SULFATION PHENOMENA UNDER OXY-FUEL CIRCULATING FLUIDIZED BED CONDITIONS

By

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Statement of Contribution of Collaborators

I, Michael Stewart, hereby declare that I am the sole author of each chapter in this thesis, unless otherwise indicated, as in the case of Chapters 2 – 5. In these chapters, I am the primary author, and performer of the work, with the exception of Chapter 3, wherein I was responsible for 50% of the authoring and experimentation work.

My supervisors, Dr. Arturo Macchi of the Department of Chemical and Biological Engineering, University of Ottawa, and Dr. Edward John Anthony of CanmetENERGY, Natural Resrouces Canada, Ottawa, supervised my work during the M.A.Sc. program.

Signature: ________________________________ Date: ___________________

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Abstract

Oxy-fuel fired circulating fluidized bed combustion (CFBC) provides a means to generate electrical power while reducing anthropogenic CO_2 while at the same time reducing the acid-rain precursor, SO_2 by utilizing *in-situ* limestone addition. Although the technology has been around for 30 years, it has only recently been gaining considerable attention, with a handful of pilot-scale units worldwide. Oxy-fuel is largely similar to standard air-fired combustion but differs in a few key respects, one of which is in the elevated concentrations of CO_2 and H_2O (up to 90% and 30%, respectively).

The effects and mechanism of action of these gasses on limestone sulfation have long been a matter of debate in the literature. Using a thermogravimetric analyzer (TGA) and tube furnace (TF), the effects of elevated gas concentrations on the sulfation of limestone are studied using synthetic air-fired and oxy-fired flue gases (SO_2: 3800 ppm, CO_2: 12.5 – 82.5%, O_2: 2.5%, H_2O: 0 – 30%) at 850 °C. An explanation is provided for the contradictory findings in the literature in terms of the TGA/TF results. Microstructural analysis of sulphated samples using scanning electron microscopy (SEM), nitrogen adsorption analysis, and helium pycnommetery is used to support a mechanism based on solid-state diffusion.

Further TF experiments are used to elucidate the effects and mechanism of action of H_2O and CO_2 on agglomeration of limestone particles during sulfation under oxy-fuel conditions.

Finally, using a pilot-scale oxy-fuel fired CFBC, the observations from the bench-scale experiments are tested in a realistic combustion environment. The effects of elevated CO_2 and H_2O associated with oxy-fuel combustion of petroleum coke on the catalytic NO_X formation over limestone are discussed and related back to the proposed mechanism of action H_2O and CO_2 on sulphation

Sommaire

La combustion avec de l'oxygène pur (i.e., oxy-combustible) en lit fluidisé circulant (LFC) permet de produire de l'électricité tout en réduisant les émissions anthropiques de CO_2 ainsi que le précurseur des pluies acides, du SO_2, en utilisant du calcaire de façon in-situ. Bien que la technologie existe depuis 30 ans, il a récemment pris de l'attention avec l'opération de quelques unités à l'échelle pilote dans le monde. La combustion avec de l'oxygène pur est en grande partie semblable à la combustion standard avec de l'air, mais diffère sur quelques points clés, dont l'un est les concentrations élevées de CO_2 et H_2O (jusqu'à 90% et 30%, respectivement).

Les effets et le mécanisme d'action de ces gaz sur la sulfatation du calcaire ont longtemps été un sujet de débat dans la littérature. A l'aide d'un analyseur thermogravimétrique (ATG) et un four tubulaire (FT), les effets de concentrations élevées de gaz sur la sulfatation du calcaire sont étudiées en utilisant des gaz d'échappement typiques de la combustion à l'air et à l'oxygène pur (SO_2: 3800 ppm, CO_2: de 12,5 à 82,5% , O_2: 2,5%, H_2O: 0 à 30%) à 850 ° C. Une explication est fournie pour les résultats contradictoires dans la littérature en termes de résultats obtenues avec les ATG/FT. Une analyse microstructurale des échantillons sulfatés utilisant la microscopie électronique à balayage (MEB), l'analyse d'adsorption d'azote et la pycnométrie d'hélium est utilisée pour soutenir un mécanisme basé sur la diffusion à l'état solide.

