
\]  

(4-1)

Where:

- \(R\) = 8.314 472 J/(mol\(\cdot\)K)
- \(M_{\text{Hg}}\) = 200.59 g/mol
- \(T_c\) = 1764 K, Critical Temperature
- \(p_c\) = 167 MPa, Critical Pressure
Table 4-5. Experimental design used for the mercury and SO\(_x\) competition experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Inlet gas Hg(^0) µg/m(^3)</th>
<th>SO(_2) (SO(_3)) ppm</th>
<th>H(_2)O %v</th>
<th>Bag Filter Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: Variable Hg(^0)</td>
<td>0, 5, 10</td>
<td>667 (10)</td>
<td>2</td>
<td>150</td>
</tr>
<tr>
<td>2: Variable SO(_x)</td>
<td>5</td>
<td>0 (0), 667 (10), 1000 (15)</td>
<td>2</td>
<td>150</td>
</tr>
<tr>
<td>3: Variable H(_2)O</td>
<td>5</td>
<td>667 (10)</td>
<td>0, 2</td>
<td>150</td>
</tr>
<tr>
<td>4: Variable BF Temp</td>
<td>5</td>
<td>667 (10)</td>
<td>2</td>
<td>90, 120, 150, 200</td>
</tr>
</tbody>
</table>

Table 4-6. Mercury coefficients, \(a\), used in the Wagner equation for determining partial pressures.

<table>
<thead>
<tr>
<th>(i)</th>
<th>(a_i)</th>
<th>Std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-4.576 183 68</td>
<td>0.0472</td>
</tr>
<tr>
<td>2</td>
<td>-1.407 262 77</td>
<td>0.8448</td>
</tr>
<tr>
<td>3</td>
<td>2.362 635 41</td>
<td>0.8204</td>
</tr>
<tr>
<td>4</td>
<td>-31.088 998 5</td>
<td>1.3439</td>
</tr>
<tr>
<td>5</td>
<td>58.018 395 9</td>
<td>2.4999</td>
</tr>
<tr>
<td>6</td>
<td>-27.630 454 6</td>
<td>1.1795</td>
</tr>
</tbody>
</table>

\[
\tau = 1 - \frac{T}{T_c} \tag{4-2}
\]

Equation (4-2) was used to normalise the sample temperature and critical temperature in the Wagner equation (4-1). Each experimental run lasted 30 minutes. After completion of the experiment, the ash in the simulated bag filter was removed and analysed for Hg and S. The Hg adsorbed in the ash was determined by placing the ash in the Ohio Lumex RA-915+ pyrolyser where the temperature was kept above 680°C to convert all Hg\(^{2+}\)/Hg\(^p\) to Hg\(^0\). This was converted to Particulate Hg (Hg\(^p\)) as given in Equation (4-3). Any Hg that is neither measured (i.e. Hg\(^0\), Hg\(^p\)) nor calculated (i.e. Hg\(^{2+}\)) is collectively termed in this study as unaccounted Hg and is calculated by difference and given by Equation (4-4).

\[
\%Hg^p = \frac{Hg_{in\ ash}}{Hg_{input}} \times 100\% \tag{4-3}
\]
where $H_{\text{g in ash}}$ represents the measured amount of Hg in the filter ash in ng Hg and $H_{\text{g input}}$ represents the total amount of mercury introduced into the gas stream prior to the simulated bag filter over the entire experimental time (ng/Nm$^3$ Hg).

\[
\text{Unaccounted Hg} = 100\% - \left( \%Hg^0 + \%Hg^{2+} + \%Hg^p \right)
\] (4-4)

4.3 ANALYTICAL METHODS

4.3.1 Gas Analysis

Gas phase detection of flue gas components (e.g. $SO_2$, CO, $O_2$) were accomplished online by using a Testo 350 XL analyser while the Ohio Lumex RA-915+ was used for the gas phase mercury measurements.

4.3.1.1 Testo 350 XL for Flue Gas Analysis

The Testo 350XL is an online flue gas analyser (electrochemical measure) which draws in sample gas 1-2 litres per minute (1 L/min to the analyser and less than 1 L/min vented to ensure adequate supply) with a maximum positive pressure of 20” $H_2O$ and maximum negative pressure of 80” $H_2O$ [112]. Testo 350XL can simultaneously measure $SO_2$, NO, NO$_2$, O$_2$, CO, CO$_2$, C$_x$H$_y$, H$_2$S, H$_2$, flue gas temperatures and differential pressure with the capability of fresh air rinsing and zeroing. The analyser (Figure 4-9) was used during ash decomposition experiments to measure $SO_2$ (with a resolution of 1 ppm), CO (0.1 ppm for values below 500 ppm, 1 ppm for values up to 10,000 ppm), and $O_2$ (0.1% vol.). Accuracy of measurement is reading plus maximum 2% and the details for the measurement ranges of the flue gas components and some screen parameters are shown in Table 4-7.

Table 4-7. Testo 350XL Flue Gas Analyser measurement range for selected gases used in the study [112]
4.3.1.2 Ohio Lumex RA-915+ Zeeman Mercury Spectrometer for gas phase Hg Analysis

The Ohio Lumex RA-915+ Zeeman Mercury Spectrometer was manufactured by Ohio Lumex Corporation. The RA-915+ analyser (Figure 4-10) was used in the online measurements and Hg in ash analyses in Section 4.2.4. The Ra-915+ analyser is based on the differential Zeeman atomic absorption spectrometry using high frequency modulation of light polarization (ZAAS-HFM) [113]. The system utilises a mercury lamp as a radiation source (wavelength, $\lambda = 254$ nm) placed in a permanent magnetic field. A photodetector then detects the radiation propagated along the direction of the magnetic field which has passed through a polarisation module and the multi-path cell (with a length of about 10 m). This signal is then converted to Hg concentration.
In all of the gas phase Hg determinations, the multi-path cell (optical bridge 3) was used due to its higher detection limit in gas measurements even though the range is limited. Table 4-7 shows the comparison between the single-path and multi-path options for Hg measurements. For the gas phase measurements of Hg, a combined constant flowrate of 3 L/min (298 K, 1 atm) of gas was maintained using Brooks mass flow controllers. Table 4-9 presents the detection limits and techniques applied in measuring the Hg concentrations of gas and solid samples from Section 4.2.4.

Table 4-8. Comparison between the Single-Path and Multi-Path Detection Cells of the Ohio Lumex RA-915+ Zeeman Mercury Spectrometer [113].

<table>
<thead>
<tr>
<th>Options</th>
<th>Detection Limit (ng/m$^3$)</th>
<th>Detection Range (ng/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-Path Cell</td>
<td>500</td>
<td>200,000</td>
</tr>
<tr>
<td>Multi-Path Cell</td>
<td>2</td>
<td>20,000</td>
</tr>
</tbody>
</table>
Table 4-9. Detection limit of the Ohio Lumex RA-915+ Zeeman Mercury Spectrometer and techniques used in the experiment [113].

<table>
<thead>
<tr>
<th>Matrix (Sample)</th>
<th>Detection Limit</th>
<th>Sample parameters (flow rate, volume, weight)</th>
<th>Detection Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient Air</td>
<td>2 ng/m³</td>
<td>20 L/min</td>
<td>Direct</td>
</tr>
<tr>
<td>Natural / Industrial gases</td>
<td>2 – 500 ng/m³</td>
<td>1 – 20 L/min</td>
<td>Direct</td>
</tr>
</tbody>
</table>

4.3.2 Liquid Analysis

Liquid analyses are accomplished either using an in-house Ion Chromatogram (Dionex DX-100) or sent to external accredited laboratories.

4.3.2.1 Dionex DX-100 Ion Chromatography for Sulfate Analysis

Ion chromatography using Dionex DX-100 (Figure 4-11) was used to identify and quantify SO₃ in liquid samples as sulfates (SO₄²⁻) for Sections 4.2.3 and 4.2.4. The Dionex DX-100 performs analysis using conductivity detection. The column employed in the experiments used sodium bicarbonate as eluent.

Sample analysis was carried out with 1 mL of liquid samples at an injection rate of 1 mL/min and conductivity detector of 100 µS to obtain a measurable concentration for analysis. Samples were injected using a 1 mL syringe (as shown in Figure 4-11). The Chromeleon chromatography software calculates the concentrations of the anions (i.e. SO₄²⁻) by integrating the area under the generated curve. Sodium sulfate (Na₂SO₄) was dissolved in DDI to prepare different standards for the calibration. Elution time of sulfates are typically around 10.5 - 12 minutes. Standards at concentrations of 0.05, 0.1, 0.2, 0.4 and 0.5 mmol/L were prepared for the calibration. The sulfate calibration curve used for this study is presented in Figure 4-12.
Figure 4-11. Dionex DX-100 Ion Chromatogram

Figure 4-12. Sulfate calibration curve completed at 1 L/min flowrate.
4.3.3 Solid Analysis

For the analyses of solid samples (*i.e.* fly ash), the Malvern Mastersizer 2000 was used to measure the Particle Size Distribution ([Section 4.2.2](#)), total sulfur in the fly ash ([Sections 4.2.2 and 4.2.4](#)) utilised the Eschka method [114] and mercury in fly ash ([Section 4.2.4](#)) was accomplished by using the Ohio Lumex RA-915+ analyser.

### 4.3.3.1 Malvern Mastersizer 2000 for Particle Size Distribution

In order to measure the particle size of the fly ash coming from [Section 4.2.1](#), a Malvern Mastersizer 2000 was used ([Figure 4-13](#)). The mastersizer has been designed to measure the size of particles, specifically the distribution of different sizes within a sample [115]. Fly ash samples are placed in DDI water for preparation and properly dispersed to the correct concentration before taking measurements. The dispersant used in the measurement was Gardisperse 810P (Naphthalene sulfonate formaldehyde condensates) dissolved in DDI.

The background is first measured for electrical noise caused by any floating dust on the optics and any floating contaminant in the dispersant (DDI + Gardisperse). Then the added sample (*i.e.* fly ash) is added to the dispersant until a certain obscuration is reached. Obscuration is the fraction of light lost from the analyser beam when the sample is introduced [115]. The light scattering from the sample was then measured giving the particle size distribution. The particle sizer used in the experiments has a detection limit of 1 µm. Submicron particles were not reported due to limitation in the calibration of the Malvern particle sizer and measurements of very small particle sizes were not completed.

The results were then reported as volume percentage of the sample per particle size distribution. Standard percentile readings $D(v, 0.5)$, $D(v, 0.1)$ and $D(v, 0.9)$ were reported also by the analyser where $D(v, 0.5)$ stands for size of the particle below which 50% of the sample lies.
Apart from thermal decomposition of the fly ash in Section 4.2.2, total sulfur in samples were also determined by the Eschka method as per the Australian Standards [116] and Mott, et al.[114]. The Eschka method involves the ignition of a known mass of the sample in intimate contact with the Eschka mixture in an oxidising atmosphere at 800°C to decompose organic material and to convert all sulfur to sulfate. The sulfate was then dissolved in dilute hydrochloric acid and determined gravimetrically by precipitation with barium chloride [116] to obtain barium sulfate as the product. The amount of total sulfur is given by Equation (4-5):

\[
S_{ad} = \frac{m_2 - (m_3 - 0.0335m_4)}{m_1} \times 13.74
\]  

where:
- \( S_{ad} \) = percentage of total sulfur in the analysis sample, %
- \( m_1 \) = mass of the sample taken, g
- \( m_2 \) = mass of barium sulfate found in the determination, g
- \( m_3 \) = mass of barium sulfate found in the blank determination, g
- \( m_4 \) = mass of potassium sulfate per litre of solution, g
Figure 4-14 shows the sample mixed and covered with the Eschka mixture (MgO : Na₂CO₃, 2:1 ratio by mass) and the final product precipitated as barium sulfate (BaSO₄) by

![Image of sample mixture and final product](image)

**Figure 4-14.** Total Sulfur Determination by the Eschka Method showing product before and after acid digestion.

### 4.3.3.3 Ohio Lumex RA-915+ with RP-M-324M: Sorbent Trap Testing for Mercury in Solid Samples

The basic principles of measurement of the Ohio Lumex RA-915+ have been presented in the previous section. For Hg in the fly ash measurements, the optical bridge was set to position 1 and analysed using a furnace and controller RP-M-234M that is attached to RA-915+ (Figure 4-15). This analyser is intended for direct testing of solids, *i.e.* ash and coal. Quartz ladles are used as sorbent traps for solid testings. The ladle is inserted into the analyser’s thermo-catalytic conversion chamber heated to 680°C where bound mercury (Hg⁰, Hg²⁺, Hg⁰⁺) is thermally decomposed and converted to Hg⁰ to be measured by the analyser.

The mercury measurement takes place in the heated cell zone of the converted, directly coupled to the spectrometer. This technique, having high temperature and short residence times, prevents mercury atoms to recombine with any active species.
generated from the sample matrix. For a solid sample of ~0.5 g, the pyrolyser can give a detection limit of as accurate as 0.5 µg/kg [113]. The furnace and controller was constructed with an external pump to control the suction of gas, *i.e.* 0.5 L/min, 2 L/min and 4 L/min, depending on the expected mercury concentration. Technical specifications of the analyser are presented in Table 4-10.

**Table 4-10.** Technical Specifications of the Ohio Lumex RA-915+ with RP-M-324M.

<table>
<thead>
<tr>
<th><strong>Feature</strong></th>
<th><strong>Values</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limit</td>
<td>0.3 ng – 100,000 ng</td>
</tr>
<tr>
<td></td>
<td>1 µg/kg – 1000 µg/kg</td>
</tr>
<tr>
<td>Precision</td>
<td>± 5%</td>
</tr>
<tr>
<td>Accuracy</td>
<td>± 5%</td>
</tr>
<tr>
<td>Direct Analysis (minimum time)</td>
<td>2 minutes</td>
</tr>
<tr>
<td>Calibration</td>
<td>Spiking with Hg standard solution, HgNO₃</td>
</tr>
<tr>
<td>Set-up / Take-down time</td>
<td>&lt; 1 h</td>
</tr>
<tr>
<td>Utilities</td>
<td>110 V / 60 Hz, 1000 Watts</td>
</tr>
</tbody>
</table>

**Figure 4-15.** Ohio Lumex RA-915+ with RP-M-324M showing Furnace, Ladles and the Controller.
Quartz ladles were used for the sorbent trap (solid) testings. During analysis, ~0.7 g of fly ash was placed in the ladle then covered completely with Na₂CO₃ to absorb acidic gases. A pump flowrate of 0.5 L/min was maintained for each test. Analysis of each sample was completed in 2 minutes. Mercury standards were prepared using 2 – 20 µL and 20 – 200 µL calibrated pipettes. Daily calibrations using freshly prepared standard solutions were completed prior to each experiment. A sample calibration curve used in the study is presented in Figure 4-16.

![Figure 4-16. Sample calibration curve for Hg analysis (2014 07 09)](image)

4.4 THERMODYNAMIC MODELLING

FactSage is a thermodynamic modelling software containing a comprehensive set of databases for inorganic systems and several modules to perform data calculations [43]. FactSage 6.0 was used in the calculations used in the thesis. The equilibrium module of the software allows the calculation of equilibrium composition of a selected set of reactants, providing products predicted by Gibb’s energy minimisation. FactSage 6.0’s compound and solution databases in conjunction with equilibrium, phase diagram, and reaction modules were used to aid in identifying sulfate decomposition temperatures during ash decomposition.
(section 4.2.2), equilibrium compositions and formation temperatures of the different SO$_x$ species (section 4.2.3).

The input settings for the thermodynamic models for the fly ash decomposition were the XRF composition of the fly ash and the metal sulfates for the pure salt decomposition. On the other hand, for the conversion of SO$_2$ to SO$_3$ experiments, input settings are the concentrations of the oxidant gas. Calculations were completed at 1 atm pressure and at 100°C temperature intervals. For the products, the possible product species are dependent on the database used and the species selection from the chosen database [43].

4.5 CHAPTER SUMMARY

This chapter introduced the coal, materials, reagents and gases used in the conduct of the experiments and detailed the experimental setups used in each of the four major experimental studies completed in this thesis. Apart from Chapter 5 which is a stand-alone chapter detailing the objectives, experimental description, results and discussions, the experimental descriptions for Chapters 6, 7 and 8 were presented in this chapter.

Some photos of actual setup are presented for clarification and visual purposes. Calibration curves and essential equations were also presented in each of their corresponding sections. On the other hand, some equations are also presented in their corresponding chapters for emphasis.
5 COMBUSTION EXPERIMENTS WITH THE 20 KW\textsubscript{TH} DROP TUBE FURNACE AT THE INSTITUTE OF COMBUSTION AND POWER PLANT TECHNOLOGY (IFK), UNIVERSITÄT STUTTGART, GERMANY

5.1 INTRODUCTION

In this chapter, experimental results produced at the 20-kW\textsubscript{th} experimental rig, relevant to the overall aims of the thesis, are discussed. The experiments were conducted at the Institute of Combustion and Power Plant Technology (IFK) under a University of Stuttgart and University of Newcastle (Australia) collaboration funded by Xstrata Coal Low Emissions R&D Project CC08-71 on “Coal Impurity Impacts and Gas Quality Control in Oxy-fuel Technology for CCS” [117]. The author visited the institute (IFK) in June to July of 2012 to conduct some measurements and observe the operation, nevertheless the experimental work were performed mainly by IFK’s staff.

IFK’s 20 kW\textsubscript{th} once-through combustion rig is unique in that it applies a novel methodology [21] that allows investigation of different oxy-fuel configurations; \textit{i.e.} different levels of impurity injection (SO\textsubscript{2}, SO\textsubscript{3}, H\textsubscript{2}O, Hg) simulating different extents of flue gas recycling options (full cleaning, partial cleaning and no cleaning) for oxy-fuel. Whilst oxidant impurity levels are varied to accommodate differing extents of cleaning options, the 20 kW\textsubscript{th} once-through rig was kept with similar volumetric flow through the burner to have comparable residence times [11, 17]. The experiments performed at IFK focused on the flue gas impurity formation and reactions with fly ash under air and controlled oxy-fuel atmospheres utilising three commercial Australian coals A, B and C [117].
5.2 SECTION OBJECTIVES

The general objective of this section is to study the coal quality impacts and SO\textsubscript{x} and Hg injections on the combustion and emissions behaviours in air and oxy-fuel combustion conditions in a pilot scale reactor.

In order to carry out the main objective, the effects of the following specific objectives were established:

1) Investigate the differences in the emissions behaviour between conventional air (O\textsubscript{2}/N\textsubscript{2}) and oxy-fuel (O\textsubscript{2}/CO\textsubscript{2} with flue gas recycling) combustion environments.

2) Investigate effects of differing SO\textsubscript{2} input levels from air and oxy on SO\textsubscript{3} formation and bag filter capture.

3) Investigate the effects of differing SO\textsubscript{2}/SO\textsubscript{3} levels from air and oxy on the mercury speciation and capture by fly ash.

Fly ash obtained from the bag filters during the air and oxy-fuel studies in this chapter were used for the sulfur capture by fly ash study (Chapter 6); homogeneous and catalytic conversions with fly ash of SO\textsubscript{2} to SO\textsubscript{3} (Chapter 7); and competition between SO\textsubscript{x} and Hg in fly ash study (Chapter 8).

5.3 EXPERIMENTAL

5.3.1 Description of the 20 kW\textsubscript{th} Once-Through Furnace

The 20 kW\textsubscript{th} electrically heated coal-fired furnace is a once-through combustion rig which was operated at a combustion temperature of 1350°C. The schematic of the coal-fired once-through furnace of IFK is presented in Figure 5-1 with sampling locations identified. The rig is fired by a top-mounted burner [117] and is highly flexible for feeding impurities (e.g. SO\textsubscript{2}, NO, and Hg) with the oxidant gases (i.e. O\textsubscript{2}, CO\textsubscript{2}, N\textsubscript{2} and H\textsubscript{2}O) to evaluate air and oxy-fuel firing conditions [11]. The rig was controlled to have a constant product gas rate of 11.5 m\textsuperscript{3}/hr (STP) to maintain comparable residence times in the system for different oxidant settings [11, 17, 21, 117]. Out of the total
product gas flow from the end of the furnace, approximately 9-10 m³/hr (STP) was drawn through a short, unheated flue gas extraction section before going through an electrically heated flue gas duct (diameter = 200 mm, length = 2500 mm) wherein the gas temperature dropped from 700°C to 200°C within ~4 seconds, with the remaining product gases sent to the exhaust [17, 117]. The temperature – residence time approximation graph for the combustion rig is shown in Figure 5-2.

The fuel was fed using a system that consisted of a gravimetric conveyor and a screw feeder [17, 31] allowing 0.5 – 3 kg/h of pulverised coal to be fed with a carrier oxidant gas stream and additional primary and secondary oxidant gas streams [117]. The furnace utilised three commercially available Australian sub-bituminous coals A, B and C, similar to the pilot scale tests completed in 2006 at the Aioi Facility by Ishikawajima-Harima Heavy Industries (IHI) [45, 118, 119]. Flue gas with temperature of approximately 200°C to 280°C [117] then entered the heated bag filter which was maintained at 225°C (±30 K) and exited at about 195°C (±30 K) [11, 17]. Fly ash samples were obtained from the bag filter (encircled in Figure 5-1) of the rig. The same fly ash samples were used in the experiments presented in the succeeding chapters.