D'autres expériences dans le FT sont utilisées pour élucider les effets et le mécanisme d'action de H_2O et CO_2 sur l'agglomération des particules de calcaire au cours de la sulfatation dans des conditions d'oxy-combustible. Enfin, en utilisant un LFC à l'échelle pilote, les observations des expériences en laboratoire ont été testés dans un environnement réaliste de combustion. Les effets de concentrations élevées de CO_2 et H_2O associés à la combustion oxy-combustible du coke de pétrole sur la formation catalytique de NO_x sur du calcaire sont discutés et reliés au mécanisme proposé de H_2O et CO_2 sur la sulfatation

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Preface

The work described in this thesis is an amalgamation of the work performed by the author between September 2009 and December 2010. All of the work described herein has been published, submitted for publication, or presented at symposiums amongst the author's fellow researchers. This thesis has been written in a manner that is consistent with the format of others, that have consisted of a collection of similarly identified material, submitted to the University of Ottawa over the years. As such, this thesis is divided into six chapters. The first chapter serves as an introduction and background to the work performed. This chapter is intended to underline the importance of the work performed, and as a supplement to the introductions of subsequent chapters. In some cases, the introduction to another chapter was sufficient such that further expansion on the topic was not necessary in the first chapter. Chapters 2 – 5 reflect individual publications or conference papers and are the core of this thesis. In these chapters, the arguments of Chapter 1 are put to the test and expanded upon. Finally, Chapter 6 concludes the thesis by reflecting upon the interaction between, and results of, the studies performed, and provides recommendations for future work in the area.

CHAPTER 1 : INTRODUCTION

Introduction

The Case for Coal

There is no question that average global temperatures are on the rise. This past year (2010), average surface temperatures in Canada exceeded the mean by over 3°C, the largest deviation recorded since Environment Canada began collecting climate data in 1948 *(1)*. At the same time, atmospheric concentrations of CO_2 have steadily increased since the industrial revolution, and have seen an exponential increase in recent years *(2)*. Whether the trends of these two environmental anomalies imply a causal relationship or mere coincidence is still a matter of great debate. However, the adverse influence of human kind on the rapid increase of CO_2 in the atmosphere through the burning of fossil fuels is no longer refutable.

Some governments take responsibility for their country's greenhouse gas emissions, and so they encourage innovation in the renewable energy technology sector and implement strategies to mitigate or eliminate emissions from the more carbon-heavy sectors. Electrical power generation from coal or other fossil fuels such as natural gas represents the single largest emitter of CO_2 worldwide, and thus presents itself as a clear target for reducing anthropogenic carbon emissions. In 2010, Canada's Minister of the Environment announced a plan to phase out all 51 of the country's coal-fired power plants at the end of their service lives, plants which satisfy nearly 20% of the country's electrical power demand. By 2025, 33 out of 51 of these coal-fired plants will be closed. A lesser-known detail of the plan is that all of the shuttered plants will be replaced by natural gas-fired boilers to meet increasing demand *(3)*. While the switch from coal to natural gas will increase the net efficiency of each facility (and thus lower CO_2 emissions, overall), there are also limitations and uncertainties associated with the use of natural gas. Without additional back-end technologies, such as carbon capture and sequestration

(CCS), the replacement of coal plants by natural gas plants only implies a small reduction in GHGs, not their elimination. Furthermore, the price of natural gas has fluctuated by 700% over the last 10 years *(4)*, calling into question the economical sustainability of such installations. And perhaps the most obvious but nevertheless important limitation to such a unilateral plan is the inevitable exhaustion of remaining natural gas reserves. As the plan places an increasing demand on existing gas reserves, they will be depleted even faster than ever.

While some reports suggest that we have more than 60 years of coal remaining, a more conservative (radical) estimate of the worldwide "peak" production year of coal is 2025, followed by a steady decline in production thereafter, until about 2100 when production ceases altogether *(5)*. Canada alone has more than 10 billion tonnes of coal reserves, amounting to a resource more energy-rich than all of the country's oil, natural gas, and oil sands combined *(6)*. Thus, in the absence of revolutionary new technology, or new source of energy in the next 25 or so years, coal will likely continue to be used or at least eventually used once the "cleaner" resources are exhausted. It is projected that coal will continue to be mined and, for the most part, burned at the rate of about 4500 million tonnes per year worldwide, adding to the atmosphere 1000 billion tonnes of CO_2 until coal resources are finally depleted.