Figure 5-1. Schematic diagram of the 20 kWe experimental rig used for Air and Oxy-fuel investigations at IFK, University of Stuttgart, Germany [11, 17, 117].
Figure 5-2. Temperature - residence time profile approximation of the 20 kWth IFK combustion rig [117].

In order to simulate impurity levels in the flue gas recycling during oxy-fuel runs, impurity feeding systems for H\textsubscript{2}O vapour, SO\textsubscript{2}, NO and Hg\textsuperscript{0} were set in place [117].

1) H\textsubscript{2}O Vapour was fed using a water evaporator capable of injecting ~5 m\textsuperscript{3} (STP) superheated steam (~4 kg/hr) injected into the secondary injection point just before the burner.

2) SO\textsubscript{2} coming from a pure SO\textsubscript{2} gas cylinder was injected to the secondary injection point.

3) NO coming from a pure NO gas cylinder was injected to the secondary injection point.

4) Hg\textsuperscript{0} was injected to the secondary injection and was generated using an evaporator – condenser system where a known amount of gas (controlled with a mass flow controller) was passed into a temperature controlled vessel that contained liquid mercury (Figure 5-3). The gas that is highly concentrated with Hg\textsuperscript{0} then passes through a second vessel (the Hg\textsuperscript{0} condensation vessel) kept between 15°C and 25°C where Hg\textsuperscript{0} condenses until the gas reaches the Hg\textsuperscript{0} saturation for the set temperature. The Hg\textsuperscript{0} concentration was then calculated with the same principles as discussed in Section 4.2.4 using the Wagner Equation.
5.3.2 Fuel Characterisation

The analyses for the Australian coals A, B and C are summarised in Table 5-1. From amongst the three coals, it is noteworthy to mention for this thesis that the ash content of coal A is high followed by B then C in a ratio of 3:2:1. Hence in order to maintain the flue gas production at a constant rate of 11.5 m³/hr (STP), frequent cleaning of the bag filters had to be made during the combustion runs utilising coal A. In terms of sulfur content, which is essential in this study, although all sulfur contents of the three coals are not very high, the trend was opposite that of ash content. Coal C has 0.72% S, followed by B with 0.67% S then lastly A with 0.32% S. For the XRF analyses, coals A and B can be seen to have high SiO₂ contents of roughly the same magnitude (~60%) whilst C only had roughly half of A and B (33%). On the other hand the Fe, Ca and Mg contents of the coals are highest for C, followed by A, then lastly B. The mean particle size distributions (PSD) D₁₀, D₅₀ and D₉₀ of each coal used are also shown in the table.

Figure 5-3. Schematic of the mercury feeding system used in IFK [17].
Table 5-1. Proximate, Ultimate, ash oxide analysis (XRF) and Particle Size Distribution Analyses of the coals used in this study [117].

<table>
<thead>
<tr>
<th>Item</th>
<th>Units</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCV</td>
<td>kJ/kg</td>
<td>18026</td>
<td>24956</td>
<td>26748</td>
</tr>
<tr>
<td><strong>Proximate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water (W)</td>
<td>%, ad</td>
<td>3.9</td>
<td>1.5</td>
<td>3.7</td>
</tr>
<tr>
<td>Ash (A)</td>
<td>%, db</td>
<td>32.5</td>
<td>23.0</td>
<td>9.8</td>
</tr>
<tr>
<td>Volatile Matter (VM)</td>
<td>%, daf</td>
<td>35.9</td>
<td>50.6</td>
<td>35.9</td>
</tr>
<tr>
<td>Fixed Carbon (FC)</td>
<td>%, daf</td>
<td>64.1</td>
<td>49.4</td>
<td>64.1</td>
</tr>
<tr>
<td><strong>Ultimate Analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>%, daf</td>
<td>73.8</td>
<td>78.3</td>
<td>77.2</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>%, daf</td>
<td>4.3</td>
<td>6.7</td>
<td>5.2</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>%, daf</td>
<td>1.06</td>
<td>1.09</td>
<td>1.98</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>%, daf</td>
<td>0.32</td>
<td>0.67</td>
<td>0.72</td>
</tr>
<tr>
<td>Oxygen* (O)</td>
<td>%, daf</td>
<td>20.5</td>
<td>13.2</td>
<td>15.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>%, daf</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>Mercury in Coal</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>µg/kg, daf</td>
<td>66.4</td>
<td>41.5</td>
<td>22.2</td>
</tr>
<tr>
<td><strong>XRF Analysis (from coal ashing)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>%, db</td>
<td>58.91</td>
<td>64.39</td>
<td>33.20</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>%, db</td>
<td>26.18</td>
<td>21.53</td>
<td>23.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>%, db</td>
<td>6.84</td>
<td>1.24</td>
<td>11.40</td>
</tr>
<tr>
<td>CaO</td>
<td>%, db</td>
<td>1.19</td>
<td>0.35</td>
<td>6.95</td>
</tr>
<tr>
<td>MgO</td>
<td>%, db</td>
<td>0.71</td>
<td>0.68</td>
<td>1.79</td>
</tr>
<tr>
<td>Na₂O</td>
<td>%, db</td>
<td>0.13</td>
<td>0.24</td>
<td>1.33</td>
</tr>
<tr>
<td>K₂O</td>
<td>%, db</td>
<td>0.43</td>
<td>0.41</td>
<td>0.90</td>
</tr>
<tr>
<td>TiO₂</td>
<td>%, db</td>
<td>2.35</td>
<td>3.92</td>
<td>1.24</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>%, db</td>
<td>0.19</td>
<td>0.03</td>
<td>1.80</td>
</tr>
<tr>
<td>SO₃</td>
<td>%, db</td>
<td>3.07</td>
<td>7.21</td>
<td>22.70</td>
</tr>
<tr>
<td><strong>Particle Size Distribution</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D₁₀</td>
<td>µm</td>
<td>1.83</td>
<td>7.63</td>
<td>4.32</td>
</tr>
<tr>
<td>D₅₀</td>
<td>µm</td>
<td>11.09</td>
<td>44.14</td>
<td>21.77</td>
</tr>
<tr>
<td>D₉₀</td>
<td>µm</td>
<td>31.59</td>
<td>104.12</td>
<td>49.78</td>
</tr>
</tbody>
</table>

NCV – Net Calorific Value, ad – air dried, db – dry basis, daf – dry ash free basis

*Calculated by difference
5.3.3 Oxidant Concentrations

During conventional air combustion mode, “Air”, the burner was fed with cleaned and dried air. During oxy-fuel combustion mode, the burner was fed with a mix of 28% O\textsubscript{2} and CO\textsubscript{2} corresponding to the pilot scale tests done in 2006 by Ishikawajima-Harima Heavy Industries (IHI) [118, 119] and based on the matched radiative heat transfer with air firing [11]. Impurities NO\textsubscript{x}, SO\textsubscript{2}, Hg\textsuperscript{0} and H\textsubscript{2}O were introduced to simulate the practical oxy-fuel combustion with partial flue gas cleaning conditions (with simulated removal of nominal 20% H\textsubscript{2}O, 20% SO\textsubscript{2} and 50% Hg\textsubscript{tot} from flue gas based on theoretical maximum conversion [17]), referred in the thesis as “Oxy” for convenience. The practical case was based on the need to cool the primary recycle in order to prevent condensation of the H\textsubscript{2}O in the coal mill [11]. Theoretical maximum conversions for H\textsubscript{2}O, SO\textsubscript{2} and Hg impurities to simulate actual oxy-fuel conditions with an exit of 3 %vol. O\textsubscript{2} concentration were calculated using Equation (5-1) [117]. Varying injection concentrations reflect different removal rates of the impurities from the recycled flue gas (RFG) stream. The experimental configurations with associated removal rates and oxidant concentrations used as input for each experiment are summarised in Table 5-2.

\[
c_{i, \text{max, oxy}} = \frac{f_i \gamma_j M_{M,j}}{\left(\frac{\gamma_S M_{M,S}}{M_{M,S}} + \frac{\gamma_C M_{M,C}}{M_{M,C}} + \frac{\gamma_N M_{M,N}}{M_{M,N}}\right) 100} \left(100 - \gamma_{O_2}\right)
\]

where:
- \(c_i\) = mass concentration of component \(i\) in the flue gas (ppm, dry)
- \(\gamma_{ij}\) = weigh fraction of component \(i, j\) in the fuel (%wt, raw)
- \(M_{M,j}\) = molecular weight of component \(j\) (g/mol)
- \(\gamma_{O_2}\) = volume fraction of component O\textsubscript{2} in the flue gas (%vol., dry)
- \(f_i\) = stoichiometric factor for each component \(i\) (1 = SO\textsubscript{2} / Hg, 0.5 = H\textsubscript{2}O)
- \(i\) = index for flue gas components: H\textsubscript{2}O, SO\textsubscript{2} and Hg\textsuperscript{0}
- \(j\) = index for fuel component belonging to the respective flue gas component \(i\): H, S & Hg
Table 5-2. Experimental configuration showing removal rates to simulate Air and practical Oxy-fuel Combustion conditions [117].

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Units</th>
<th>Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>Oxy</td>
</tr>
<tr>
<td>Simulated Capture Rate</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>H₂O</td>
<td>%</td>
<td>-</td>
</tr>
<tr>
<td>SO₂</td>
<td>%</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>%</td>
<td>-</td>
</tr>
</tbody>
</table>

Oxidant Composition

<table>
<thead>
<tr>
<th>Coal feed</th>
<th>kg/hr</th>
<th>2.1</th>
<th>2.8</th>
<th>1.5</th>
<th>2.1</th>
<th>1.4</th>
<th>1.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>%vol. dry</td>
<td>21</td>
<td>28</td>
<td>21</td>
<td>28</td>
<td>21</td>
<td>28</td>
</tr>
<tr>
<td>CO₂</td>
<td>%vol. dry</td>
<td>0</td>
<td>66.3</td>
<td>0</td>
<td>64.8</td>
<td>0</td>
<td>66.1</td>
</tr>
<tr>
<td>H₂O</td>
<td>%vol. wet</td>
<td>0</td>
<td>16.9</td>
<td>0</td>
<td>20.5</td>
<td>0</td>
<td>17.5</td>
</tr>
<tr>
<td>SO₂</td>
<td>ppm, dry</td>
<td>0</td>
<td>824</td>
<td>0</td>
<td>1569</td>
<td>0</td>
<td>1687</td>
</tr>
<tr>
<td>NO</td>
<td>ppm, dry</td>
<td>0</td>
<td>654</td>
<td>0</td>
<td>631</td>
<td>0</td>
<td>634</td>
</tr>
<tr>
<td>Hg</td>
<td>μg/m³ (STP) dry</td>
<td>0</td>
<td>17.8</td>
<td>0</td>
<td>8.9</td>
<td>0</td>
<td>3.7</td>
</tr>
</tbody>
</table>

5.4 RESULTS

5.4.1 Conversion Rates of SO₂ to SO₃

Air and oxy-fuel combustion were carried out for coals A, B and C. Table 5-3 presents flue gas compositions (average) taken at the end of the furnace using a tempered sample probe (~180°C) [117] for each of the coals fired during the tests. The table clearly shows that during oxy-fuel (28% O₂) run with flue gas recycling, CO₂ concentrations of 95 %vol. (dry) and greater could be achieved. With a stable flue gas O₂ of ~3 %vol. (dry), CO concentrations remained low and the burnout was good with just about < 0.1% unburned carbon (by LOI) [11, 17, 21]. SO₂ concentrations in the table represented flue gas concentrations resulting from air and oxy-fuel combustion with flue gas recycling. Mean SO₃ values showed that increasing SO₂ input concentrations result in increased SO₃ output concentrations in the flue gas.
Based on the emissions presented in Table 5-3, SO$_2$ and SO$_3$ were compared and plotted. Figure 5-4 presents compiled results of SO$_2$ versus SO$_3$ measurements conducted at 0.8 MW$_{th}$ rig at IHI, Japan [45, 118] and this study at 20 kW$_{th}$ rig at IFK, Germany [21, 117] for coals A, B and C from Spörl, et al. [21]. Two sets of data were compared for SO$_3$ vs SO$_2$ from coals with same qualities. The graph shows three coals A (diamond), B (square) and C (triangle) marked hollow for IHI studies and solid for studies conducted in IFK. Also, in the graph a diagonal separator line divides the air combustion runs (left downwards of the separator) from oxy-fuel combustion runs (right upwards of the separator). Sets of positively sloped lines are also in the plot to represent 0.5, 1, 2 and 3% SO$_2$ to SO$_3$ conversions, respectively. Although coals of similar qualities were run in both studies, the scatter in SO$_3$ measurements is expected as two different rigs are being compared and experimental approaches were differing [21].

Table 5-3. Average flue gas composition measured from the end of the furnace [117].

<table>
<thead>
<tr>
<th>Coal</th>
<th>Units</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Air</td>
<td>Oxy</td>
<td>Air</td>
</tr>
<tr>
<td>O$_2$</td>
<td>%vol., dry</td>
<td>3.0</td>
<td>3.6</td>
<td>3.1</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>%vol., dry</td>
<td>17.6</td>
<td>95.4</td>
<td>16.0</td>
</tr>
<tr>
<td>CO</td>
<td>ppm, dry</td>
<td>1.4</td>
<td>55.8</td>
<td>0.0</td>
</tr>
<tr>
<td>NO</td>
<td>ppm, dry</td>
<td>845.8</td>
<td>1410.0</td>
<td>861.3</td>
</tr>
<tr>
<td>NOx</td>
<td>ppm, dry</td>
<td>845.8</td>
<td>1410.0</td>
<td>862.4</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>%vol. wet</td>
<td>6.4</td>
<td>23.5</td>
<td>7.6</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>ppm, dry</td>
<td>198.7</td>
<td>1234.6</td>
<td>367.5</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>ppm, dry (mean)</td>
<td>1.3</td>
<td>24.1</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Note: H$_2$O concentrations were calculated based on fuel composition and steam injection to the oxidant gases.

SO$_2$ input concentration significantly influences the SO$_3$ output concentration. What is interesting in this plot is that although air combustion results for IHI and IFK give lower SO$_3$ concentrations and oxy-fuel combustion for IHI and IFK gave higher SO$_3$ concentrations, the conversion rates do not differ much especially and lie roughly
on the same conversion line. In IHI Coal A (hollow diamond), it can be noted that SO₃ measurements of 2 ppm (Air) and 7 ppm (Oxy) corresponded to higher SO₂ inputs due to change in mode of firing; 182 ppm to 556 ppm, but both points lie on the same conversion line of approximately 1%. Average SO₂ to SO₃ conversion rates are found to be within 0.5% to 3% with Coal A (Air – 0.66%, Oxy – 1.95%), Coal B (Air – 2.25%, Oxy – 2.01%) and Coal C (Air - 0.04%, Oxy – 1.28%). There is a scatter but it can be observed that for Coal B, conversion is the same for air and oxy while Coals A and B showed greater conversions in oxy. Spörl, et al. [21] compared the IFK results to the existing results and concluded that IFK results are within 0.5 and 4.5% conversion rates from literature.

**Figure 5-4.** SO₂ input versus SO₃ output concentrations comparing results of the 0.8 MWₑ IHI pilot scale studies in 2006 [45, 118] and 20 kWₑ IFK measurements in 2012[21, 117] taken before the bag filter for similar coals A, B and C. Diagonal lines in the plot represent SO₃/SO₂ % conversion values of 0.5, 1, 2 and 3%.
Although most of the SO$_2$ to SO$_3$ conversion rates lie within 0.5 to 3%, it can be noted from Table 5-3 that the SO$_3$ concentration for Coal C in air-firing was 0.2 ppm while it is 36.5 ppm for oxy-fuel firing. Sulfur contents of the coals B and C are roughly similar (Table 5-1) but it can be seen from Figure 5-4 that IFK Coal C – Air is nowhere near coal B, in fact it is not in the plot since the conversion rate is only 0.04%. Spörl, et al. [21] stated that while sulfur in coal is the main driver for SO$_2$ (and eventually SO$_3$) production, it is probable that the SO$_2$ generation was too low to reach a measurable conversion to SO$_3$. The low amount of SO$_3$ produced might have also been captured by the alkali and alkaline-earth metals which is relatively high in Coal C compared to Coals A and B (Section 5.3.2). Fe$_2$O$_3$ has been known to catalyse the conversion of SO$_2$ to SO$_3$ [39, 66, 70, 120] as discussed in Chapter 2. Although Coal C has the highest iron content (IFK - Air), it has a much lower SO$_3$ output concentration. On the other hand Coal C also has the highest CaO and MgO contents which captures SO$_2$ and SO$_3$. Whereas Coal B which has the lowest alkali and alkaline-earth metals (AAEMs) generated higher SO$_3$ for both air (8.3 ppm, dry) and oxy-fuel (52.5 ppm, dry) combustion runs. The effect of the AAEMs on the sulfur capture by fly ash is further discussed in Chapter 6. Furthermore, laboratory experiments on the effects of SO$_2$, O$_2$, H$_2$O and fly ash on the conversion rates of SO$_2$ to SO$_3$ is further discussed in Chapter 7.

**5.4.2 SO$_3$ capture by fly ash across the bag filter**

It was presented in the Section 5.4.1 that SO$_2$ input concentration indeed greatly influences the output concentration of SO$_3$ in the flue gas. On the other hand, the % conversion of SO$_2$ to SO$_3$ did seem slightly affected by the mode of firing from air to oxy-fuel for coals A and C but only slightly for coal B. It was also stated that the fluctuations of these SO$_3$ measurements could be due to the some coal and ash specific factors, e.g. ash content, AAEM oxides content. This section now looks into the effects of the bag filter fly ash on the measured SO$_3$ concentrations.

Figures 5-5 (a) and (b) presents the mean SO$_3$ measurements taken before and after the bag filter, respectively. The plots clearly show that there are differences between the SO$_3$ values of before and after filter [21] which indicates that SO$_3$ (and not
just \( \text{SO}_2 \) could be captured by some active species in the fly ash (\textit{e.g.} \text{CaO}, \text{MgO}). Minimal differences are observed for the air modes whilst a greater reduction (concentration units) are observed for oxy-fuel modes and this is due to the already low concentrations obtained during the air combustion mode.

\textbf{Figure 5-5.} Mean \( \text{SO}_3 \) concentrations (a) before and (b) after the bag filter house showing high and low values.
Figure 5-6 presents the average SO$_3$ capture rates across the bag filter for the three coals in both air and oxy-fuel combustion conditions. This clearly indicated that bag filter is effective in capturing SO$_3$ in the flue gas. Average capture rates for air runs ranged from 50 to 80% whereas oxy-fuel runs only averaged from 7 to about 50% were observed. Again, as in Figures 5-5 (a) and (b), lower SO$_3$ concentrations in air combustion runs resulted to higher removal rates compared to high SO$_3$ concentrations found in oxy-fuel combustion runs. SO$_3$ capture rates were calculated by Spörl, et al. [21] using Equation (5-2):

\[
\eta_{SO_3} = \frac{y_{SO_3}^{bf} - y_{SO_3}^{af}}{y_{SO_3}^{bf}} \times 100\%
\]  

(5-2)

Where:
- $\eta_{SO_3}$ = bag filter capture efficiency
- $y_{SO_3}$ = volumetric concentration (ppm, dry)
- $bf$ = before the bag filter
- $af$ = after the bag filter

**Figure 5-6.** SO$_3$ capture efficiencies (%) at the bag house filters for air and oxy-fuel combustion for coals A, B and C [17].
Spörl, et al. [21, 117] stated that after the bag filters, repeatability of SO\(_3\) measurements after the bag filter could not be established (for A-Oxy) hence showing almost no removal. Possible explanation was attributed to the fluctuations of inlet (±30°C) and outlet (±15°C) temperatures of the bag filter which could directly affect the acid dew point temperatures. According to Cao, et al. [121], increased SO\(_3\) sorption is expected when working with temperatures closer to ADP. ADPs of 92 – 163°C (before) and 86 – 157°C (after) the bag filter were calculated using ZareNezhad’s correlation [50] as presented in Chapter 2 with ADP temperatures of oxy-fuel with recycling 41–67°C higher than air combustion [21]. This capture of SO\(_3\) by the bag filter resulted to H\(_2\)SO\(_4\) dew point reductions between 1 and 16°C [21].

### 5.4.3 Mercury Speciation and Capture by Fly Ash

Combustion tests conducted by Spörl, et al. [17, 117] at IFK allowed differing mercury injection levels during air and oxy-fuel tests. Interaction between SO\(_x\) species and mercury and their capture on fly ash are presented in this section. Extensive studies have stated that SO\(_2\) and SO\(_3\) compete with mercury for adsorption sites on the unburned carbon (UBC) in fly ash [97, 100, 104, 122]. This study is unique in that the unburned carbon present in the fly ash is low (< 0.1%) and the effects of inorganics in the fly ash and not the carbon is the main focus.