Oxy-fuel combustion

To mitigate the amount of CO_2 that would be released to the atmosphere by the burning of fossil fuels and/or biomass, a fleet of new CO_2 capture technologies are being developed. CO_2 capture technologies go about converting a fuel source into energy while producing a near pure (90-95%) stream of CO_2 for sequestration. The technologies currently receiving the most attention are:

1. Integrated gasification combined cycle (IGCC) with air separation to produce O_2
2. Chemical looping combustion, wherein a solid metal oxygen carrier is cycled between a reactor and regenerator (e.g. Ni, Cu, or Fe as oxygen carriers, or alternatively CaO as in calcium-looping technology as a CO_2 carrier)
3. Standard pulverized fuel coal combustion with back end flue gas scrubbing (such as by amines or NH_3)
4. Oxy-fuel combustion with an external solids heat exchanger to regulate the combustion temperature in the case of oxy-fuel FBC
5. Oxy-fuel combustion with internal recycle via oxygen jets to regulate the combustion temperature.

For a more detailed review of pre-combustion, *in-situ* and post-combustion capture technologies, the interested reader is referred to *(7)*.

One CO_2 capture technology that has shown considerable promise is oxy-fuel combustion. Oxy-fuel combustion is largely similar to standard air-fired combustion but differs in one key respect: instead of using air to fuel the combustion, pure or near-pure oxygen is used. With combustion in an atmosphere of pure oxygen, the resultant flue gas is nearly-pure H_2O and CO_2, and after condensation of the H_2O component, CO_2 can then be sent for sequestration in deep geological formations. Figure 1-1 shows a simplified block flow diagram of the process.

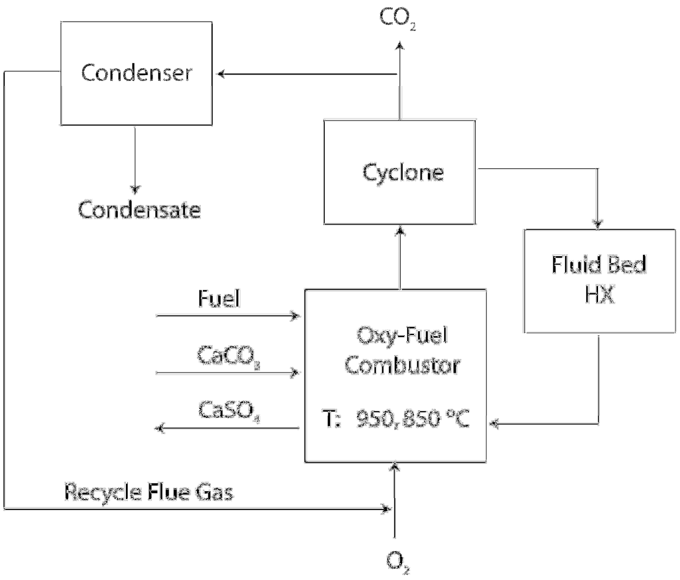

Figure 1-1 Simplified process schematic of a typical oxy-fuel fluidized-bed combustion scheme.

Since the boiler materials required to sustain the high temperatures associated with the adiabatic combustion of a solid fuel in pure oxygen are not yet available, the recycle of 60-80% of the flue gas is required to reduce flame temperatures. The recycle can be either wet or dry or somewhere in between to control the concentration of $H_2O_{(g)}$ in the boiler.

Due to the similarities to air-firing technology, oxy-fuel is especially attractive as a means for clean power generation since it can be retrofitted to existing power generation stations. Due to the increased proportions of CO_2 and $H_2O_{(g)}$ with oxy-fuel combustion, the emissivity of the flue gas is increased, so retrofitted pulverized fuel or fluidized bed combustors can utilize existing heat transfer surfaces. For new installations, since the amount of flue gas produced is reduced by up to 80%, oxy-fuel combustion is associated with a reduction in boiler area of about 50%, and thus, substantial cost savings over its air-fired counterpart and competing technologies *(8)*.