**Figure 5-7** shows the differences between the measured Hg\(^0\) and Hg\(^{2+}\) for air and oxy-fuel combustion runs for the three experimented coals. It may be noticed from the IFK experiments that a change from air combustion to oxy-fuel combustion runs for all three coals gave similar trends with respect to speciation of mercury, with a higher Hg\(^{2+}\) during oxy-fuel runs. However, even though greater Hg\(^{2+}/Hg_{\text{tot}}\) can be seen in the graph as there is a change from air to oxy-fuel, 2 variables were simultaneously changed in the shifting from air to oxy, namely; SO\(_x\) and Hg. Therefore it is difficult to isolate in this case whether SO\(_x\) or Hg is the main driver for increased Hg\(^{\text{tot}}\) and Hg\(^{2+/Hg_{\text{tot}}\) speciation.
Tests were also conducted to determine whether capture across the bag filter differed as the impurity levels were varied from air mode to simulated oxy-fuel mode. Figure 5-8 shows the capture behaviour across the bag filter in IFK. Spörl, et al. [117] discussed in detail that although Hg$^{\text{tot}}$ capture efficiencies from 13 to 51% were observed, a clear trend in Hg capture and speciation between air and oxy-fuel could not be determined. Decreasing capture for coal A, increasing capture for coal B and similar capture levels for coal C were noted. The negative capture efficiencies in Figure 5-8 indicates an oxidation as the flue gas interacts with the fly ash in the bag filter and the resulting Hg$^{2+}$ after the bag filter is higher than the inlet. One possible reason is the high Fe$_2$O$_3$ content of coal C compared to coals A and B.
Figure 5-8. Speciated Hg capture across the bag filter during air and simulated oxy-fuel for coals A, B and C. Speciation (as Hg$^0$ and Hg$^{2+}$ are also shown).

In order to investigate the isolated effect of SO$_3$ concentration on the Hg capture in fly ash, Spörl, et al. [117] conducted an experiment for coal A using the same Hg concentration (17.8 µg/m$^3$ (STP)) but varied the amount of SO$_3$ input in the bag filter (Figure 5-9). In the graph, it can be deduced that as the SO$_3$ concentration increased, the capture extent of Hg$^{\text{tot}}$ by the fly ash also increased. Capture extents of 8.6 to 23.8% were observed as the SO$_3$ increased from 16 to 37 ppm (dry) before the bag filter. Spörl, et al. [117] stated that in regards to competition between Hg and SO$_3$, the behaviour could not be established from this graph. Kellie, et al. [104] which investigated mercury speciation in a 100 MW coal fired boiler concluded that during coal combustion, sulfur was shown to be a major factor in the oxidation of Hg$^0$ but it inhibits adsorption of Hg onto the fly ash carbon. Studies by Presto and Granite [122] have revealed that between SO$_2$ and SO$_3$, SO$_3$ was seen to inhibit capture of Hg on activated carbon. On the other hand, Wilcox, et al. [97] also stated that depending on the species of sulfur, it can either have a positive or negative effect on the oxidation and capture of Hg$^0$ on the activated...
carbon surfaces. However, most of the studies conducted dealt with either high UBC fly ash or activated carbon injection tests whereas this study dealt with fly ash with very low (< 0.1%, LOI) unburned carbon.

Figure 5-9. Hg\text{tot} capture efficiency vs inlet SO$_3$ concentration before bag filter using coal A [117].

5.5 CHAPTER SUMMARY AND CONCLUSIONS

A comprehensive set of experiments of air and oxy-fuel combustion with different extents of flue gas recycling were completed by Spörl, et al. [17, 21, 117] at the Institute of Combustion and Power Plant Technology (IFK), Stuttgart, Germany. The work investigated the combustion behaviour of three Australian coals A, B and C during air and oxy-fuel combustion. The effects of differing SO$_x$ levels during air and oxy-fuel with impurity injection (simulating flue gas recycle) has been studied. The following conclusions and recommendations were used to drive some of the scientific works in Chapters 6, 7 and 8.
5.5.1 On Fly Ash

The experiments at IFK indicate that SO$_3$ was found to be effectively captured in the bag filter. Higher capture were observed in air (50 – 80%) than during oxy-fuel (7 – 50%).

It is expected that with similar residence times, higher SO$_2$ and O$_2$ partial pressure in the flue gas during oxy-fuel combustion, SO$_3$ formation may be altered [11] and is said to be more efficient [123]. Liu, et al. [123], Wang, et al. [124] studied simultaneous sulfation and carbonation of CaO which is one of the active species capturing sulfur that can be found in fly ash; they have stated that with an increasing SO$_2$ concentration, greater sulfation of CaO was observed. On the other hand an increased in CO$_2$ concentration from 70 to 90% CO$_2$ caused the sulfation ratio of CaO to decrease from ~0.41 to ~0.33 [124]. With this, SO$_2$ (and SO$_3$) may be captured more or less efficiently during oxy-fuel combustion. Therefore, the differences in sulfur capture by fly ash using the bag filter ash obtained during air and oxy-fuel firing were then investigated and presented in Chapter 6.

5.5.2 On SO$_2$ to SO$_3$ Conversion

During combustion testing, the average SO$_2$ to SO$_3$ conversion rates were found to be within 0.5% to 3%. Similar conversion rates for the same coals were observed with slightly higher conversions during oxy-fuel combustion compared to air combustion. SO$_3$ capture on the bag filter reduced the H$_2$SO$_4$ dew point by around 1 and 16°C. ADP temperatures were observed to be around 41–67°C higher in oxy-fuel combustion than in air.

Literature suggested that SO$_2$ to SO$_3$ conversion is a function of some or all of the following, namely; SO$_2$ partial pressure [86, 125-127], O$_2$ partial pressure [86, 126, 127], presence or absence of moisture [66, 86, 125-127], presence of catalytically active components in the fly ash (e.g. Fe$_2$O$_3$) [66, 86, 125, 127], and the temperature-residence time profile of the plant [86]. Similar residence times and temperature profile were maintained for air and oxy-fuel during IFK experiments, hence conversions have been focused mainly on the effects of SO$_2$, O$_2$, moisture and fly ash. With this, an attempt to
conduct conversion experiments were carried out with simulated flue gas (variable [SO₂], [O₂], [H₂O], temperature, residence time) to investigate the effects of contacting the oxidant gases (synthetic flue gas) with fly ash generated from the IFK experiments. Chapter 7 presents the results of the conversion experiments with and without the presence of fly ash in the system.

### 5.5.3 On Mercury Capture and Speciation

*Increased Hg\text{tot} and Hg^{2+}/Hg\text{tot} were observed when switching from air combustion to oxy-fuel combustion during the IFK experiments. Changing between air and oxy-fuel firing did not result to a clear trend with respect to capture by the bag filter. On the other hand, increasing SO₃ concentrations with Hg input held constant increased capture of Hg by the bag filter fly ash.*

Several researchers [97, 100, 104, 122] have studied capture of Hg on activated carbon during combustion. In cases where the fly ash contains almost negligible unburned carbon (< 0.1%, LOI), such as this study, focus will not be on the capture by activated carbon but by the inorganic portions in the fly ash. In the experiments detailed in Section 5.4.3, the effects of the change between air and oxy-fuel firing resulted to increased Hg and SOₓ inputs making it difficult to isolate the individual effects of increasing Hg, SO₂, SO₃ and H₂SO₄ on the capture efficiencies. Therefore in Chapter 8, the individual effects of pure Hg, pure SO₂, SO₂/SO₃, SO₂/SO₃/H₂SO₄ and bag filter temperature will be investigated and discussed.
6 DIFFERENCES IN SULFUR CAPTURE BEHAVIOUR BY FLY ASH IN AIR AND OXY-FUEL PF COMBUSTION

6.1 INTRODUCTION

Chapter 5 concluded that due to considerable differences in the SO$_2$ and O$_2$ partial pressures in the flue gas between air and oxy-fuel combustion, the formation and capture of sulfates can be altered. SO$_2$ concentrations was found to be roughly 4 times in oxy-fuel compared to air. Conversions of SO$_2$ to SO$_3$ were around 0.5 to 3% across the three coals for air and oxy-fuel combustion with slightly higher conversions during oxy-fuel runs. SO$_3$ was also found to be captured by the bag filter fly ash effectively ranging from 50 – 80% during air combustion and 7 – 50% during oxy-fuel combustion. Together with the capture of SO$_3$ by the bag filter is the reduction of the H$_2$SO$_4$ acid dew point by around 1 and 16°C. From literature [123, 124], it is expected that with longer residence times and higher SO$_2$ concentrations due to flue gas recycling during oxy-fuel combustion conditions, higher capture of sulfur occurs in the fly ash. This is however not the case for the experiments conducted at IFK [17, 21, 117] where the capture efficiency by the bag filter was lower in oxy-fuel. During the combustion tests at IFK, in order to observe purely the effects of gas interactions at different environments with different rates of flue gas recycling, the wall temperature and the volumetric flow across the boiler were kept constant to have comparable conditions between air and oxy-fuel.

This chapter focuses on understanding the sulfur transformations in a flue gas followed by its capture in fly ash during air and oxy-fuel combustion. Bag filter fly ash resulting from experiments detailed in Chapter 5 were utilised in this chapter to study the differences in sulfur capture by fly ash coming from different modes of firing, i.e. air firing and oxy-fuel firing. Two techniques for comparing sulfur from air and oxy-firing are presented in this
chapter; the thermally evolved gas method by heating fly ash to 1400°C using the setup discussed in Section 4.2.2 and the Eschka method by acid digestion.

### 6.2 SECTION OBJECTIVES

The reduction in the gas volume, change in the combustion environment and increase in SO\textsubscript{2} and SO\textsubscript{3} concentrations during oxy-fuel combustion is expected to alter the extent of sulfation of alkali and alkaline earth metals in fly ash as well as adsorption/condensation dynamics of the SO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} by fly ash in the bag filter [11]. In the case where combustion temperatures and residence times are kept similar, the isolated effect of flue gas impurities on sulfur capture by fly ash can then be evaluated.

The main objective therefore of this chapter is to evaluate the difference in sulfur captured by fly ash obtained during air and oxy-fuel combustion tests conducted using the 20-kW\textsubscript{th} once-through furnace located at IFK, Stuttgart [17, 21].

In order to carry out the general objective of the study, the following specific objectives were established:

1) To characterise the fly ash in terms of particle size distribution, XRF and XRD to determine the differences in the physical and chemical properties of air and oxy-fired fly ash.

2) To carry out gas evolved thermal decomposition and digestion of fly ash to evaluate the differences in sulfur capture behaviour of fly ash exposed to differing levels of SO\textsubscript{2} levels (apparatus as outlined in Section 4.2.2).

3) To identify the possible active species in the fly ash that capture SO\textsubscript{x}.
6.3 RESULTS: FLY ASH CHARACTERISATION

6.3.1 Particle Size Distribution

Previous investigators [128-131] have described three peaks (trimodal PSD) in the particle size distribution of combustion ash; these are the ultrafine region, fragmentation region and the supermicron region. In this study, submicron particles (< 1 µm) were not reported due to limitation in the calibration of the Malvern particle sizer. The fragmentation region (approximately 1 µm – 2 µm) and a bulk or supermicron fragmentation region (>5 µm diameter, centered approximately around 10 µm) are observed in all of the fly ashes studied. A peak between 30 µm and 60 µm is also observed in the PSD for fly ash B. According to Yu, et al. [129] previous researchers noted peaks (approx. 10 µm) correspond to alumino-silicate rich particles [130] while larger particle sizes, coarse region, (>10 µm, around 40-50 µm) correspond to carbon enriched particles. However, particle sizes greater than 50 µm correspond to mineral rich particles.

Figure 6-1 shows the PSD for each of the fly ashes used in this thesis, produced in both air and practical oxy-fuel combustion. In Figure 6-1 (a) and Figure 6-1 (c), both fly ash A and C exhibit a peak centred at around 1 to 2 µm (fragmentation region) and another one at about 10 µm (supermicron fragmentation region). In Figure 6-1 (b), it can be observed that the presence of an additional peak around 30 µm is observed. While previous researchers [128, 129] stated carbon enriched particles are responsible for peaks > 10 µm, the amount of unburned carbon (UBC) present in fly ashes A, B and C are low (refer to Table 6-1). In order to verify the behaviour of the sizing of the fly ash, they were compared against the PSD of the original coal samples. As per the PSD of the original coal samples, the D_{90} (particle diameter at which 90% of the population fall) of coals A, B and C are 32 µm, 104 µm, and 50 µm, respectively.

Particle sizing was conducted on the fly ash samples in order to test whether mode of firing, i.e. Air and Oxy-fuel, would have an effect on the fragmentation, ash formation and potentially sulfur capture. Marier and Dibbs [66] indicated that apart from the flow of gas, amount of metal oxides to capture sulfur, the availability of large surface
area for capture is necessary. However the PSDs for air and oxy ash were similar. The same conclusion was reached by the studies by Wall, et al. [110] and Jia, et al. [132].

Figure 6-1. Particle Size Distribution of the bulk fly ashes A, B and C using the Malvern Mastersizer 2000.
6.3.2 Fly Ash Chemistry

6.3.2.1 X-Ray Fluorescence (XRF): Alkali and Alkaline Earth Metals (AAEMs) and Sulfur Compositions

From the XRF analysis including unburned carbon by LOI of the three Australian coal fly ash samples, as can be seen in Table 6-1, the major oxides are SiO$_2$ > Al$_2$O$_3$ followed by Fe$_2$O$_3$, it can however be observed that compared with fly ashes A and C, fly ash B has a relatively low Fe$_2$O$_3$ content. CaO, MgO, TiO$_2$ and MnO$_2$ are present in small fractions for fly ash A and B; fly ash C however has higher CaO. Figures 6-2 (a), 6-2 (b) and 6-2 (c) show the Alkali and Alkaline Earth Metals (AAEMs) composition from the XRF of the bulk ash.

Table 6-1. XRF and %Unburned Carbon Analyses of the Fly Ash Samples from the IFK combustion tests used in this set of experiments.

<table>
<thead>
<tr>
<th>Dry Basis %$_{w}$</th>
<th>Fly Ash Sample</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td></td>
<td>B</td>
<td></td>
<td>C</td>
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<td>Air</td>
<td>Oxy</td>
<td>Air</td>
<td>Oxy</td>
<td>Air</td>
<td>Oxy</td>
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<tr>
<td>SiO$_2$</td>
<td>55.2</td>
<td>52.9</td>
<td></td>
<td>68.7</td>
<td>69</td>
<td>53.8</td>
<td>53</td>
<td></td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>33.3</td>
<td>34</td>
<td></td>
<td>25.2</td>
<td>24.2</td>
<td>25.9</td>
<td>26.5</td>
<td></td>
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<tr>
<td>Fe$_2$O$_3$</td>
<td>6.55</td>
<td>7.13</td>
<td></td>
<td>1.62</td>
<td>2.16</td>
<td>8.55</td>
<td>8.34</td>
<td></td>
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<tr>
<td>CaO</td>
<td>0.95</td>
<td>1.41</td>
<td></td>
<td>0.73</td>
<td>0.87</td>
<td>4.55</td>
<td>4.66</td>
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<tr>
<td>MgO</td>
<td>0.741</td>
<td>0.98</td>
<td></td>
<td>0.716</td>
<td>0.737</td>
<td>1.558</td>
<td>1.667</td>
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<td>Na$_2$O</td>
<td>0.144</td>
<td>0.158</td>
<td></td>
<td>0.25</td>
<td>0.275</td>
<td>0.971</td>
<td>0.979</td>
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</tr>
<tr>
<td>K$_2$O</td>
<td>0.512</td>
<td>0.518</td>
<td></td>
<td>0.627</td>
<td>0.604</td>
<td>1.11</td>
<td>1.058</td>
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<tr>
<td>TiO$_2$</td>
<td>2.06</td>
<td>2.16</td>
<td></td>
<td>1.77</td>
<td>1.65</td>
<td>1.15</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>0.097</td>
<td>0.113</td>
<td></td>
<td>0.002</td>
<td>0.008</td>
<td>0.04</td>
<td>0.041</td>
<td></td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.178</td>
<td>0.275</td>
<td></td>
<td>0.134</td>
<td>0.176</td>
<td>1.364</td>
<td>1.508</td>
<td></td>
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<tr>
<td>SO$_3$</td>
<td>0.132</td>
<td>0.243</td>
<td></td>
<td>0.186</td>
<td>0.28</td>
<td>0.932</td>
<td>0.969</td>
<td></td>
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<tr>
<td>BaO</td>
<td>0.042</td>
<td>0.056</td>
<td></td>
<td>0.067</td>
<td>0.063</td>
<td>0.067</td>
<td>0.072</td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td>0.049</td>
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<td></td>
<td>0.034</td>
<td>0.036</td>
<td>0.094</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100.0</td>
<td></td>
</tr>
<tr>
<td>% Carbon (Unburned)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>0.106</td>
<td>&lt; 0.1</td>
<td>0.134</td>
<td>0.199</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calcium and magnesium are known to be very active species that capture SO$_2$ in power plants; they play a significant role in the sulfur capture and retention in the ash. Furthermore, it has been stated that among other AAEMs, calcium is the most
effective species at capturing sulfur after deposition onto heat transfer surfaces in the cooler regions of the combustion system, *e.g.* economizer [41, 133, 134].

It can however be noted that the XRF results across all three fly ash samples are consistent between Air and Oxy runs, and that no significant differences were observed. It could be seen that Fly Ash C has higher SO$_3$, about 1.2%mol, compared to both A and B which have values approximately 0.2%mol. Then again, this may be justified by the fact that Fly Ash C contains higher amounts of alkaline oxides, *i.e.* CaO and MgO, which are essential in sulfur capture [41, 42, 66]. In Figure 6-2 (e), Fly ash C shows a higher CaO and MgO contents, 8% mol and 4%, respectively whilst A and B similarly contain approximately 2%mol CaO and 1.8% mol MgO.

**6.3.2.2 X-Ray Diffraction Analysis (XRD)**

As part of the identification of the active species in the fly ash that captures sulfur, XRD analyses were performed on the bag filter fly ash samples A, B and C for both air and oxy-fuel cases. Figure 6-3 shows the XRD spectra for fly ash sample A-Air. The spectra shows that the fly ash is composed mostly of aluminosilicates, mullite (3Al$_2$O$_3$•2SiO$_2$) and quartz (SiO$_2$) followed by Hematite (Fe$_2$O$_3$) and Magnetite (Fe$_3$O$_4$). An attempt to search for Alkali and Alkaline-Earth Metal oxides was carried out but no peaks were found. A comparison of spectra was also carried out for fly ash A-Oxy (Appendix A) however the spectra did not show significant differences. XRD for fly ash B and C for both Air and Oxy also revealed aluminosilicates followed by oxides of iron. An identification of the metal sulfates from the XRD spectra was carried out but no peaks corresponded with the metal sulfates. It could be that the crystal structure has broken down and not melted. These sulfates could be present together with the background and were regarded as amorphous.
Figure 6-2. Alkali and Alkaline-Earth Metals (AAEMs) and SO$_3$ Content of fly ash A, B and C.
Figure 6-3. XRD Spectra of Fly Ash A-Air showing peaks for Magnetite, Hematite, Mullite and Quartz.
6.4 FLY ASH DECOMPOSITION

Fly ash decomposition experiments were performed in order to decompose the sulfur-containing species which may evolve upon heating the fly ash and provide a measure of identification from ambient temperatures up to 1400°C. In Figure 6-4, it can be noted that for all fly ash samples used, changing between samples from Air to Oxy has increased the amount of sulfur species (as ppm SO\textsubscript{2} in N\textsubscript{2}) evolved during the decomposition. The light blue lines in the figures show air-firing derived fly ash whilst the red lines represent the fly ash derived from oxy-fuel firing, Oxy. Five main points which are noteworthy can be deduced from this plot.

1. The evolution of sulfur species was found to be aligned when the plots were drawn against one another indicating that similar sulfur species evolve at similar temperatures from different samples with only a slight shifting of the evolution temperature.

2. Oxy fly ash SO\textsubscript{2} release is 2-3 times greater compared to Air fly ash, upon integration of the area under the curve. This finding is significant since it follows claims of other researchers that during oxy-fuel combustion with flue gas recycling, SO\textsubscript{2} and other impurities were found to be 3-4 times greater than in air; resulting to more sulfur retention by ash [133]. Differences between the areas of Oxy and Air are shaded in the figure.

3. Between 400°C and 800°C, a wide primary peak of sulfur release with a smaller shoulder peak is observed from all fly ash samples (enlarged image: Figure 6-4(a)).

4. Between 800°C and 1100°C, a strong secondary peak with a shoulder peak can be observed especially in samples B and C. These peaks are quite significant in all Oxy samples indicating that due to its higher flue gas concentrations, an improved sulfur capture mechanism might be involved. In the Air fly ash samples however, the secondary peaks was only strongly visible with sample C.

5. It can be noted that a third set of peaks, occurring roughly at temperatures higher than 1300°C could be observed from all fly ash samples for both air and oxy-fuel and evolved roughly at the same concentration level. This may indicate that during
the sintering of the fly ash, some high temperature sulfur species, possibly associated with slag particles are still evolved.

Figure 6-4. Thermal Gas Evolution from the Decomposition of Fly Ash under an inert atmosphere, N₂. Shaded region is the difference between Oxy and Air fly ash.
Figure 6-5 presents the sample coming from the fly ash decomposition experiments. It can be noted that in Figure 6-5 (a), using fly ash A, the product after heating to 1400°C is a pellet-like fused slag (emphasised in Figure 6-5 (b)). Fly ash B produces similar pellet-like slag. On the other hand, all decomposition products coming from fly ash C fuses to the alumina crucible as shown in Figure 6-5 (c). Also, in the crucible was cut lengthwise on its cross-section to show that the slag has fused to the walls and the base of the alumina.

![Figure 6-5](image)

Figure 6-5. Fly Ash Samples (a) before and after decomposition of fly ash A; (b) showing fused pellet-like slags; (c) sintered slag from fly ash C fusing to the walls of the crucible.
6.5 THERMODYNAMIC MODELLING AND PURE SALTS THERMAL DECOMPOSITION

In order to be able to identify the active species capturing sulfur in the fly ash, pure salts of the AAEMs (*i.e.* CaSO$_4$, MgSO$_4$, Na$_2$SO$_4$, K$_2$SO$_4$) and other metal sulfates (Al$_2$(SO$_4$)$_3$ and Fe$_2$(SO$_4$)$_3$) were thermally decomposed. These decomposition temperatures from experiments were then compared with FactSage 6.0 model. In the pure salts decomposition, the same conditions to the fly ash decomposition tests were employed. For the FactSage 6.0 model, the conditions used were [SO$_2$] = 0 – 1000 ppm, [O$_2$] = 5% vol., N$_2$ balance and Alkaline Salts calculated from XRF data (Table 6-1).

6.5.1 Thermodynamic Model: FactSage 6.0

The FactSage thermodynamic model for the decomposition of pure CaSO$_4$ under N$_2$ is presented in Figure 6-6. It can be observed from the figure that the decomposition of CaSO$_4$ under pure N$_2$ starts at about 960 to 980°C and continues to 1150 to ~1200°C. Input of SO$_2$ in the model was made in order to account for any SO$_2$ partial pressure above the fly ash sample that may have evolved from other sulfates prior to CaSO$_4$ decomposition.

6.5.2 Pure Salts Thermal Decomposition

A sample decomposition of pure salt, *i.e.* CaSO$_4$, is presented in Figure 6-7 showing the actual thermal decomposition of the pure salt and the cumulative decomposition (as % total sulfur released) versus sample temperature used to obtain the decomposition temperatures in Table 6-2. Thermal decomposition values obtained from FactSage 6.0 model and SI Chemical Data [135] were used to guide the pure salt decomposition experiments; the model shows the initial decomposition temperature of the metal sulfates.
Figure 6-6. Thermodynamic model used in determining the decomposition temperature of sulfates (CaSO₄). Model Inputs: [O₂] = 5% vol., [SO₂] = 0 – 1000 ppm, balance N₂.

Figure 6-7. Decomposition of CaSO₄ under 1.5 L/min (298 K, 1 atm) of N₂, 5°C/min heating rate.
Table 6-2. Decomposition Temperatures of the Pure Salts of the Metal Oxides.

<table>
<thead>
<tr>
<th>Metal Sulfate Species</th>
<th>Decomposition Temperatures, °C</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model</td>
<td>Experiment</td>
</tr>
<tr>
<td></td>
<td>FactSage 6.0</td>
<td>Start of Decomposition</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃</td>
<td>520</td>
<td>546</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>505</td>
<td>793</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>680</td>
<td>903</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>1035</td>
<td>962</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>1085</td>
<td>1129</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>980</td>
<td>1141</td>
</tr>
</tbody>
</table>

The values in Table 6-2 suggest that the initial peaks between 400°C and 800°C in Figure 6-4 may be a combination of Iron (III) Sulfate, Fe₂(SO₄)₃, and Aluminium Sulfate, Al₂(SO₄)₃. The secondary peaks between 800°C and 1100°C may be a combination of Magnesium Sulfate (MgSO₄) and Potassium Sulfate (K₂SO₄). The third peak which occurs at temperatures greater than 1300°C may well be a combination of Calcium Sulfate (CaSO₄) and Sodium Sulfate (Na₂SO₄).

Although in the pure salts decomposition and in the thermodynamic modelling, all of the Na, Ca and K salts are decomposed well before 1400°C, it could be that during fly ash experiments these sulfur species may have been encapsulated in the sintered slag, needing a longer time period for release. Preliminary experiments using varying heating rates showed no difference in the decomposition temperatures of the peaks; however higher temperature shifts were observed at higher heating rates similar to the ones in literature [136]. Fly ash C was also observed to have a lower sintering/melting temperature based on the experiments performed (< 1200°C).

Sulfur may be retained as solids due to the sulfation of the alkaline oxides CaO, MgO, Al₂O₃, Fe₂O₃, K₂O, Na₂O especially in the cooler condensing zones of a combustion system [41, 134, 137]. According to Cheng, et al. [137], one possibility is the formation of calcium alumina sulfate (3CaO·3Al₂O₃·CaSO₄) and/or calcium silicate
sulfate (Ca$_5$(SiO$_4$)$_2$SO$_4$) which are thermally stable products at high temperatures. Another possibility is the presence of the Fe–Si–Ca melt (e.g. CaFe$_3$(SiO$_4$)$_2$OH) in the fly ash sample which is very heat resistant and can physically enwrap/encapsulate the sulfation product CaSO$_4$ preventing its thermal decomposition. Also, due to the crystal structure of CaSO$_4$, it does not form a solid solution with the silicates at high temperature but is only encapsulated by the Fe-Si-Ca melt. In their study [137], the Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analysis showed that the silicates with Si and Fe contents closely encapsulate the CaSO$_4$ preventing it from decomposing at high temperature.

Slight shifts in the formation and decomposition temperatures of sulfates in the fly ash could be observed between Air and Oxy-fuel ashes. This suggests higher concentrations of impurities during oxy-fuel firing might have some effects on the improved capture and retention mechanisms, or that minerals may not be pure and their compositions vary slightly throughout the combusted coal resulting in various sulfate compounds with variable purity.

6.6 SULFUR IN FLY ASH

6.6.1 Species Identification: Normal Distribution Modelling

Peak identification with the aid of a normal distribution modelling using MS Excel was carried out for the fly ash samples examined in the study. A sample normal distribution model is given in Figure 6-8 using fly ash A-Oxy. The figure shows the models (species), the total from the model and the actual SO$_2$ data evolved from the sample (ppm SO$_2$ in N$_2$ per gram of fly ash). Each model shows an area and a mean temperature ± standard deviation. The model was fitted to the data and it can be noticed that the peaks are not entirely made of single species, the presence of shoulder peaks indicates more than one species may exist per set of peaks. The actual data on the plot was discontinued at 1416°C (1400°C ± 20 K) sample temperature. After staying at approximately 1400°C for 2 hours, the temperature drops at a rate of 20°C/min.
However, the normal curves (5th and 6th species) used in the prediction were continued until they reached zero ppm SO2.

Temperatures from FactSage 6.0 thermodynamic modelling and pure salts decomposition were used as guides in the species identification. Presented in Table 6-3 is the identification of the possible active species in the fly ash that capture sulfur for fly ash sample A-Oxy. From the table, it can be noted that the mean temperatures ± standard deviations are quite close to the predicted values from thermodynamics and pure salt decomposition experiments. With the aid of FactSage 6.0 and the pure salt experiments, the predicted active species responsible for sulfur capture and retention are Fe (III), Al, Mg, K, Na and Ca, in the order of increasing decomposition temperatures.

Table 6-3. Peak identification based on the normal distribution.

<table>
<thead>
<tr>
<th>Possible Sulfate Species</th>
<th>Species 1</th>
<th>Species 2</th>
<th>Species 3</th>
<th>Species 4</th>
<th>Species 5</th>
<th>Species 6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe2(SO4)3</td>
<td>Al2(SO4)3</td>
<td>MgSO4</td>
<td>K2SO4</td>
<td>Na2SO4</td>
<td>CaSO4</td>
</tr>
<tr>
<td>% in Ash (%)</td>
<td>10%</td>
<td>11%</td>
<td>11%</td>
<td>45%</td>
<td>4%</td>
<td>19%</td>
</tr>
<tr>
<td>Mean T (°C)</td>
<td>575</td>
<td>660</td>
<td>810</td>
<td>940</td>
<td>1400</td>
<td>1450</td>
</tr>
<tr>
<td>Std. Dev (±°C)</td>
<td>40</td>
<td>60</td>
<td>50</td>
<td>52</td>
<td>38</td>
<td>40</td>
</tr>
</tbody>
</table>

Figure 6-8. Normal Distribution Modelling to Identify Active Species for Sulfur Capture, Fly Ash A-Oxy.
6.6.2 Total Sulfur in Fly Ash: the Eschka Method

Table 6-4 presents the mass balance of sulfur by comparing the sulphur released from the ash samples during heating by the Ash Decomposition method used in the experiment and the total sulfur in samples determined by the Eschka method as per the Australian Standards [116] and Mott et al.[114]. In order to obtain the amount of sulfur in the decomposition column, the areas under the curves from the decomposition experiments (Figure 6-4) were calculated by integration. These values were then used to estimate sulfur released from ash upon heating as mg S/g FA sample and % fuel S captured by ash (as presented in Table 6-4).

Eschka results, which measure total sulfur in a given sample, gave higher sulfur than the ones from the ash decomposition results. This may be due to the slagging of the fly ash at temperatures which may have caused some of the sulfur to not be released due to encapsulation in the slag and alumino-silicates present in the fly ash [134, 137] as discussed in the previous section.

<table>
<thead>
<tr>
<th>Fly Ash Sample</th>
<th>Sulfur Content mg S/g FA</th>
<th>Decomposition Total</th>
<th>Eschka Coal sulfur % fuel S captured by Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition</td>
<td>Total % of ash S from decomposition</td>
<td>% fuel S captured by Ash</td>
<td></td>
</tr>
<tr>
<td>A-Air</td>
<td>0.85</td>
<td>1.71</td>
<td>50%</td>
</tr>
<tr>
<td>A-Oxy</td>
<td>1.67</td>
<td>2.00</td>
<td>83%</td>
</tr>
<tr>
<td>B-Air</td>
<td>0.48</td>
<td>1.29</td>
<td>38%</td>
</tr>
<tr>
<td>B-Oxy</td>
<td>1.09</td>
<td>1.59</td>
<td>68%</td>
</tr>
<tr>
<td>C-Air</td>
<td>1.65</td>
<td>4.21</td>
<td>39%</td>
</tr>
<tr>
<td>C-Oxy</td>
<td>4.05</td>
<td>4.95</td>
<td>82%</td>
</tr>
</tbody>
</table>
Sulfur XRF data, *i.e.* SO$_3$, was not used in the calculations to represent sulfur species in the ash as some of the sulfur species may be lost during the fusion and preparation of the XRF sample at around 700°C, where as shown in Figure 6-4, the first peak of sulfur evolution occurs between 500°C and 700°C.

From Table 6-4 there is a significant difference between the sulfur coming from decomposition experiments, *i.e.* ‘decomposable’ sulfur species which could be released upon heating, and the total sulfur which is a combination of both decomposable sulfur and sulfur which remained in the fly ash. Oxy ash gives 2-3 times greater sulfur than Air from decomposition whereas from the Total sulphur results it only contains 17% to 23% more sulphur. This significant finding requires further study.

### 6.6.3 Sulfur Capture by Fly Ash

Calcium is known to be a very active species that capture SO$_2$ in power plants; it plays a significant role in the sulfur retention in the ash. It has also been found that among other AAEMs, Calcium is the most effective species at retaining sulfur after deposition onto heat transfer surfaces in the cooler regions of the combustion system, *e.g.* economizer [41, 133, 134]. This is vital especially in the cooler zone where the fly ash is in contact with the flue gas.

The Ca/S molar ratio is one of the main characteristics governing sulfur capture in fly ash [11, 66, 134]. The effects of Ca and AAEMs content were plotted against the total sulfur of the fly ash as per Eschka method (Figure 6-9 and 6-10). Fly ash A and B has similar molar amounts of calcium and they were found to have captured similar amounts of sulfur. Fly ash C on the other hand has the highest calcium content and was found to have the highest S retention among the three fly ash samples tested (See Table 6-4). In oxy-fuel, the flue gas is recycled through the boiler raising the sulfur content in the furnace hence the effect of Ca and AAEMs on the sulfur content of the ash was not compared to the coal S content but rather their molar percentages.
Figure 6-9. Calcium Oxide content versus the amount of sulfur present in the fly ash (determined by Eschka).

Figure 6-10 showing the relationship between AAEMs versus capture established an increasing linear trend in sulfur in fly ash as the AAEMs content increased. It can also be noticed that from both Figures 6-9 and 6-10, the amount of sulfur (as determined by Eschka) from oxy is more compared to air (5th column, Table 6-4), the plots show that the amount of sulfur captured is more influenced by the amount of alkali and alkaline earth metal oxides (Ca, Mg, Na and K) than the mode of firing although it can be viewed that in all oxy-fuel cases, the amount of sulfur captured is slightly higher.

The amount of sulfur in the fly ash is also plotted against the amount of sulfur-to-ash in the original coal in Figure 6-11. It can be observed that for fly ash B, the amount of sulfur is lower than in fly ash ‘A’ even if the S/Ash ratio is higher, an increasing linear trend was not observed. It should however be noted that the Ca and other AAEMs content of A is greater than that of B. This highlights the importance of all basic oxides in the ash collecting sulfur, while other coal-specific factors, i.e. coal particle size, the way the sulfur, alkali and alkaline earth metals are bound, the amount of other basic oxides in the ash, the amount of aluminosilicates that could encapsulate the sulfur species, the heating value of the coal that directly impacts combustion temperature, and changes in the chemistry during the change of mode Air to Oxy-fuel may play key role in sulfur capture and retention of the fly ash.
Figure 6-10. Alkali and Alkaline Earth Metal (AAEM) Oxide content versus the amount of sulfur present in the fly ash (determined by Eschka).

Figure 6-11. Amount of sulfur in ash (by Eschka) versus the ratio of sulfur-to-ash in coal.
6.7 CHAPTER SUMMARY AND CONCLUSIONS

A series of experiments were undertaken to investigate the sulfur capture behaviour of fly ash from air and oxy-fuel firing experiments simulating flue gas recycling of three Australian coals. Thermally evolved gas analysis under N₂ was also employed during the decomposition of the fly ash at atmospheric pressure. The results indicate that there is greater sulfur capture by the fly ash in oxy-fuel combustion.

(1) The particle size distribution (PSD) of the fly ash is not found to be a function of the mode of firing, Air firing versus Oxy-fuel firing, but was mostly coal specific. Nor did the bulk ash chemistry from XRD and XRF differ between Air and Oxy fly ash samples. However, the effect of PSD of fly ash, i.e. size segregated ash, on sulfur capture is recommended for future studies.

(2) The extent of sulfur species released upon heating the Oxy fly ash is 2 to 3 times greater than their Air condition counterparts. Three sets of peaks were observed during the fly ash heating experiments.
   a. 400°C-800°C: First set of peaks were evident in both Air and Oxy,
   b. 800°C-1100°C: Second set of peaks are most evident for Oxy fly ash,
   c. >1300°C: Third set of peaks.

These peaks from ash decomposition are consistent with thermodynamic predictions. Oxy fly ash showed consistently higher amounts of SO₂ capture in the second set of peaks.

(3) The Eschka Method was used for total ash sulfur determination. The amount of decomposable sulfur evolved that was released upon heating was found to vary from 38% to 83% of the ash sulfur whereas the Eschka sulfur for oxy fly ash is only 17% to 23% higher than the air fly ash.

(4) The amount of basic oxides, i.e. Ca, Mg, Na, K, was found to have a more significant effect on the capture of sulfur in the fly ash than the differences due to mode of firing.
7 DIFFERENCES BETWEEN THE HIGH TEMPERATURE HOMOGENEOUS AND FLY ASH CATALYTIC CONVERSIONS OF SO₂ TO SO₃ FROM AIR AND OXY-FUEL PULVERISED FUEL COMBUSTION

7.1 INTRODUCTION

During oxy-fuel combustion, the increased amount of O₂ and SO₂ has the potential of affecting the degree of oxidation of SO₂ to SO₃, which has been evidenced in Chapter 5 and are also reported in several studies [6, 7, 21]. However, limited literature exists on the conversion of SO₂ in the absence of combustibles. Spörl, et al. [138] noted that the ratios between heterogeneous and homogeneous SO₃ formation are still vague. Fleig, et al. [64], Jorgensen, et al. [86] and Cullis and Mulcahy [60] stressed that even though photochemical oxidation of SO₂ had been studied in the past, there is limited convincing evidence of an uncatalysed homogeneous reaction at temperatures below 900°C. However according to Cullis and Mulcahy [60] and Rees, et al. [120], oxidation of SO₂ to SO₃ is rather difficult but it can be achieved catalytically.

Chapter 5 concluded that with similar residence times SO₂ to SO₃ conversions were between 0.5 and 3% for coals A, B and C, with slightly higher conversions observed during oxy-fuel firing. SO₃ was also shown to be efficiently captured by the bag filter ash. On the other hand, apart from the gaseous components being around 4 times higher in oxy-fuel, dust and ash loading is also said to be higher than conventional air firing due to the reduced flow [43, 45]. Chapter 6 showed that higher sulfur capture was observed in fly ash coming from oxy-fuel firing. It has been stated that fly ash can either capture SO₂ to form basic sulfates
or can act as a catalyst [39, 66, 86] for SO\(_2\) to form SO\(_3\) even at temperatures as low as 400°C [60, 139]. The presence of SO\(_3\) is significant in power plants because increasing amounts of SO\(_3\) in the flue gas increases the acid dew point (ADP) and this dictates the extent of flue gas cleaning [16]. Therefore, the aim of this chapter is to focus on understanding the mechanisms of conversion of SO\(_2\) to SO\(_3\) as a function of SO\(_2\), O\(_2\) and H\(_2\)O in post-flame conditions in the absence of combustibles. The extent of catalytic conversion due to fly ash was also investigated.

### 7.2 SECTION OBJECTIVES

The main objective of this chapter is to understand and evaluate the mechanism of SO\(_3\) production by conducting homogeneous experiments and heterogeneous experiments using fly ash derived from air and oxy-fuel combustion performed at the 20 kW\(_{th}\) once-through furnace of the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Germany [17, 21], outlined in Chapter 5.

In order to carry out the general objective of the study, the following specific objectives were established:

1) To carry out homogeneous gas phase experiments as a function of residence time, oxidant concentrations ([SO\(_2\)], [O\(_2\)], [H\(_2\)O]), and reaction temperature to determine the impacts of different post flame conditions on SO\(_2\) to SO\(_3\) conversion.

2) To quantify SO\(_3\) production by applying the principles of controlled condensation method.

3) To carry out heterogeneous experiments with the presence of fly ash to study the extent of catalytic effect brought about on the SO\(_2\) to SO\(_3\) conversion.
7.3 PRELIMINARY CONSIDERATIONS

The section is divided into two major parts, the homogeneous and the heterogeneous conversions. In the homogeneous conversion experiments, the quartz tube reactor as discussed in Section 4.3.2 was empty apart from the oxidant gases consisting of SO$_2$, O$_2$, H$_2$O vapour and N$_2$/CO$_2$. The condenser section to account for SO$_3$ as H$_2$SO$_4$ consisted of a quartz tube containing quartz wool and maintained at temperature with cooling water.

Prior to the experiments, several preliminary tests and thermodynamic models were first considered to aid in selecting values for the parameters ([SO$_2$], [O$_2$], [H$_2$O], flowrate, temperature) in the homogeneous conversion experiments. FactSage 6.0 was used to model reactions between SO$_2$, O$_2$ and H$_2$O. Chapter 2 has discussed that SO$_2$ is the thermodynamically favoured species at temperatures greater than 900°C while SO$_3$ is favoured at lower temperatures with a maximum conversion at 500°C. The principal mechanisms for SO$_3$ production in combustion systems are:

\[
SO_2 + O_2 \rightleftharpoons SO_3 + O \quad \text{Reaction 7-1}
\]

\[
SO_2 + O(+M) \rightleftharpoons SO_3(+M) \quad \text{Reaction 7-2}
\]

where M is a third body and with Reaction 7-2 occurring at flame temperatures. Burdett et al. [65] stated that unless there is a high concentration of O atoms present, the concentration is not high enough to facilitate SO$_3$ production via Reaction 7-2. Hence, this section will only concentrate its investigation on Reaction 7-1 for SO$_3$ production.

Figure 7-1 presents the thermodynamic modelling result on the effect of increasing [SO$_2$] in the oxidant on the SO$_2$-SO$_3$-H$_2$SO$_4$ equilibria. It can be seen that with increasing amounts of [SO$_2$] to simulate, medium – medium-high to high sulfur concentrations found in power plants, no notable effect on the equilibrium between SO$_2$ and SO$_3$ was observed; i.e. intersections between SO$_3$ and SO$_2$ lie on the same temperature, as well as between H$_2$SO$_4$ and SO$_3$. However, even if SO$_3$ is found to be maximum at 500°C kinetics of SO$_2$ to SO$_3$ is expected to be slower as discussed in Chapter 2.
Figure 7-1. FactSage 6.0 thermodynamic model on the effects of variable SO$_2$ concentration on the SO$_2$-SO$_3$-H$_2$SO$_4$ equilibria. Model inputs: [SO$_2$] = 500 – 2000 ppm, [O$_2$] = 3% vol., [H$_2$O] = 3% vol., balance N$_2$. Temperature range 0 – 1000 °C.