Oxy-fuel technology for pulverized fuel combustors has been well-studied, but investigation into oxy-fuel fluidized bed combustion (FBC) has only just recently been gaining attention *(9)*. FBC connotes a number of additional advantages, summarized by Dennis in his PhD dissertation *(10)*:

1. Lower combustion temperature in comparison to other technologies such as pulverized coal combustion serves to eliminate production of thermal NO_x, as well as the potential for ash fusion, thereby reducing fouling of heat transfer surfaces. It also reduces the potential for vaporization of alkali metal salts, thus producing lower metals emissions.
2. High heat fluxes are possible, resulting in a reduction of equipment size and cost.
3. FBC is highly adaptable and can burn almost any fuel or biofuel and in any combination.
4. The main advantage of FBC is that in-situ sulphur capture can be employed with limestone, reducing sulphur emissions from stack gasses and eliminating the need for downstream flue gas desulfurization.

While FBC technology is highly adaptable to burning any type of fuel, pulverized fuel combustion requires high quality coals, and cannot be readily adapted to fire biomass. Furthermore, if biomass is considered a carbon-neutral fuel, oxy-fuel FBC with carbon capture and sequestration presents itself as a carbon-negative technology (where CO_2 is scrubbed from the atmosphere by the biomass, and then stored underground).

As a slight variant to FBC, circulating fluidized bed combustion (CFBC) utilizes higher superficial gas velocities to achieve higher solids fluxes. CFBC is a well-established combustion technology for firing marginal fuels such as biomass, waste-derived biomass and high sulfur fuels. The technology began to achieve commercial importance in the 1970s and there are now several hundred large scale utility-operated boilers throughout the world *(11)*.

Based on the advantages of oxy-fuel technology for CO_2 capture, and of CFBC technology, it is logical that oxy-fuel fired CFBC technology has been the target of considerable attention in recent years. However, to this day, there are very few pilot-scale units in operation worldwide. Most tests are being done at the <100 kW scale, or with bottled flue gasses and are thus not ideal for scale-up purposes. To the knowledge of the author, there are only two facilities that are operating pilot-scale oxy-fuel CFBC units with flue gas recycle: VTT (the Technical University of Denmark) and CanmetENERGY in Ottawa. At Canmet, there are two units in operation, a 0.8MW unit and a smaller 100 kW unit on which the tests described in this thesis were performed.

Limestone in FBC

Sulfur is present to some degree in most carbonaceous fuels ranging from 0.1% for low sulfur coal up to 6% for petroleum coke. When the fuel is burned, most of the sulfur is released as SO_2, a precursor to acid rain and other detrimental environmental effects. In the 1980s, there was growing concern over the effects of SO_2 emitted from stationary combustion facilities and as a result, stringent environmental controls were put in place by most developed nations on emissions of SO_2 and NO_X.

One of the advantages of (C)FBC is its ability to utilize *in-situ* limestone for a high degree of sulfur capture. Limestone crushed to an appropriate particle size is injected into the furnace with the fuel. At combustion temperatures, the limestone undergoes a reaction with SO_2

that is termed sulfation. The resultant product is environmentally benign and can be landfilled with the remaining ash components or recycled for use in the cement and drywall industry.

At combustion temperatures, limestone is in dynamic equilibrium with its products, lime (CaO) and CO_2, as shown in reaction (1). The equilibrium relationship given by Baker *et al. (12)* (2) dictates at what CO_2 concentration (or temperature) does limestone undergo calcination to form lime.