The effect of oxygen concentration is shown in Figure 7-2; it can be inferred that the increase in oxygen concentration from 1 to 10% vol. shifts the 50% equilibrium conversion between SO$_2$ and SO$_3$ from about 600°C to 700°C. On the other hand the equilibrium between SO$_3$ and H$_2$SO$_4$ remained the same. Lastly, the effect of H$_2$O in the system was investigated and it can be seen from Figure 7-3 that the equilibrium between H$_2$SO$_4$ (g) and H$_2$SO$_4$ (l) was not affected. However, what is interesting is that as the H$_2$O is increased, the equilibrium conversion of SO$_3$ to H$_2$SO$_4$ was shifted to a higher temperature. This is noteworthy since according to discussions in Chapter 2, H$_2$O in the system reacts readily with SO$_3$ and that the presence of higher H$_2$O increases the ADP of the system. This instance of shifting H$_2$SO$_4$ (l) temperature is not evident in this thermodynamic modelling.
Figure 7-2. FactSage 6.0 thermodynamic model on the effects of variable O₂ concentration on the SO₂-SO₃-H₂SO₄ equilibria. Model inputs: [SO₂] = 1000 ppm, [O₂] = 1% - 10% vol., [H₂O] = 3% vol., balance N₂. Temperature range 0 – 1000 °C.

Figure 7-3. FactSage 6.0 thermodynamic model on the effects of variable H₂O concentration on the SO₂-SO₃-H₂SO₄ equilibria. Model inputs: [SO₂] = 1000 ppm, [O₂] = 3% vol., [H₂O] = 1% - 10% vol., balance N₂. Temperature range 0 – 1000 °C.
From the preliminary experiments and thermodynamic calculations, [SO$_2$], [O$_2$] and [H$_2$O] were found to have effects on the SO$_2$-SO$_3$-H$_2$SO$_4$ equilibria. This was then investigated in the succeeding sections by observing if the kinetics and thermodynamics agree with each other. Results of other preliminary experiments and the experimental design are presented in Chapter 4.

### 7.4 HOMOGENEOUS CONVERSION

Experiments with different flue gas volumetric flowrates and flue gas impurity concentrations (SO$_2$, O$_2$ and H$_2$O vapour) were investigated and compared with an existing kinetic model from the literature. Data and results for this set of Experiments are presented in Appendix B.

#### 7.4.1 Effect of Varying Residence Times

Experiments with varying gas velocities were performed in order to obtain an insight into the effect of residence time at the desired temperature on the system. Gas velocities of 0.5 – 1.5 L/min (dry; STP) were utilised to obtain residence times of 0.3 – 0.9 seconds in the isothermal zone in the quartz tube reactor as previously presented in the Experimental Section 4.2.3. Figure 7-4 presents the effect of residence time on SO$_2$ conversion to SO$_3$.

The experimental results were then compared to a previous study completed by Flint and Lindsay [85] who used a minimum residence time of 1 second and generated an SO$_3$/SO$_2$ conversion of about 0.4%. The experimental results were also compared to a kinetic model produced by Burdett, et al. [65]. The previous kinetic studies [65] were conducted at a temperature range from 900 K – 1350 K with the assumptions that:

1. The operative reaction is

\[ SO_2 + O_2 \rightleftharpoons SO_3 + O \]  

\textit{Reaction 7-3}
(2) The equilibrium concentration of SO$_3$ is magnitudes greater than the measured concentrations hence the reverse reaction of SO$_3$ to SO$_2$ in Reaction 7-1 is neglected.

(3) The temperature dependence of the rate of reaction is given by the Arrhenius equation: $k_1 = Ae^{(-B/T)}$.

With these assumptions, the Burdett’s global kinetic model is given by Equation (7-1):

$$\frac{d[SO_3]}{dt} = \frac{k_1}{RT} [SO_2][O_2] = \frac{A[SO_2][O_2]}{RT} e^{(-B/T)} \tag{7-1}$$

where:

$A = 2.6 \, (\pm 1.3) \times 10^{12} \, \text{mol}^{-1} \, \text{cm}^{3} \, \text{s}^{-1}$

$B = 23000 \pm 1200 \, \text{K} \, (\text{leading to } B/R = 190 \pm 10 \, \text{kJ mol}^{-1})$

[SO$_2$], [O$_2$] and [SO$_3$] are partial pressures.

Increasing SO$_3$/SO$_2$ conversions were observed as the residence time in the reactor was increased. It could be noted that at about 0.3 seconds of residence time, there was almost negligible conversion observed (average 0.03%). On the other hand, at ~0.9 seconds, conversions from 0.14% to 0.36% were observed (average 0.24%). Longer residence times were not observed as they are difficult to achieve due to limitations in equipment. Conversions were calculated by using the formula given:

$$\text{% Conversion} = \frac{\text{moles SO}_3}{\text{moles SO}_2} \times 100 \tag{7-2}$$
Effect of Residence Time on the Homogeneous Conversion of SO\textsubscript{2} to SO\textsubscript{3}. Inlet Gas Mixture: SO\textsubscript{2} = 1000 ppm, O\textsubscript{2} = 5% vol., H\textsubscript{2}O = 3 % vol., balance N\textsubscript{2}, at Temp = 900°C (Flint and Lindsay [85] and Burdett, et al. [65]).

Figure 7-4. Effect of residence time on the homogeneous conversion of SO\textsubscript{2} to SO\textsubscript{3}. Inlet Gas Mixture: SO\textsubscript{2} = 1000 ppm, O\textsubscript{2} = 5% vol., H\textsubscript{2}O = 3 % vol., balance N\textsubscript{2}, at Temp = 900°C (Flint and Lindsay [85] and Burdett, et al. [65]).

7.4.2 Effect of Impurity Concentrations (SO\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O)

7.4.2.1 Effect of SO\textsubscript{2} Concentration

The effect of input SO\textsubscript{2} concentration on the SO\textsubscript{3} output and SO\textsubscript{2} to SO\textsubscript{3} conversion is presented in Figures 7-5 (a) and (b). As anticipated, SO\textsubscript{3} concentrations were higher when the input SO\textsubscript{2} partial pressure is increased, as shown in Figure 7-5 (a). Plotted in the figure is the kinetic prediction based on Burdett’s model together with the experimental data. Grey lines were also drawn as the range for ±35% of the predicted values. It can be seen that the data produced a linear trend but with a gradient that is much smaller than the kinetic model. The experiment results fall within ±35% of the predicted values. Based on the trend of the data a higher disparity would be expected with increasing SO\textsubscript{2} input, i.e. 2000 ppm onwards.

Average conversions ranged from 0.48% for 500 ppm SO\textsubscript{2} input, 0.33% for 1000 ppm SO\textsubscript{2}, 0.24% for 1500 ppm SO\textsubscript{2} and 0.25% for 2000 ppm SO\textsubscript{2} (Figure 7-5 (b)). It can be seen that as the input SO\textsubscript{2} is increased, a decreasing conversion is observed. This behaviour was also reported by other investigators [64, 82, 83].
Schwaemmle, et al. [83] stated that conversions at lower concentrations start high but decrease as the input SO\textsubscript{2} concentration becomes higher giving a pseudo-first order reaction. Supporting the claim, Svachula, et al. [82] stated that an apparent kinetic order in SO\textsubscript{2} is higher than 1 for low concentrations (0 – 200 ppm) and decreases to a fractional order (i.e. < 1) at higher SO\textsubscript{2} inlet concentrations. Conversely, other studies [82, 84, 140] indicated that a first order dependence may provide a reasonable approximation between 0 – 1000 ppm SO\textsubscript{2}. With this premise, the use of Burdett’s first order kinetics with respect to SO\textsubscript{2} is compared here with the data.

**Figure 7-5.** Effect of input SO\textsubscript{2} concentration on (a) the output SO\textsubscript{3} concentration (b) the conversion of SO\textsubscript{2} to SO\textsubscript{3}. Flowrate = 0.5 L/min (298K, 1 atm), Inlet Gas Mixture for the experiment: SO\textsubscript{2} = variable ppm, O\textsubscript{2} = 5% vol., H\textsubscript{2}O = 3% vol., balance N\textsubscript{2} at Temperature = 900°C. The grey dots in the figures representing the highest and lowest values obtained in the experiments.
7.4.2.2 Effect of \(O_2\) Concentration

Experiments with varying \(O_2\) concentration were performed to investigate the effect of \(O_2\) on the homogeneous, uncatalysed oxidation of \(SO_2\). Bayless et al. [88] stated that previous studies established that at least 1\% excess \(O_2\) is needed for the conversion of \(SO_2\) to \(SO_3\). Typically, coal fired plants use between 3\% and 5\% excess \(O_2\) [88]. In this study, 3\%, 5\%, and 10\% were used as the \(O_2\) levels. The results are plotted in Figures 7-6 (a) and 7-6 (b).

![Figure 7-6. Effect of input \(O_2\) concentration on (a) the output \(SO_3\) concentration (b) the conversion of \(SO_2\) to \(SO_3\). Flowrate = 0.5 L/min (298K, 1 atm), Inlet Gas Mixture for the experiment: \(SO_2 = 1000\) ppm, \(O_2 = \) variable \% vol., \(H_2O = 3\%\) vol., balance \(N_2\) at Temperature = 900°C. The grey dots in the figures representing the highest and lowest values obtained in the experiments.](image)
Similar to the effects of SO$_2$, an increasing O$_2$ input gives an increasing SO$_3$ output. However, the SO$_3$ output data is similar to the kinetic prediction at lower O$_2$ of 3% but falls to 40% below the predicted value at an oxygen concentration of 10%. The conversion at varying O$_2$ input concentrations gave a similar trend. This behaviour could suggest that the effect of input O$_2$ concentration on the SO$_3$ production rate is of fractional order and not first order with respect to O$_2$ as predicted by Burdett, et al. [65] Although Glueck and Kenney [141] proved independence of the SO$_3$ production on O$_2$ concentration, Svachula, et al. [82] and Forzatti [84] stated that a dependence on O$_2$ only manifests when the concentrations of O$_2$ and SO$_2$ are comparable. Therefore similar to SO$_2$, a first order approximation as stated by Burdett, et al. [65] for ease of calculations would deem justifiable.

7.4.2.3 Effect of H$_2$O Concentration

To evaluate the effect of moisture content on the conversion of SO$_2$ to SO$_3$, measurements between 3% vol. and 9% vol. were completed. Conversions at 0% vol. moisture (dry gas) was not performed due to the need to condense the sulfuric acid aerosols for the quantification of SO$_3$ formed for CCM. It can be seen in Figures 7-7 (a) and 7-7 (b) that increasing moisture concentration from 3% vol. to 9% vol. did not have much effect on the output and conversion of SO$_2$ to SO$_3$.

The effect of changing H$_2$O concentration is not as pronounced as the effects of SO$_2$ and O$_2$ concentrations. Average conversions of 0.36% to 0.39% have been observed. This suggests that the conversion of SO$_2$ to SO$_3$ is independent of the water content being studied (between 3% and 9% vol.). Although Forzatti [84] stated that the addition of water inhibits SO$_2$ conversion at low concentrations but levels off at above 5% v/v water content. However, the absence of the effect of H$_2$O concentration in the homogeneous oxidation of SO$_2$ was also evidenced in the works of Burdett et al.[65], Schwaemmle, et al. [83], Svachula, et al. [82].
7.4.3 Effect of Temperature: Conversions at Temperatures from 400°C to 1000°C

The temperature dependence of the homogeneous oxidation of SO₂ to SO₃ was investigated at 1000 ppm SO₂, 5% vol. O₂, 3% vol. H₂O, balance N₂. The effect of temperature is presented in Figure 7-8. The figure shows the SO₂ to SO₃ conversion data and the thermodynamic model, along with Burdett’s [65] global kinetic model and its associated range of error (the upper and lower light dashed lines) as shown in the variability of the pre-exponential factor presented in Equation 2-1. It can be seen that thermodynamically the maximum SO₃ is expected at about 500°C and as the temperature
is increased to 900°C and 1000°C, the SO$_3$ decreased to about 6.75% and 3.21%, respectively.

**Figure 7-8.** Homogeneous Conversion of SO$_2$ to SO$_3$ at different temperatures. Flowrate = 0.5 L/min (298K, 1 atm), Inlet Gas Mixture for the experiment: SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., balance N$_2$. Burdett, *et al.* [65].

In summary, a positive correlation was found between SO$_3$/SO$_2$ conversion and temperature. Increasing conversions from 0.04 to 0.77% were observed as the temperature was increased from 400 to 1000°C during the post-flame homogeneous conversion experiments. Temperatures of around 900°C or greater are required to obtain an observable conversion with the available residence times provided by the uncatalysed homogeneous reactor. This is consistent with the findings of Bayless, *et al.* [88] and Burdett, *et al.* [65].
7.5 FLY ASH CATALYSED CONVERSION

Equilibrium calculations from 400°C to 1000°C in Chapter 2 show that the maximum conversion of SO$_2$ to SO$_3$ happens at around 500°C and that the equilibrium shifts to the formation of SO$_2$ at higher temperatures, approximately 10% at 900°C [66]. Whilst SO$_3$ formation is favoured at lower temperatures, the kinetics is relatively slow and is said to be ‘frozen’ at low temperatures [6, 66, 139]. Literature suggests that it is in this region where catalysis by iron oxides in the fly ash could enhance rapid formation of SO$_3$ [16, 66].

In this regard, the effect of temperature on the catalytic conversion of SO$_2$ to SO$_3$ in the presence of fly ash supported by quartz wool was investigated and is presented in Figure 7-9. To simulate air and oxy-fuel flue gas compositions, the concentrations of the gas mixtures used in this study were:

- **Air**: SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., balance N$_2$;
- **Oxy**: SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., CO$_2$ = 85% vol., balance N$_2$.

The results of this study were plotted against a previous study by Marier and Dibbs [66]. Fly ash A derived from air firing is the sample used for this plot. From Figure 7-9, it can be seen that as with homogeneous conversion (Figure 7-8), temperature has a significant impact on the heterogeneous conversion of SO$_2$ to SO$_3$ with fly ash as catalyst. Marier and Dibbs [66] found that conversion is negligible at 500°C and increases significantly at 700°C with SO$_3$/SO$_2$ conversion of 27% before falling to about 16% between 800 and 900°C. Similarly, the post-flame experiments in this study produced negligible SO$_3$/SO$_2$ conversions at temperatures below 500°C. A maximum conversion of 1.7% at 700°C was obtained before the conversion decreased to 1.4% at 900°C and then increasing again to about 1.6% at 1000°C. It is however noteworthy that the concentrations used by Marier and Dibbs [66] were roughly 10 times greater than the concentrations typically found in the flue gas and that the residence time in their reactor was 1.8 seconds as opposed to ~1 second in this study. Nevertheless, the temperature dependence trend found in this study was similar to that of Marier and Dibbs [66].
The effect of varying flue gas concentrations, *i.e.* gas concentrations equivalent to flue gas concentrations in air and oxy-fuel combustion, was also looked into. Changing the gas composition from O$_2$/N$_2$ to O$_2$/CO$_2$ to simulate air and oxy-fuel flue gas conditions did not have a significant effect on the conversion. Hence, for post-flame conditions, conversion of SO$_2$ to SO$_3$ is not a function of the mode of firing but of temperature and presence of catalyst. It could be observed from Figure 7-9 that the overall SO$_3$/SO$_2$ conversions at 700°C and 1000°C are similar; however, it should be noted that homogeneous and fly ash catalysis have combined effects on the overall conversions.

![Figure 7-9. Fly Ash Catalytic Conversion of SO$_2$ to SO$_3$ at different temperatures. Fly ash used: A – Air. Flowrate = 0.5 L/min (298 K, 1 atm). Inlet Gas Mixture for the experiment: (Air) SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., balance N$_2$. (Oxy) SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., CO$_2$ = 85% vol., balance N$_2$. Marier and Dibbs Settings: Residence time = 1.8 sec, flow rate = 185 cc/min, Gas composition: H$_2$O = 18.9% vol, O$_2$ = 32.4% vol., SO$_2$ = 8.4% vol., N$_2$ = 40.4% vol. [66].](image-url)
7.5.1 Contribution of Fly Ash

Figure 7-10 presents the contribution of homogeneous and catalytic effects on the overall conversions at different temperatures. The overall conversion at 400°C started at 0.04% and peaked at 1.78% at 700°C then decreased to 1.31% at 900°C similar to the trend given by Marier and Dibbs [66]. The experimental run tested the catalytic effect of fly ash A – Air from 400°C to 900°C (Figure 7-9). However, extending the test to 1000°C revealed an increase in average conversion to roughly 1.79% which is similar to the conversion obtained at 700°C. It is noteworthy that although similar total conversions were observed at 700°C and 1000°C, total conversions consist of both homogeneous and catalytic conversions. Table 7-1 shows that the conversion which could be attributed to fly ash, i.e. catalytic, is negligible at 400°C and is greatest at 700°C accounting for about 95% (3rd bar) of the total conversion (approximately 1.78%) of SO$_2$ to SO$_3$. With further increase in temperature, the catalytic component drops to 57% (5th bar) of the total conversion at 1000°C.

Figure 7-10. Temperature effects on the catalytic and homogeneous conversions of SO$_2$ to SO$_3$ using Fly Ash A – Air.
Table 7-1. Homogeneous, catalytic and total conversions of SO$_2$ to SO$_3$ from 400°C to 1000°C using Fly Ash A - Air.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>%</th>
<th>Homog.</th>
<th>Total</th>
<th>Catalytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.041</td>
<td>1</td>
<td>0.042</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.062</td>
<td>19</td>
<td>0.077</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>0.098</td>
<td>95</td>
<td>1.784</td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.361</td>
<td>72</td>
<td>1.308</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>0.773</td>
<td>57</td>
<td>1.791</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.5.2 Effect of Iron Oxide in fly ash on the Conversion of SO$_2$ to SO$_3$

Iron Oxide, Fe$_2$O$_3$, which is naturally occurring in fly ash of coal-fired boilers is known to catalyse the formation of SO$_2$ to SO$_3$ [39, 66, 120] via Reaction 7-4:

$$SO_2 + \frac{1}{2}O_2 \xrightarrow{Fe_2O_3\text{ catalyst}} SO_3$$

Reaction 7-4

In order to observe the effect of Fe$_2$O$_3$ content of the fly ash on the conversion of SO$_2$ to SO$_3$, fly ash samples A, B and C from the three coals fired at different modes were investigated and used in the study. Plotting the overall SO$_3$/SO$_2$ conversions against the Fe$_2$O$_3$ content (% weight) (Table 7-2) of the fly ash at 1000 ppm SO$_2$, 5% vol. O$_2$, 3% vol. H$_2$O conducted at 700°C revealed that a general linear trend can be observed (Figure 7-11). A previous study [66] using roughly 10 times higher gas concentrations showed a linear trend in their conversions using fly ash with Fe$_2$O$_3$ content ranging between 7 and 25 %w.

Table 7-2. Fe$_2$O$_3$ content (by XRF) of the fly ash used in this chapter.

<table>
<thead>
<tr>
<th>Fly Ash</th>
<th>Fe$_2$O$_3$ Content (% weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air derived</td>
</tr>
<tr>
<td>A</td>
<td>6.55</td>
</tr>
<tr>
<td>B</td>
<td>1.62</td>
</tr>
<tr>
<td>C</td>
<td>8.55</td>
</tr>
</tbody>
</table>
It can be observed from the plot that even at lower Fe$_2$O$_3$ contents typically found in the Australian coals and with 10 times lower gas concentrations, a linear trend was obtained (Figure 7-11). The hollow triangle markers (Δ) in the plot denote fly ash derived from air firing and the shaded triangle markers denote fly ash obtained from oxy-fuel firing. It could be said that based on the plot, the catalytic conversion of SO$_2$ to SO$_3$ is a function of the iron oxide content of the fly ash and that how the fly ash was derived, *i.e.* air-derived ash or oxy-fuel derived ash, did not seem to have any effects on the conversion. It is interesting though that although other coal-ash factors such as surface area, porosity, form of iron oxides could play a vital role in the catalysis, a strong linear correlation was obtained between Fe$_2$O$_3$ and conversion. On the other hand, the effect of varying oxide concentrations (one species at a time) as well as residence time on the conversion should be considered as part of future studies.

**Figure 7-11.** Effect of the amount of Fe$_2$O$_3$ (% weight) in fly ash on the catalytic conversion of SO$_2$ to SO$_3$. Inlet Gas Mixture for the experiment: SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., balance N$_2$. Temperature = 700°C. Marier and Dibbs Settings: Residence time = 1.8 sec, flow rate: 185 cc/min, Gas composition: H$_2$O = 18.9% vol., O$_2$ = 32.4% vol., SO$_2$ = 8.4% vol., N$_2$ = 40.4% vol. [66].
7.5.3  Effect of Metal Oxides in the fly ash on the Conversion of SO$_2$ to SO$_3$

In the preceding section, it was shown that the amount (% weight) of Fe$_2$O$_3$ in the fly ash has a significant effect on the catalysed conversion of SO$_2$ to SO$_3$. The individual effects of the other metal oxides (e.g. TiO$_2$) apart from Fe$_2$O$_3$ were investigated here for catalytic enhancement. Figures 7-12 (a) and (b) show individual correlations between SO$_3$/SO$_2$ conversion and the molar amounts of Fe$_2$O$_3$ and TiO$_2$, respectively. Molar percentages of the fly ash samples derived from air firing and oxy-fuel combustion completed in Chapter 5 are presented in Table 7-3. It shows that as the Fe$_2$O$_3$ content has a linear trend with SO$_3$/SO$_2$ conversion, the same is not true for TiO$_2$ where there is just a scatter (see Figure 7-12 (b)).

Table 7-3. Molar percentages of the metal oxide of the fly ash samples A, B and C used in this section.

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>Composition (% mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fly Ash A</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>24.01</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.01</td>
</tr>
<tr>
<td>CaO</td>
<td>1.25</td>
</tr>
<tr>
<td>MgO</td>
<td>1.35</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.17</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.40</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.90</td>
</tr>
</tbody>
</table>
Marier and Dibbs [66] and Jorgensen, et al. [86] stated that CaO, another metal oxide, can also be a potential catalyst for SO$_2$ to SO$_3$ conversions. With this, the effects of individual metal oxides (CaO, MgO, Na$_2$O and K$_2$O) as well as combined metal oxides were plotted against SO$_3$/SO$_2$ % conversions. The strength of the correlation was also worked out. Pearson’s product moment correlation coefficient (“r”) or simply known as correlation coefficient was used to provide an effective index of association between two variables, metal oxide content and conversion [142, 143]. The formula used to solve for “r” is presented in Equation (7-3):

---

**Figure 7-12.** Effect of the molar amounts (% mole) of (a) Fe$_2$O$_3$, (b) TiO$_2$ in fly ash on the catalytic conversion of SO$_2$ to SO$_3$. Inlet Gas Mixture for the experiment: SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., balance N$_2$, Temperature = 700°C.
Where:
\[ x = \text{tested variable} \]
\[ y = \text{response variable} \]
\[ r = \text{Pearson’s correlation coefficient} \]

Table 7-4 shows the results of the correlation calculations on the effects of metal oxides on the conversion of SO\(_2\) to SO\(_3\) using air-derived fly ash, oxy-fuel derived fly ash and combined results from air and oxy-derived ash. It can be noted that individually, air and oxy-fuel derived ash gave a very high positive correlation with 0.80 and ≈1.00 correlation coefficients and an overall score of 0.88 for Fe\(_2\)O\(_3\). On the other hand, TiO\(_2\) was seen to play minimal effects on the catalytic conversion (Figure 7-12 (b)) and gave a very weak overall correlation \( r = 0.11 \).

Table 7-4. Correlation table for the individual, combined and overall effects of metal oxides concentration (% mole) on SO\(_2\) to SO\(_3\) conversion.

<table>
<thead>
<tr>
<th>Metal Oxide (% mol.)</th>
<th>Correlation Coefficient</th>
<th>Air Fly Ash</th>
<th>Oxy Fly Ash</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_2)O(_3)</td>
<td></td>
<td>0.80</td>
<td>1.00</td>
<td><strong>0.88</strong></td>
</tr>
<tr>
<td>TiO(_2)</td>
<td></td>
<td>0.29</td>
<td>-0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>CaO</td>
<td></td>
<td>0.22</td>
<td>0.74</td>
<td><strong>0.43</strong></td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>0.23</td>
<td>0.84</td>
<td><strong>0.48</strong></td>
</tr>
<tr>
<td>Ca + Mg Oxides</td>
<td></td>
<td>0.23</td>
<td>0.77</td>
<td><strong>0.44</strong></td>
</tr>
<tr>
<td>Na(_2)O</td>
<td></td>
<td>0.09</td>
<td>0.59</td>
<td>0.29</td>
</tr>
<tr>
<td>K(_2)O</td>
<td></td>
<td>0.08</td>
<td>0.58</td>
<td>0.27</td>
</tr>
<tr>
<td>Na + K Oxides</td>
<td></td>
<td>0.09</td>
<td>0.59</td>
<td>0.28</td>
</tr>
<tr>
<td>AAEMs</td>
<td></td>
<td>0.20</td>
<td>0.74</td>
<td><strong>0.42</strong></td>
</tr>
</tbody>
</table>
Figures 7-13 (a) and 7-13 (b) show the individual effects of CaO and MgO on SO$_2$ to SO$_3$ conversion, respectively. It can be observed that for both CaO and MgO, air-derived fly ash gave a more scattered plot whilst the oxy-derived fly ash gave a more evident increasing trend. This was also justified when the r-value gave weak correlations for air FA (CaO = 0.22 and MgO = 0.23) and stronger linear correlations from both oxy FA (CaO = 0.74 and MgO = 0.84). The overall effect, regardless of whether air or oxy-derived gave a moderate correlation from both CaO (r = 0.43) and MgO (r = 0.48).

![Figure 7-13. Effect of the molar amounts (% mole) of (a) CaO and (b) MgO in fly ash on the catalytic conversion of SO$_2$ to SO$_3$. Inlet Gas Mixture for the experiment: SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., balance N$_2$, Temperature = 700°C.](image_url)

The effects of alkali metal oxides Na$_2$O and K$_2$O were also investigated (see Figures 7-14 (a) and 7-14 (b)). It can be seen that the plots for Na and K produced scattered data for both air and oxy-fuel derived fly ashes. When the correlations were
calculated, it revealed zero correlations from air-derived FA while moderately strong correlations from oxy-derived ash. However, when the overall effect of alkali oxides were correlated against the conversion, a weak correlation was obtained. This suggests that alkali (group I metal) oxides do not play a big role on the catalytic conversion of SO$_2$ to SO$_3$.

Figure 7-14. Effect of the molar amounts (% mole) of (a) Na$_2$O, (b) K$_2$O and (c) Alkali and Alkaline-Earth Metal Oxides in fly ash on the catalytic conversion of SO$_2$ to SO$_3$. Inlet Gas Mixture for the experiment: SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., balance N$_2$, Temperature = 700°C.
The overall effects of AAEM oxides (CaO + MgO + Na₂O + K₂O) were also tested and found that for air-derived FA, there was more scatter than for oxy-fuel derived FA (Figure 7-14 (c)). The correlation was also true where for air-derived FA, \( r = 0.20 \) whilst for oxy-fuel derived FA, \( r = 0.74 \) giving an overall \( r = 0.42 \), a moderate positive linear correlation between AAEM oxides and \( \text{SO}_2 \) to \( \text{SO}_3 \) conversion. Fleig, et al. [39] noted that production of \( \text{SO}_3 \) is favoured by fly ash containing catalytically active species, e.g. \( \text{Fe}_2\text{O}_3 \) and \( \text{V}_2\text{O}_5 \), on the other hand if the alkalinity of the fly ash is high, fly ash might capture \( \text{SO}_3 \). This occurrence is evident in Section 6.6.3 where an increasing overall amount of AAEM oxides increases the total amount of sulfur retained in the fly ash (Figure 6-10).

Due to the differences between the scatter behaviour in oxy-derived and air-derived ash, a plot is generated showing relationships between the conversions using air and oxy-fuel derived fly ash (Figure 7-15). Conversions utilising fly ashes A and B were found to lie on the one-to-one correspondence line denoting similar conversions. For fly ash C on the other hand, it can be noted that conversions using oxy-fuel derived fly ash gave slightly higher conversions, roughly around 30% higher than its air counterpart. In order to clarify the relationship between conversions and source of fly ash, a correlation between how the fly ash was derived, i.e. from Air firing or Oxy-fuel firing, was also calculated. In order to solve for the correlation coefficient, a score of “0” was assigned for fly ash derived from air-firing and a score of “1” was assigned for fly ash derived from oxy-fuel firing. Table 7-5 shows the correlation between \( \text{SO}_2 \) to \( \text{SO}_3 \) conversion and source of fly ash. With this, it can be inferred that although conversions using FA derived from oxy-fuel firing gave a more consistent linear trend than using FA from air-firing, the mode of firing where the fly ash were derived from and the \( \text{SO}_2 \rightarrow \text{SO}_3 \) conversion capability has a very weak to almost no correlation, \( r = 0.21 \).
Figure 7-15. Percentage SO3/SO2 conversions using Air and Oxy-derived Fly Ashes A, B and C.

Table 7-5. Correlation between SO2 to SO3 conversion and the mode of firing where the fly ash were derived.

<table>
<thead>
<tr>
<th>Source of FA</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.21</td>
</tr>
</tbody>
</table>

Overall, even with 0.5 grams of fly ash for every 30 L (STP) of oxidant gases, *i.e.* simulated flue gas, SO3 concentrations of 0.98 ppm SO3 and 17.84 ppm SO3 were obtained at 700°C for homogeneous and heterogeneous conversions, respectively. Therefore with 0.5 g of FA containing 6.55%w of Fe2O3 in the ash, a change in SO3 from 0.98 to 17.84 ppm at 3% vol. moisture and a contact time of 41 ms with the ash, is expected to change the ADP from 100°C to 130°C (*Figure 7-16*), a 30°C increase based on ZareNezhad’s [50] correlation (*Section 2.4.2.4*). It can also be viewed from the graph that in cases where water concentrations are higher, *i.e.* Oxy-fuel combustion with full flue gas recycling (30% vol. H2O), H2SO4 ADP could easily be higher by another 20 to 30°C compared to the one at 3% vol. H2O.
Figure 7-16. Estimated Acid Dew Point with and without fly ash. Acid dew points estimated using ZareNezhad ADP Correlation [50]. Input flowrate = 0.5 L/min (298 K, 1 atm), SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol, flue gas contact time with fly ash = 41 ms, using fly ash A – Air. Assumption of 30% vol. H$_2$O concentration was used for Oxy-fuel runs using full flue gas recycling.

Correlations were carried out for SO$_3$/SO$_2$ conversion versus metal oxide content and SO$_3$/SO$_2$ conversion versus the source of fly ash, i.e. air-fired or oxy-fuel fired. Based on the strength of correlations for the set of metal oxides tested, the order of catalytic activity is:

Fe$_2$O$_3$ > CaO, MgO > AAEM Oxides (combined) > Na$_2$O, K$_2$O > TiO$_2$

The presence of metal oxides definitely played a huge role in the extent of conversion of SO$_2$ to SO$_3$. On the other hand, the mode at which the fly ash was derived seemed to not play much effect on the extent of conversion.

7.6 CHAPTER SUMMARY AND CONCLUSIONS

The homogeneous (uncatalysed) and heterogeneous (catalysis by fly ash) conversions of SO$_2$ and O$_2$ to SO$_3$ in the absence of combustibles were investigated experimentally between 400°C and 1000°C using a quartz flow reactor.
Homogeneous (uncatalysed) oxidation of SO$_2$ to SO$_3$ was examined and compared with a kinetic model by Burdett et al. [65].

1) The effect of increasing SO$_2$ concentrations gave an apparent order in SO$_2$ of greater than 1 at low SO$_2$ concentrations, decreasing to a fractional order as the input concentration is increased.
2) O$_2$ concentration was found to have an influence on the oxidation of SO$_2$ at concentrations of 3% to 10% vol.
3) SO$_2$ oxidation was also found to be independent of H$_2$O vapour concentration in the flue gas.
4) Temperatures of at least 900°C are required for an observable conversion to occur for a residence time of ~1 s.

Heterogeneous (fly ash catalysed) conversions were found to be greatest at 700°C for the temperature range of 400°C – 1000°C accounting for 95% of the overall conversions.

1) Fly ash coming from different modes of firing, i.e. Air and Oxy-fuel gas atmospheres, was found to have no effect on the conversion of SO$_2$ to SO$_3$ when the concentration of SO$_2$ were the same.
2) The atmosphere associated with the mode of firing, i.e. predominantly N$_2$ or CO$_2$, had no impact on the conversion of SO$_2$ to SO$_3$.
3) The presence of Fe$_2$O$_3$ catalytically enhances conversion of SO$_2$ to SO$_3$.
4) Correlations showed that the order of catalytic activity for the oxides in the fly ash is: Fe$_2$O$_3$ > CaO, MgO > AAEM Oxides (combined) > Na$_2$O, K$_2$O > TiO$_2$

With greater SO$_2$, H$_2$O and ash loading during oxy-fuel, higher SO$_3$ and therefore an increased acid dew point are expected.
8 IMPACT OF SULFUR OXIDES ON MERCURY SPECIATION AND CAPTURE BY FLY ASH

8.1 INTRODUCTION

Chapter 5 has focused on the flue gas compositions and interactions between sulfur and mercury with fly ash for air and oxy-fuel combustion. Chapters 6 and 7 focused on the interactions between the increased SO\textsubscript{x} present in oxy-fuel flue gas and the fly ash generated during combustion. Fly ash either captures SO\textsubscript{x} components (Chapter 6) or promotes oxidation of SO\textsubscript{2} to SO\textsubscript{3} (Chapter 7). At higher SO\textsubscript{x} (oxy-fuel conditions), Chapter 6 has concluded that decomposable sulfur is 38% to 83% of the ash sulfur -- much higher than air-derived fly ash. Also at 700°C as the flue gas passes the convection zone, SO\textsubscript{2} to SO\textsubscript{3} oxidation from 0.10% (homogeneous) to 1.78% (catalytic, fly ash) was observed even with 41 ms flue gas contact with fly ash. It has been concluded that increased Hg\textsuperscript{tot} and Hg\textsuperscript{2+}/Hg\textsuperscript{tot} were observed when switching from air to oxy-fuel combustion. However a clear trend on Hg capture efficiency could not be established. SO\textsubscript{3} was also found to be effectively captured by the bag filter fly ash. Consequently, SO\textsubscript{2}/SO\textsubscript{3} are known to compete with Hg for active sites of adsorption on the fly ash [104, 122]. In this chapter, SO\textsubscript{2}/SO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4} and mercury interaction on fly ash will be discussed.

At the Callide Oxy-fuel Plant, the SO\textsubscript{x} and mercury-laden flue gas passes the bag filter and is expected to be partially captured by the unburned carbon (UBC) in the fly ash. As UBC in fly ash has always been correlated with Hg capture, several researchers [97, 109] have examined mechanisms of adsorption of Hg onto the UBC. The fly ash generated in Chapter 5 and used in Chapters 6, 7 and this Chapter contains very low unburned carbon (< 0.1%w [11, 17]), and that investigations will be focused on the competition between Hg\textsuperscript{0}/Hg\textsuperscript{2+}/Hg\textsuperscript{P} and SO\textsubscript{x} interaction with fly ash rather than the UBC. Therefore during oxy-
fuel combustion where concentrations of impurities are higher, competition, capture and speciation may be different.

8.2 SECTION OBJECTIVES

The general objective of this section is to evaluate the extents of competition between mercury and SO\textsubscript{x} capture by the inorganic portion of fly ash during pulverised coal combustion in oxy-fuel and air combustion conditions.

In order to carry out the above objective, the effects of the following parameters on the speciation and capture of Hg were investigated and correlations were carried out:

1) Effects of mercury (Hg\textsuperscript{0}) input concentration
2) Effects of varying SO\textsubscript{x} (SO\textsubscript{2}/SO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4}) inputs
3) Effects of water vapour (H\textsubscript{2}O) concentrations
4) Effects of bag filter temperature

Fly ash A was used in the conduct of this section of the thesis. Refer to Section 4.2.4, Figure 4-8 for the experimental setup.

8.3 RESULTS

The effects of input mercury concentration, SO\textsubscript{x} gases and bag filter temperature were tested for capture and speciation of Hg on fly ash. Table 8-1 shows the properties of the fly ash used in this study. Data and results are presented in Appendix C.

Table 8-1. Physical properties of fly ash A – Air used in the study. (Refer to Table 6-1 for the XRF analyses and Table 7-3 for the Metal Oxide molar composition of the said fly ash)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3} content (wt %, dry basis)</td>
<td>6.55</td>
</tr>
<tr>
<td>Unburned Carbon (wt %, dry basis)</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Mean diameter, d50 ((\mu\text{m}))</td>
<td>7.45</td>
</tr>
<tr>
<td>Initial Hg\textsuperscript{0} content (ng/g fly ash)</td>
<td>5.34</td>
</tr>
<tr>
<td>BET surface area (m\textsuperscript{2}/g of fly ash)</td>
<td>0.9455</td>
</tr>
</tbody>
</table>

Note: Fly ash A was the ones used by the Callide Oxy-fuel Power Plant and thus was chosen to be the test ash. Further testing utilising other fly ashes is recommended for future studies.
8.3.1 Effect of Mercury Concentration

The effects of increasing Hg\(^0\) vapour concentration was evaluated (Figure 8-1). It can be seen from the plot that the Hg\(^p\) captured by the fly ash associated with doubling the Hg\(^0\) input increases the amount of Hg\(^0\) which may have been converted to Hg\(^2+\) and captured by ash from 1.6% to 2.8%, roughly double the amount. Similarly, increasing the partial pressure of Hg\(^0\) has increased the proportion of unaccounted Hg from 5.8% to 18.1%. This mercury is not retained in the ash but may be adsorbed on surfaces throughout the experimental rig, in particular the section between the heated bag filter simulator and the impinger train where the gas undergoes cooling.

![Figure 8-1](image)

*Figure 8-1.* Effect of increasing Hg\(^0\) concentration on fly ash capture. Input: Hg\(^0\) = varied 5 – 10 \(\mu g/Nm^3\), SO\(_2\) (SO\(_3\)) = 667 (10) ppm, O\(_2\) = 3.33% vol., H\(_2\)O = 2% vol., balance N\(_2\). BF Temp = 150°C.
8.3.2 Effect of SO$_x$ (SO$_2$ / SO$_3$ / H$_2$SO$_4$)

Previous studies [17, 97, 100, 104] have shown that Hg competes with SO$_x$ during capture in fly ash. Wilcox, et al. [97] noted that sulfur can have either a positive or a negative impact in oxidising and capturing Hg$^0$ on activated carbon depending on its form, species and presence. In order to investigate the effects of different forms of SO$_x$ in the flue gas on the Hg capture of inorganic fly ash, this paper divided the effects of SO$_x$ as follows: (1) purely SO$_2$, no SO$_3$ present, where the gas mixture (SO$_2$, O$_2$, H$_2$O, N$_2$) does not pass through the SO$_3$ generator bed of fly ash; (2) SO$_2$, SO$_3$ and H$_2$SO$_4$ wherein the gas mixture passes through a fixed bed of fly ash to generate SO$_3$ which then comes in contact with water vapour to produce H$_2$SO$_4$ vapour and (3) SO$_2$ and SO$_3$ only, where water was absent to test the effect of the absence of H$_2$SO$_4$. For all these experiments the simulated bag filter (BF) temperature was set at 150°C.

8.3.2.1 SO$_2$

Figure 8-2 presents the effect of SO$_2$ input on the Hg capture of fly ash when no SO$_3$ is present, i.e. no generator ash was used. With the input Hg$^0$ fixed at ~5 $\mu$g/Nm$^3$, increasing the concentration of input SO$_2$ from 0 ppm to 1000 ppm shows that Hg$^0$ measured by the analyser decreased. The amount of Hg$^P$ did not vary greatly ranging from 1.2% to 2.3% of the input Hg, while the amount of unaccounted Hg increased significantly. Research completed by Kellie, et al. [104] noted that as SO$_2$ concentration in the flue gas is increased, the Hg$^0$ decreases while Hg$^{2+}$ increases. The same is true with the measured Hg$^0$ by the online Hg analyser but in this case instead of Hg$^{2+}$ increasing, the amount of unaccounted Hg increased. It may be that Hg$^0$ fed was oxidised and was not captured by the fly ash but captured elsewhere in the system.
An experiment with and without water vapour at the same SO\textsubscript{2} input concentration was also investigated (3\textsuperscript{rd} and 4\textsuperscript{th} bars Figure 8-2), it showed that purely addition of H\textsubscript{2}O vapour does not have much effect on the capture of Hg on fly ash, Hg\textsuperscript{P}. The Hg\textsuperscript{P} captured by the fly ash were 2.3% when water is not present and 1.2% with water in the system. However, the addition of 2% vol. H\textsubscript{2}O vapour to the system, decreased the unaccounted Hg from 13.4% and 17.3%. It is also worth noting that even though the study completed by Kellie, et al. [104] performed a correlation between Hg speciation and SO\textsubscript{2} in the flue gas, it did not account for the SO\textsubscript{3} formed in the boiler.

\textbf{8.3.2.2 Combined SO\textsubscript{2}, SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4}}

Using the SO\textsubscript{3} generator (refer to Figure 4-8), the effect of varying SO\textsubscript{3} concentration has been investigated and the result is plotted in Figure 8-3. It can be seen from the plot that increasing SO\textsubscript{3} concentrations from 0 to 15 ppm corresponding
to an SO$_2$ input increase from 667 to 1000 ppm, the graph produced three notable points:

1) The Hg$^0$ in all three levels of SO$_2$ (SO$_3$) are similar in magnitude, ranging from 1.5% to 1.9%. However there is a slight decrease in the Hg$^0$ as the SO$_3$ is increased. Krishnakumar and Niksa [90] stated that in power plants, using SO$_3$ injection as a conditioning agent diminishes Hg capture by activated carbon sorbent. Although there is practically no activated carbon in the fly ash used in this study, it follows the same trend in that as there is more SO$_3$ passing through the system, less Hg is being captured by the fly ash.

2) As the SO$_x$ concentration is increased, the unaccounted Hg increases from 4.7% to 16.1%. This similar trend was found in a study by Spörl, et al. [17] focusing on mercury emissions and removal by ash utilising the same coal A, where the capture efficiency of the fly ash in the bag filters is reduced as SO$_2$/SO$_3$ concentrations were higher, i.e. air to oxy.

3) With an input of 15 ppm SO$_3$ (and 1000 ppm SO$_2$) into the system, a measured Hg$^{2+}$ of 7.1% was observed. The speciation was not fully evident without the presence of SO$_3$ (Figure 8-2), however similar to the findings of Spörl, et al. [17] where increased impurity concentration, i.e. SO$_2$ and SO$_3$, increased the amount of oxidised mercury, Hg$^{2+}$, found to be captured in the fly ash. Also, at higher SO$_3$ the Hg$^{2+}$ was not found to be captured by the FA which could suggest competition with SO$_3$.

It could be deduced that enhanced Hg$^0$ oxidation can be observed at higher SO$_3$ (and SO$_2$) input concentrations. The capture behaviour exhibited in this plot is similar to works completed by investigators [17, 100, 103, 104] where in the absence of SO$_x$, the Hg$^0$ adsorption effectiveness of the sorbents is lower whilst with SO$_2$ (and SO$_3$), the adsorption was enhanced. The unaccounted Hg has increased as SO$_x$ input was increased.
Fernandez-Miranda, et al. [100] noted that in simple combustion atmospheres, Hg\(^0\) oxidation may occur via:

\[
2\text{Hg}^0(g) + 2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{HgO}(g) + 2\text{SO}_3(g) \text{ fast } \quad \text{Reaction 8-1}
\]

However in this study where baseline Hg\(^0\) was kept constant at \(\sim 5\ \mu\text{g/Nm}^3\), the presence of 10 ppm SO\(_3\) (667 ppm SO\(_2\)) (Figure 8-3) did not change the oxidation of mercury compared to the equivalent system without SO\(_3\) (667 ppm SO\(_2\), 2\textsuperscript{nd} bar Figure 8-2), but when the SO\(_3\) concentration increased to 15 ppm, 1000 ppm SO\(_2\), a significant oxidation amounting to 7.1\% \(\text{Hg}^{2+}/\text{Hg}_{\text{Tot}}\) was observed. This oxidation was not observed at the same SO\(_2\) (with and without SO\(_3\)) but was observed when the SO\(_2\) was 1000 ppm (and much higher SO\(_3\)) following the forward reaction of Reaction 8-1. This homogeneous and/or heterogeneous Hg oxidation on the fly ash by SO\(_2\) and/or SO\(_3\)/H\(_2\)SO\(_4\) was also observed by Spörl, et al. [17] where changing configuration from air combustion to oxy-fuel combustion (with flue gas recycling).
It is quite difficult to discern whether the oxidation of Hg$^0$ and eventual capture is due to SO$_2$/SO$_3$ or SO$_3$/H$_2$SO$_4$ from the above set of experiments. Another set of experiments that involved feeding SO$_2$ + SO$_3$ with and without the presence of H$_2$O vapour was also designed to investigate whether the presence of H$_2$SO$_4$ will enhance Hg$^0$ oxidation and its eventual capture by providing acidified surface or compete against Hg species for active sites on the fly ash.

**8.3.2.3 SO$_2$ + SO$_3$ with and without H$_2$O vapour**

Producing SO$_3$ and cooling the gas in the presence of water will produce H$_2$SO$_4$. Therefore it was not clear whether SO$_3$ or H$_2$SO$_4$ is producing the enhanced oxidation of Hg$^0$ observed. Figure 8-4 shows the effect of purely SO$_2$/SO$_3$ and SO$_2$/SO$_3$/H$_2$SO$_4$ on mercury. A practical oxy-fuel SO$_2$ input (667 ppm) giving rise to SO$_3$ of 10 ppm was used. Wilcox et al. [97] stated that Hg in its atomic state acts as a base and can readily react with acidic sites on carbon surfaces. Hower, et al. [109] stated that Hg$^0$ oxidation is promoted by addition of acid, not only HCl but even small amounts of H$_2$SO$_4$. Similarly, introducing water vapour in the system to produce H$_2$SO$_4$ from SO$_3$ provides acid sites on the fly ash surface by [100]:

$$SO_3(aq, g) + H_2O(l, g) \rightarrow H_2SO_4(aq, g) \quad \text{fast} \quad \text{Reaction 8-2}$$

Once Hg$^0$ is oxidised and becomes acidic, it will compete with other acidic gases on the basic sites that are available on carbon surfaces. However, the fly ash used in this study is very low in UBC (< 0.1%w) and so the effect of fly ash as an adsorbent (with its inorganic mineral content) is observed [17, 97].

It can be seen that with a similar SO$_3$ input, both systems have roughly the same Hg$^0$ measured but the BF fly ash without water vapour in the system has captured roughly 4 times Hg$^p$ (from 1.6% to 6.8%). Fernandez-Miranda, et al. [100] compared the effect of different water concentrations simulating air and oxy-fuel combustions and found that Hg$^0$ oxidation was favoured by the presence of more H$_2$O vapour. Hence, without H$_2$O the Hg measured as Hg$^p$ may have been Hg$^0$ captured
by the fly ash while with H₂O there could have been oxidation but not fully captured by the fly ash.

![Graph showing Hg speciation measured by analyser](image)

**Figure 8-4.** Effect of H₂O vapour input in the fly ash capture. Input: Hg⁰ ~ 5 µg/Nm³, SO₂ (SO₃) = 667 (10) ppm, O₂ = 3.33% vol., H₂O = 0 and 2% vol., balance N₂. BF temp = 150°C.

With the presence of H₂O vapour, it can also be seen that the amount of unaccounted Hg has increased which could mean that Hg⁰ may have oxidised to Hg²⁺ but is not present in the ash. One more important point in this plot is that without H₂O, there is no unaccounted mercury. In fact, the total is slightly higher than 100%, which can be due to the errors associated in the online measurements, error in analytical techniques and possible baseline drifting of the online mercury analyser. These variation in the amounts of Hg⁰ and the Hg unaccounted requires further investigation and may be carried out as part of future studies.

### 8.3.3 Effect of Temperature

In order to test the saturation of fly ash on Hg capture, different temperatures were tested to check whether temperature would have an effect on the capture capacity of the bag filter fly ash.
Figure 8-5 shows the Hg captured in fly ash (Hg\(^\text{P}\)) at different temperatures. The analysis is completed by heating the ash above 680°C where Hg\(^\text{P}\) or Hg\(^{2+}\) is converted back to Hg\(^0\) and released as a gas. The plot shows that, with similar Hg\(^0\) feed and atmosphere, lower temperatures correspond to better capture by fly ash. The lowest temperature 90°C is below the acid dew point and has resulted in a significant increase of mercury collection by the ash. Acid dew point estimations for SO\(_3\) ~ 10 ppm and H\(_2\)O = 2% vol. were calculated using ZareNezhad’s correlation [50]. One run, completed at 150°C, was performed at an extended time of 60 minutes, it was found that there is only 21% better capture (6.03 ng Hg/g FA compared to 4.98 ng Hg/g FA for exposure of 30 minutes) indicating the fly ash is approaching saturation at 60 minutes.

![Figure 8-5](image)

**Figure 8-5.** Mercury captured/retained in fly ash at different temperatures. Input: Hg\(^0\) = 5 µg/Nm\(^3\), O\(_2\) = 3.33% vol., H\(_2\)O = 2% vol. balance N\(_2\).

Figure 8-6 shows the effect of varying bag filter temperatures on the capture of Hg on fly ash. It can be noted that enhanced capture can be observed at lower temperatures. As temperatures increased from 90°C to 120°C capture by fly ash (Hg\(^\text{P}\)) was decreased from 9.1% to 2.8% and eventually to just 1.9% at 150°C and 1.2% at 200°C. Hg\(^0\) and Hg\(^\text{P}\) measurements also showed consistent trends in decreased capture as the temperature is increased. The results were in agreement with the reports by
Hover, *et al.* [109], and Serre and Silcox [96] where they have stated that temperature has negative effects on Hg capture. Serre and Silcox [96] studied Hg capture on fly ash with 8.7% carbon at bag filter temperatures of 121 to 177°C. They noted that with a temperature increase from 121 to 149°C, a reduction of 48% was observed and a further 34% reduction when temperature was further increased from 149 to 177°C.

Each of the figures shown in this article show increasing proportions of mercury that cannot be accounted for with increasing conversion to Hg$^{2+}$ or collection of the Hg by particulate matter when water is present. This suggests the same mechanism that results in the collection of mercury by particles is also affecting the loss of mercury in the experiment and this mechanism could possibly be associated with H$_2$SO$_4$ formation or condensation. It is likely that condensation of mercury on particles will also result in condensation on tubing. The PFA lines between the simulated bag filter and impinger train were washed with DDI water and resulting liquid was collected and sent out to be tested for Hg condensed, the results found no Hg on the lines.

**Figure 8-6.** Effect of bag filter temperature in the fly ash capture. Input: Hg$^0 = 5\mu\text{g/Nm}^3$, O$_2 = 3.33\%$, H$_2$O = 2\% vol. balance N$_2$. 

![Graph showing the effect of bag filter temperature on Hg capture](image-url)
Correlations among Hg species (Hg$^0$, Hg$^{2+}$, Hg$^P$ and unaccounted Hg) and experiment inputs Hg$^0$, SO$_2$, SO$_3$, H$_2$O and simulated bag filter temperature were carried out and the Pearson’s $r$ coefficients are summarised in Table 8-2. Pearson’s $r$ confirmed that temperature, similar to findings by Hower, et al. [109], has a very strong negative correlation with mercury capture. It can be seen in the table that Hg$^P$ is highly affected by temperature followed by the unaccounted Hg with a weak negative correlation coefficient.

Table 8-2. Pearson's correlation coefficient ($r$) for the correlations among the measured and calculated Hg species and the inputs Hg, SO$_2$, SO$_3$, H$_2$O and temperature.

<table>
<thead>
<tr>
<th>Factor / input</th>
<th>Pearson’s $r$ coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg$^0$</td>
</tr>
<tr>
<td>Hg input, µg/m$^3$</td>
<td>0.62</td>
</tr>
<tr>
<td>SO$_2$, ppm</td>
<td>-0.16</td>
</tr>
<tr>
<td>SO$_3$, ppm</td>
<td>-0.19</td>
</tr>
<tr>
<td>H$_2$O, % vol.</td>
<td>-0.09</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Overall, it may be seen that the unaccounted Hg increased to a great extent (5$^{\text{th}}$ column) as the Hg and SO$_2$ inputs increased and decreased with increasing BF temperature. This unaccounted Hg found in all of the figures were taken as the Hg that was not measured by the online analyser and not captured in the ash but captured elsewhere in the system. Connections presented in Section 4.2.4 were insulated to keep temperatures above water dew point (and acid dew point) to ensure no condensation in the lines occurred. However due to this unaccounted Hg, the lines were washed with known volumes of DDI water then the solutions were sent out to an accredited external laboratory to test for sulfates and mercury. It was found that the lines from the simulated bag filter to the impinger system did not contain any measurable Hg (below detectable limit < 0.0001 mg/L) nor did any of the liquids SnCl$_2$ and NaOH impinger solutions. However, when the Swagelok T-connection where the Hg was fed and the oxidant gases pass through, a measurable Hg concentration was found. It could be that even though
the connection was kept above (> 200°C) the expected acid dew point, some Hg was lost and might have formed some oxidised Hg salt (e.g. HgSO₄) with the input Hg.

### 8.4 CHAPTER SUMMARY AND CONCLUSIONS

The SO₂, SO₂/SO₃, SO₃/SO₄/H₂SO₄ and mercury interactions and speciation in fly ash during coal combustion were investigated experimentally using Hg⁰ injection and selected flue gas impurities and a simulated bag filter using a low carbon fly ash. The following conclusions were drawn:

1) Mercury capture by fly ash (Hgᵇ) associated with doubling the Hg in the flue gas, from 5 to 10 µg/Nm³, increased the amount of Hg²⁺ captured by roughly twice the amount, though the capture was relatively small: from 1.6 to 2.8% while the unaccounted Hg increased from 5.8 to 18.1%.

2) Effects of SOₓ on Hg capture by fly ash have also been investigated.
   a. Increasing SO₂ decreased the proportion of Hg⁰ in the flue gas, though the effect on Hg captured by the fly ash was minimal.
   b. The amount of unaccounted Hg increased with increasing SO₂ without SO₃ present. Allowing SO₂ to be converted to SO₃ with the presence of water, i.e. the formation of H₂SO₄, resulted in a significant conversion of Hg⁰ to Hg²⁺ in the flue gas. Even though increased Hg²⁺ was observed, this was not shown to be captured by the FA instead was left in the gas stream which could suggest competition.
   c. When water vapour is not present with SO₂+SO₃, 6.8% of the Hg was collected by the ash, and all the mercury was accounted for, however when 2% vol. H₂O vapour was added a significant decrease (1/4 the original amount) in particulate Hg was measured together with an increase in unaccounted Hg from 0 to 5.8%. This drastic change in the Hgᵇ and Hg unaccounted requires further investigation as part of future studies.
3) Bag filter temperature was seen to have a substantial impact on the mercury capture on the fly ash. Mercury capture was found to increase with decreasing bag filter temperature. Capture in fly ash decreased from 9.1% at the acid dew point (< 120°C) and 2.8% at 120°C to 1.9% from at 150°C and to zero at 200°C. An increase in BF temperature by 60°C (from 90 to 150°C) caused a decrease in Hg\(^{p}\) capture by 20%. The Hg\(^{0}\) in the flue gas increased from 77.9% at 90°C to 98.3% at 200°C.

Overall, it can be noted that as most of the trends support those found in literature, closing the Hg balance is challenging. The author recommends conducting more experiments on the interaction of SO\(_x\) and Hg in fly ash.
9 PRACTICAL IMPLICATIONS

This chapter will provide a summary relating theoretical findings and how they impact on practical situations in a power plant. Currently, the Callide Oxy-fuel Project (COP) is the largest existing oxy-fuel technology in operation and is therefore the focus of this thesis. It combines retrofit options for exiting power plants; electricity generation and CO$_2$ processing (compression). The COP, as with the Australian scenario in general, does not have dedicated removal technologies for SO$_x$, NO$_x$ and Hg due to low-S Australian coals and current government emissions regulations, fabric filters are expected to capture SO$_x$ and mercury in the flue gas. On the other hand, SO$_x$, particularly SO$_3$, is known to compete with Hg removal in the bag filters when the carbon content of the ash is significant. This then creates a challenge since Hg is known to amalgamate and attack aluminium components in the cryogenic compression of CO$_2$ for CCS.

Fly ash is known to capture SO$_x$ as sulfates. It was established from the research that by thermally decomposing fly ash under N$_2$, oxy-fuel fly ash released 2 to 3 times more sulfur than its air counterpart. These sulfur species in fly ash are responsible for fireside corrosion during combustion. SO$_x$, especially SO$_3$, is known to cause corrosion to the metal components of the fabric filters especially when hydrated, forming H$_2$SO$_4$. Condensed acid also causes fouling at the air pre-heater (APH) due to condensation on ash especially when the SO$_3$ concentration is higher and the alkalinity of fly ash is low. A shift from air to oxy-fuel combustion with full flue gas recycling, i.e. no cleaning, can increase the sulfuric acid dew point by up to around 60°C.

Apart from the technical issues brought about by the increased ADP, it also causes boiler efficiency losses. If SO$_2$/SO$_3$ is properly accounted for and capture by bag filter and pollution control devices are efficient, operational costs for coal fired power plants could be reduced. Assuming a 500 MW plant operating at 80% capacity with a heat rate of 9500 BTU/kWh utilising coal costing $1.80/MM Btu (presented in Section 2.7.1) with an 80% reduction of SO$_3$ in the flue gas from 18 ppm to 3.6 ppm, ADP reduction from 153 to
138°C (∆T = 27°F) could be achieved. With this reduction in ADP, fuels saving of up to $ 450,000/year is achievable (~93% of the fuel savings of a system with a starting SO₃ of 60 ppm with 95% reduction based on Figure 2-30).

In oxy-fuel technology where residence time is greater and dust loading is higher, better Hg capture is expected. However increased impurity concentrations (SO₂, SO₃ as well as water vapour) were observed, SOₓ (SO₃) was also found to compete with Hg capture by fly ash. It has been well established that carbon is an effective material for removal of Hg; however, it was difficult to establish a high removal based on the laboratory tests due to an almost negligible carbon-in-ash (< 0.1%). On the other hand, it has been established by the experiments that temperature has a huge impact on the adsorption of Hg in the fly ash.

In oxy-fuel technology where ADP can be raised by about 30 to 60°C compared to air-firing, the performance of bag filters is expected to decrease. In the experiments where the temperature was changed from 90°C to 150°C (∆T = 60°C) caused a reduction in HgP capture by about 20%. With these reductions in capture at the bag filters due to an increase in operating BF temperature, downstream impacts in the CO₂ processing requiring a need for secondary Hg removals could be created.
10 CONCLUSIONS & RECOMMENDATIONS

10.1 CONCLUSIONS

A comprehensive set of experiments were conducted to investigate the differences between the levels of sulfur species formed in air and oxy-fuel firing; focusing on the issues associated with differing SOₓ levels such as SO₃ output concentrations, SO₂/SO₃ capture by fly ash and its associated impact on the acid dew point, and the interaction between SOₓ and mercury in the bag filter. The following sections provide the summary and conclusions of each of the experiment goals with the conclusions of each study highlighted.

10.1.1 20 kW Pilot-scale Practical Oxy-fuel Combustion: SO₂ and SO₃ output levels

“The extent of SO₃/SO₂ conversions was found to be within 0.5 to 3%, slightly higher conversions in oxy-fuel. SO₃ was found to be effectively captured by the bag filter, which in turn reduced the sulfuric acid dew point.”

In the 20 kWₘₜ pilot scale tests utilising three different commercial Australian coals, practical oxy-fuel combustion test runs produced increased output concentration of SO₃ by up to 4 times that of air combustion. On the other hand, the change in configuration from air to oxy-fuel combustion did not seem to have significant effects on the extent of conversion of SO₂ to SO₃. Similar coals gave roughly similar conversion extents, i.e. similar % in air and oxy-fuel, consistent with what has been reported in existing literature. The SO₃ formed in the flue gas was found to be effectively captured by the bag filter, higher capture efficiencies were observed from air combustion runs than oxy-fuel runs. This SO₃ capture was observed to lower the H₂SO₄ acid dew point by as much as 16°C.
10.1.2 Sulfur Capture by Fly Ash

“Sulfur capture by fly ash is 2 – 3 times higher in oxy-fuel derived fly ash than in air fired fly ash.”

Pilot scale tests found that the bag filter is effective in capturing flue gas SO$_3$ with higher capture extents during air combustion runs. Experiments were undertaken to investigate the differences in the capture behaviours at different environments. It was found that although % overall SO$_3$ capture at the bag filters is higher during air combustion, the specific amount of sulfur (ppm SO$_2$/g FA and mg S/g FA) by the oxy-fuel fly ash is roughly 2 to 3 times greater than the air fly ash during thermal decomposition. This decomposable sulfur in the fly ash accounts for 38 to 83% of the total sulfur in the ash.

10.1.3 Catalytic Conversion of SO$_2$ to SO$_3$ by Fly Ash

“Fly ash was found to effectively catalyse conversion of SO$_2$ to SO$_3$, this accounts for up to 95% of the overall conversion at 700°C depending on the fly ash composition.”

Pilot scale tests indicated that SO$_2$ concentration in the oxidant gases does increase the SO$_3$ output concentration by around 4 times when changing from air firing to simulated oxy-fuel firing with impurity injections. However, the conversions of SO$_2$ to SO$_3$ is within 0.5 and 3% with slightly higher conversions during oxy-fuel firing. SO$_2$ was seen to be captured in the fly ash which caused the reduction of ADP by around 1 to 16°C with observed ADPs in oxy-fuel higher by around 41 to 67°C. However, some of the SO$_3$ that does not get captured in the fly ash in the bag filter is shown to be oxidised catalytically by the active components in the fly ash. The contribution of this catalytic conversion amounts to 95% of the overall conversion at 700°C. Fe oxides along with other metal oxides (Ca, Mg, Na, and K) was also shown to provide some catalytic enhancement on the conversion of SO$_2$ to SO$_3$. With greater SO$_2$, H$_2$O and ash loading during oxy-fuel, higher SO$_3$ that is not captured by the fly ash is expected to increase the acid dew point.
10.1.4 Interaction between SO$_x$ and Mercury in the Bag Filter

“Sulfur oxides (SO$_2$, SO$_3$ and H$_2$SO$_4$) were found to enhance oxidation of elemental mercury to oxidised mercury. The presence of SO$_3$ was found to lessen the Hg adsorption on fly ash. Temperature has a negative impact on Hg capture by fly ash.”

Pilot scale tests indicated that switching from air to oxy increased the proportion of Hg$^{2+}$/Hg$^{tot}$ in the flue gas. Increasing Hg (double) in the flue gas prior to the bag filter increases the proportion of the Hg$^p$ in the fly ash but increases the amount of unaccounted Hg as well. Increase in SO$_2$ showed decrease in proportion of Hg$^0$ in the flue gas and in the fly ash, but increases the amount of unaccounted Hg. Additionally, increase in SO$_3$ (and H$_2$SO$_4$) resulted in significant conversion of Hg$^0$ to Hg$^{2+}$ and a better mercury capture by fly ash. The bag filter temperature was seen to have a negative correlation on Hg capture. An increase in BF temperature by 60°C (from 90 to 150°C) caused a decrease in Hg$^p$ capture by 20%.

10.2 RECOMMENDATIONS FOR FUTURE WORK

This study was set out to establish an understanding of the impacts of SO$_x$ in oxy-fuel particularly on the flue gas cooling side before and after gas comes into contact with the bag filter. Some recommendations are suggested by the author for future considerations.

1) Sulfur capture was found to be more in the oxy-fuel fly ash. It is therefore suggested that ash decomposition be performed on size segregated fly ash and perform an analysis on each of the size fractions on metal oxides in order to relate capture with size fraction and possibly surface area.

2) Calcium, as CaO, is well known to capture SO$_x$ (as SO$_2$) forming stable CaSO$_4$. However, other AAEMs may also impact the extent of S-capture and retention. It is therefore suggested that the forms of calcium, as well as other AAEMs such as Na, be
analysed in order to have a better understanding on the capture mechanism occurring in the fly ash to be able to identify and quantify which active form of calcium, and AAEMs, in fly ash captures SO\(_x\) more effectively.

3) SO\(_3\) generated in this study was quantified with the use of controlled condensation principles and ion chromatography. It would be advantageous if simultaneous measurement of SO\(_3\) production and Acid Dew Point monitoring was completed using an ADP probe.

4) It has been determined that Fe\(_2\)O\(_3\) in the fly ash catalyses SO\(_2\) conversion to SO\(_3\). Therefore, morphology and surface area correlations of the iron-containing species in the fly ash is recommended in order to determine its effect on the catalysis of SO\(_2\) to SO\(_3\). It is also recommended that the effect of varying individual iron oxide species be tested in order to evaluate the extent of catalysis associated with different forms of oxide on the formation of SO\(_2\) to SO\(_3\).

5) SO\(_x\) was found to interact with mercury in the bag filter. Speciation of mercury was accomplished by using a solution of SnCl\(_2\)/HCl to reduce Hg\(^{2+}\) back to Hg\(^0\) to be measured by the analyser. The possibilities of using other chlorides, e.g. KCl, in series with activated carbon beds to simultaneously convert Hg\(^{2+}\) to Hg\(^0\) and capture the mercury in the activated carbon should be explored. Figure 10-1 shows a schematic of the recommended setup similar to the one presented in Chapter 5 for Hg-SO\(_x\) interaction. Highlighted in the figure is the option where offline analyses having Na\(_2\)CO\(_3\) as SO\(_2\) scrubber then KCl to account for Hg\(^{2+}\) as opposed to using impingers (option B).
Figure 10-1. Schematic diagram for the Hg and SO$_x$ interaction. Highlighted is the recommendation for possible offline measurement and speciation of Hg.

6) Different fly ash samples are recommended for testing to determine effect of varying surface area which provide capture of Hg and SO$_x$, AAEM oxide contents which could possibly affect the capture mechanisms when they either capture or catalyze SO$_x$ and possibly Hg, and higher unburned carbon on the SO$_x$-Hg interaction.
References


40. Santos, S., *Fate of Sulphur in Coal During Oxyfuel Combustion with Recycled Flue Gas (review of the current state of understanding)*, in IEA Clean Coal Centre - CCT Conference ’09. 2009: Dresden, Germany.


76. EPA, *METHOD 8 - Determination of sulfuric acid and sulfur dioxide emissions from stationary sources* United States Environmental Protection Agency. p. 733-753.


117. Spörl, R. and J. Maier, Results report: Pulverised coal air and oxy-fuel combustion experiments with three Australian coals at IFK, University of Stuttgart, G. Scheffknecht, Editor. 2013, Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart: Stuttgart, Germany.


Appendices

A. XRD ANALYSES OF DIFFERENT FLY ASH SAMPLES USED IN THE EXPERIMENTS.

This section contains all the XRD analyses for fly ash samples A (Oxy), B (Air and Oxy), and C (Air and Oxy).

Figure A-1. XRD analysis for fly ash A – Oxy-fuel fired.
Figure A-2. XRD analysis for fly ash B – Air fired.
Figure A-3. XRD analysis for fly ash B – Oxy-fuel fired.
Figure A-4. XRD analysis for fly ash C – Air fired.
**Figure A-5.** XRD analysis for fly ash C – Oxy-fuel fired
B. KINETIC EFFECTS

This Appendix section presents the formulas used in calculating the following data input in the tables used in Chapter 7. In order to solve for the concentration of SO₃ in ppm, the moles of SO₃ obtained from Ion Chromatography was divided by the total gas flow for a period of time as given in the Equations (1) and (2) below.

\[
ppm \ SO_3 = \frac{\text{moles } SO_3}{\text{moles gas}} \times 1,000,000 \quad (1)
\]

\[
\text{moles } A = \dot{q} \times t \times \left( \frac{[SO_2]}{1,000,000} \right) \left( \frac{273.15}{T} \right) \left( \frac{1}{22.414} \right) \quad (2)
\]

Where:

- \( A \) = species of gas, \( i.e. \) Air or SO₂
- \( \dot{q} \) = volumetric flow rate, L/min
- \( t \) = time, min
- \([SO_2]\) = SO₂ concentration, ppm
- \( T \) = Temperature, K (used 25°C in the experiments)
- 22.414 L = volume of 1 mole ideal gas at STP
I. Effects of SO2 Concentration

In order to test the effects of SO2 input concentration on the conversion of SO2 to SO3. The following input variables were used: flow rate = 0.5 L/min (298 K, 1 atm), Reactor Temperature = 900°C, O2 = 5 % vol., H2O = 3% vol. while the SO2 concentrations were varied from 500 ppm to 2000 ppm.

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<thead>
<tr>
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<th>O2</th>
<th>H2O</th>
<th>FROM IC MEASUREMENTS</th>
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<td>LPM</td>
<td>mins</td>
<td>C</td>
<td>ppm</td>
<td>%</td>
<td>%</td>
<td>A (IC)</td>
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<td>900</td>
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<td>1000</td>
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<td>1000</td>
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</tr>
</tbody>
</table>
II. Effects of O₂ Concentration

In order to test the effects of O₂ input concentration on the conversion of SO₂ to SO₃, the following input variables were used: flow rate = 0.5 L/min (298 K, 1 atm), Reactor Temperature = 900°C, SO₂ = 1000 ppm, H₂O = 3% vol. while the O₂ concentrations were varied from 3, 5 and 10 % vol.

<table>
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<th>Temp</th>
<th>SO₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>FROM IC MEASUREMENTS</th>
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</thead>
<tbody>
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<td>LPM</td>
<td>mins</td>
<td>C</td>
<td>ppm</td>
<td>%</td>
<td>%</td>
<td>mV-min ppm % (ppm/ppm)</td>
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<tr>
<td>11/04/2013</td>
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<td>5</td>
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<td>1000</td>
<td>3</td>
<td>3</td>
<td>3.5364 3.0618 0.306</td>
</tr>
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<td>10</td>
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</tr>
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<td>1000</td>
<td>10</td>
<td>3</td>
<td>4.8274 5.0154 0.602</td>
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III. Effects of H₂O Concentration

In order to test the effects of H₂O input concentration on the conversion of SO₂ to SO₃, the following input variables were used: flow rate = 0.5 L/min (298 K, 1 atm), Reactor Temperature = 900°C, SO₂ = 1000 ppm, O₂ = 5 % vol., while the H₂O concentrations were varied as 3, 4.5, 7 and 9% vol.

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<tr>
<th>Date</th>
<th>Flow</th>
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<th>Temp</th>
<th>SO₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>FROM IC MEASUREMENTS</th>
</tr>
</thead>
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<td>mins</td>
<td>C</td>
<td>ppm</td>
<td>%</td>
<td>%</td>
<td>mV-min ppm % (ppm/ppm)</td>
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<td>1000</td>
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<td>1000</td>
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<td>1000</td>
<td>5</td>
<td>9</td>
<td>3.83 3.9791 0.477</td>
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</table>
IV. Effects of Residence Time

In order to test the effects of residence time on the conversion of SO$_2$ to SO$_3$. The following input variables were used: Reactor Temperature = 900°C, SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 1% vol.

<table>
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<th>Temp</th>
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<th>O$_2$</th>
<th>H$_2$O</th>
<th>FROM IC MEASUREMENTS</th>
</tr>
</thead>
<tbody>
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<td>mins</td>
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<td>ppm</td>
<td>%</td>
<td>%</td>
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<td>6/03/2013</td>
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<td>1000</td>
<td>5</td>
<td>1</td>
<td>3.1622</td>
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</table>

The residence times corresponding to the flow rates corrected to temperature are as follows: 0.5 L/min = 0.86 sec, 1.0 L/min = 0.43 sec, and 1.5 L/min = 0.29 sec.
V. Effects of Temperature for with (W) and without (W/O) Fly Ash

In order to observe the catalytic effect of fly ash on the system at different temperatures, the following table presents the data where the first column shows the Sample Temperature and whether it contains FA in the reactor or not. Those with FA represent catalytic conversion whilst those without FA represent homogeneous conversions. Input gas concentrations are as follows: flow rate = 0.5 L/min (298 K, 1 atm), SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., while temperatures used in the reactor are 400, 500, 700, 900 and 1000°C. Fly ash sample used in this section is Fly Ash A – Air.

<table>
<thead>
<tr>
<th>Sample Temp</th>
<th>time min</th>
<th>Temp °C</th>
<th>QW g</th>
<th>SA m$^2$</th>
<th>Area mV-min</th>
<th>SO$_3$ moles</th>
<th>FA g</th>
<th>Conversion SO$_3$/SO$_2$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 w FA</td>
<td>60</td>
<td>400</td>
<td>1.0260</td>
<td>0.1936</td>
<td>0.4889</td>
<td>5.15E-07</td>
<td>0.5124</td>
<td>0.04</td>
</tr>
<tr>
<td>400 w/o FA</td>
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<td>400</td>
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<td>0.1886</td>
<td>0.4792</td>
<td>5.09E-07</td>
<td>0.5124</td>
<td>0.04</td>
</tr>
<tr>
<td>500 w FA</td>
<td>68</td>
<td>500</td>
<td>1.0161</td>
<td>0.1917</td>
<td>1.0121</td>
<td>1.07E-06</td>
<td>0.5149</td>
<td>0.08</td>
</tr>
<tr>
<td>500 w/o FA</td>
<td>60</td>
<td>500</td>
<td>1.0193</td>
<td>0.1923</td>
<td>0.7224</td>
<td>7.62E-07</td>
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<td>0.06</td>
</tr>
<tr>
<td>700 w FA</td>
<td>60</td>
<td>700</td>
<td>1.0145</td>
<td>0.1914</td>
<td>20.6982</td>
<td>2.19E-05</td>
<td>0.5014</td>
<td>1.78</td>
</tr>
<tr>
<td>700 w/o FA</td>
<td>60</td>
<td>700</td>
<td>1.0049</td>
<td>0.1896</td>
<td>1.1399</td>
<td>1.2E-06</td>
<td>0.5014</td>
<td>0.10</td>
</tr>
<tr>
<td>900 w FA</td>
<td>60</td>
<td>900</td>
<td>1.0276</td>
<td>0.1939</td>
<td>15.1152</td>
<td>1.6E-05</td>
<td>0.5032</td>
<td>1.31</td>
</tr>
<tr>
<td>900 w/o FA</td>
<td>60</td>
<td>900</td>
<td>1.0700</td>
<td>0.2019</td>
<td>4.1753</td>
<td>4.43E-06</td>
<td>0.5032</td>
<td>0.36</td>
</tr>
<tr>
<td>900 w FA</td>
<td>60</td>
<td>900</td>
<td>1.0700</td>
<td>0.2019</td>
<td>5.1753</td>
<td>5.44E-06</td>
<td>0.5032</td>
<td>0.44</td>
</tr>
<tr>
<td>1000 w FA</td>
<td>60</td>
<td>1000</td>
<td>1.0060</td>
<td>0.1898</td>
<td>20.7797</td>
<td>2.2E-05</td>
<td>0.5023</td>
<td>1.79</td>
</tr>
<tr>
<td>1000 w/o</td>
<td>45</td>
<td>1000</td>
<td>1.0389</td>
<td>0.1960</td>
<td>6.78</td>
<td>7.11E-06</td>
<td>0.5023</td>
<td>0.77</td>
</tr>
<tr>
<td>1000 w/o</td>
<td>50</td>
<td>1000</td>
<td>1.5180</td>
<td>0.2864</td>
<td>6.9703</td>
<td>7.38E-06</td>
<td>0.5023</td>
<td>0.72</td>
</tr>
<tr>
<td>900 w FA</td>
<td>125</td>
<td>900</td>
<td>1.0396</td>
<td>0.1962</td>
<td>32.9221</td>
<td>3.48E-05</td>
<td>0.5172</td>
<td>1.36</td>
</tr>
<tr>
<td>700 w FA</td>
<td>60</td>
<td>700</td>
<td>1.0145</td>
<td>0.1914</td>
<td>17.4345</td>
<td>1.84E-05</td>
<td>0.5059</td>
<td>1.50</td>
</tr>
<tr>
<td>700 w FA</td>
<td>65</td>
<td>700</td>
<td>1.0541</td>
<td>0.1989</td>
<td>19.4914</td>
<td>2.07E-05</td>
<td>0.5059</td>
<td>1.56</td>
</tr>
</tbody>
</table>
VI. Effects of Fe$_2$O$_3$ in FA on the conversion of SO$_2$ to SO$_3$.

The following table presents the data used to test the effects of varying Fe$_2$O$_3$ contents in three different fly ash samples on the conversion of SO$_2$ to SO$_3$ as presented in Chapter 7. Input gas concentrations are as follows: flow rate = 0.5 L/min (298 K, 1 atm), SO$_2$ = 1000 ppm, O$_2$ = 5% vol., H$_2$O = 3% vol., Temperature of reactor = 700°C. Fly ash samples used in this section are A, B and C derived from Air and Oxy-fuel with full flue gas recycling runs.

<table>
<thead>
<tr>
<th>Fly Ash Mode</th>
<th>Fe$_2$O$_3$ %w</th>
<th>QW g</th>
<th>IC Area mV-min</th>
<th>SO$_2$ moles</th>
<th>FA g</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – Air</td>
<td>3.26</td>
<td>1.0145</td>
<td>20.6982</td>
<td>2.1873E-05</td>
<td>0.5014</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.4345</td>
<td>1.8424E-05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0541</td>
<td>19.4914</td>
<td>2.0665E-05</td>
<td>0.5014</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.0934</td>
<td>2.0243E-05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A – Oxy</td>
<td>3.59</td>
<td>0.9984</td>
<td>18.0829</td>
<td>1.9015E-05</td>
<td>0.5034</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.6703</td>
<td>1.5427E-05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1097</td>
<td>22.8707</td>
<td>2.4406E-05</td>
<td>0.5077</td>
<td>1.26</td>
</tr>
<tr>
<td>B – Air</td>
<td>0.78</td>
<td>1.0016</td>
<td>9.5846</td>
<td>1.0171E-05</td>
<td>0.5012</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.8195</td>
<td>8.2977E-06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B – Oxy</td>
<td>1.09</td>
<td>1.0661</td>
<td>10.2547</td>
<td>1.0909E-05</td>
<td>0.505</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.3314</td>
<td>1.0991E-05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C – Air</td>
<td>4.21</td>
<td>1.0597</td>
<td>12.7361</td>
<td>1.3455E-05</td>
<td>0.5007</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.7437</td>
<td>1.3464E-05</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.081</td>
<td>13.2385</td>
<td>1.3985E-05</td>
<td>0.5065</td>
<td>1.24</td>
</tr>
<tr>
<td>C - Oxy</td>
<td>4.22</td>
<td>1.0701</td>
<td>18.2119</td>
<td>1.9209E-05</td>
<td>0.5058</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18.628</td>
<td>1.9648E-05</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
C. COMPETITION BETWEEN SO\textsubscript{x} AND MERCURY

The competition between SO\textsubscript{x} species and Hg in fly capture was investigated and the results of the following effects are summarised in the table below. The results are summarised in Chapter 8.

### I. Effect of Mercury Input Concentration

<table>
<thead>
<tr>
<th>Hg input (µg/m\textsuperscript{3})</th>
<th>Hg\textsuperscript{0} + Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{0} measured</th>
<th>Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{P}</th>
<th>Hg unaccounted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>5</td>
<td>91.5%</td>
<td>92.6%</td>
<td>0.0%</td>
<td>1.6%</td>
<td>5.8%</td>
</tr>
<tr>
<td>10</td>
<td>76.7%</td>
<td>79.1%</td>
<td>0.0%</td>
<td>2.8%</td>
<td>18.1%</td>
</tr>
</tbody>
</table>

### II. Effect of Input SO\textsubscript{2}+SO\textsubscript{3} Inputs

<table>
<thead>
<tr>
<th>SO\textsubscript{2} ppm</th>
<th>SO\textsubscript{3} ppm</th>
<th>Hg\textsuperscript{0} + Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{0} measured</th>
<th>Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{P}</th>
<th>Hg unaccounted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>87.1%</td>
<td>93.5%</td>
<td>0.0%</td>
<td>1.9%</td>
<td>4.6%</td>
</tr>
<tr>
<td>667</td>
<td>10</td>
<td>91.5%</td>
<td>92.6%</td>
<td>0.0%</td>
<td>1.6%</td>
<td>5.8%</td>
</tr>
<tr>
<td>1000</td>
<td>15</td>
<td>82.4%</td>
<td>75.2%</td>
<td>7.1%</td>
<td>1.5%</td>
<td>16.1%</td>
</tr>
</tbody>
</table>

### III. Effect of Water Vapour Concentration

<table>
<thead>
<tr>
<th>Water % vol.</th>
<th>Hg\textsuperscript{0} + Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{0} measured</th>
<th>Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{P}</th>
<th>Hg unaccounted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>96.2%</td>
<td>95.8%</td>
<td>0.4%</td>
<td>6.8%</td>
<td>0.0%</td>
</tr>
<tr>
<td>2</td>
<td>91.5%</td>
<td>92.6%</td>
<td>0.0%</td>
<td>1.6%</td>
<td>5.8%</td>
</tr>
</tbody>
</table>

### IV. Effect of Purely SO\textsubscript{2} (with and without H\textsubscript{2}O vapour)

<table>
<thead>
<tr>
<th>SO\textsubscript{2} ppm</th>
<th>With or without H\textsubscript{2}O</th>
<th>Hg\textsuperscript{0} + Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{0} measured</th>
<th>Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{P}</th>
<th>Hg unaccounted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>W</td>
<td>94.0%</td>
<td>92.2%</td>
<td>1.8%</td>
<td>2.1%</td>
<td>3.9%</td>
</tr>
<tr>
<td>667</td>
<td>W</td>
<td>87.1%</td>
<td>93.5%</td>
<td>0.0%</td>
<td>1.4%</td>
<td>5.1%</td>
</tr>
<tr>
<td>1000</td>
<td>W</td>
<td>81.8%</td>
<td>84.3%</td>
<td>0.0%</td>
<td>2.3%</td>
<td>13.4%</td>
</tr>
<tr>
<td>1000</td>
<td>Without</td>
<td>79.4%</td>
<td>81.5%</td>
<td>0.0%</td>
<td>1.2%</td>
<td>17.3%</td>
</tr>
</tbody>
</table>

### V. Effect of Temperature

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Hg\textsuperscript{0} + Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{0} measured</th>
<th>Hg\textsuperscript{2+} measured</th>
<th>Hg\textsuperscript{P}</th>
<th>Hg unaccounted</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>78.7%</td>
<td>77.9%</td>
<td>0.8%</td>
<td>9.1%</td>
<td>12.2%</td>
</tr>
<tr>
<td>120</td>
<td>88.8%</td>
<td>86.9%</td>
<td>1.9%</td>
<td>2.8%</td>
<td>8.3%</td>
</tr>
<tr>
<td>150</td>
<td>91.5%</td>
<td>92.6%</td>
<td>0.0%</td>
<td>1.9%</td>
<td>5.4%</td>
</tr>
<tr>
<td>200</td>
<td>93.1%</td>
<td>98.3%</td>
<td>0.0%</td>
<td>0.0%</td>
<td>1.7%</td>
</tr>
</tbody>
</table>