$$CaCO_3 \leftrightarrow CaO + CO_2 \tag{1}$$

$$\log_{10} P_{CO_{2,eq}} = 7.079 - \frac{8308}{T} \tag{2}$$

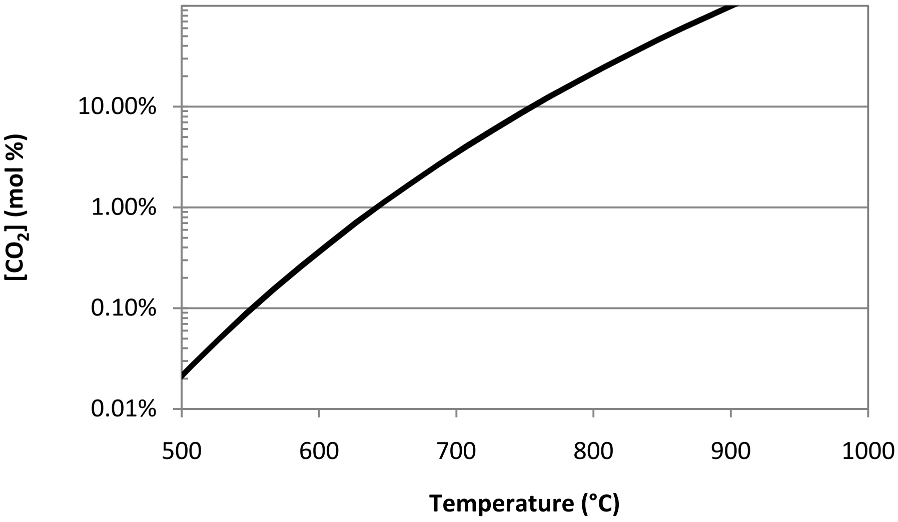

Figure 1-2 Equilibrium relationship between $CaCO_3$ and CaO, given by Baker *et al. (12).*

Figure 1-2 shows that for air-fired combustion at a typical FBC operating temperature of 850°C with an average concentration of CO_2 in the flue gas of about 15%, limestone exists as lime. Thus, for air-fired combustion, sulfation proceeds via an indirect route, *i.e.* indirect sulfation:

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 \qquad (3)$$

On the other hand, under oxy-fuel conditions, CO_2 concentrations in the flue gas are typically around 90% and thus, limestone does not calcine appreciably until 890°C. Thus, oxy-fuel sulfation proceeds via the direct route:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2 \qquad (4)$$

Sulfation via reaction (4) also occurs under pressurized fluidized bed combustion (PFBC) conditions. The exact combination and order of reaction steps have been debated by many *(13, 14)*, for example, whether SO_2 must first form SO_3 before reaction, but for all intents and purposes of this work, the assumption of overall validity of reactions (3) and (4) is deemed sufficient.

From a practical standpoint, the overarching interest in sulfation over the last thirty years has been to determine what factors influence the rate of reaction, although other incentives do exist, such as the potential to reduce sulfation-related agglomeration. In practice, sulfation rarely goes to completion, and a typical conversion value of a used sorbent that would be removed from the combustor and landfilled is 45% *(16)*. Since an increase in sorbent utilization of only 5% would reduce the amount of limestone required for, and ash produced by, a 500MW_e boiler by over 50 tonnes per day, there is a clear economic and environmental advantage associated with improvements in sulfur capture efficiency. As such, many studies have been directed towards this end.

Although indirect and direct sulfation proceed via different intermediates, most of the factors that affect one reaction affect both reactions in the same way. The classically identified factors that most affect the rate of the reactions are, in decreasing order of significance: concentration of SO_2, temperature, limestone microstructure (surface area, pore size, etc.), limestone composition (%Ca content, presence of impurities), concentration of CO_2, and concentration of O_2 *(15,16)*. In general, increasing SO_2, temperature, %Ca content, impurities and surface area all have positive effects on the reaction, while increasing CO_2 has a negative effect. However, the picture becomes less clear with most of these factors at elevated conditions or concentrations. For example, while increasing temperature has a positive effect on the reaction, there is a point at which it becomes detrimental to reaction rates. This point is termed the temperature maximum of sulfation, and is still largely unexplained, along with the mechanisms of action of the other factors *(16)*.

Influence of CO_2 on the Sulfation of Limestone

As mentioned previously, oxy-fuel combustion is associated with an increase in average CO_2 concentration in the flue gas to about 90% from the air-fired case of 15%. The effects of such a change have been reported in the literature dedicated to the direct sulfation reaction. The purpose of this review is to make a chronology of the important findings on the topic of $CaCO_3$ and CaO sulfation to see how views and theories evolved, converged and diverged over time. This is not meant to be a comprehensive presentation of all studies on the subject, but rather those that are most relevant to the current discussion. It is noted that the author is aware of the works of Hsia *et al.*, Iisa *et al.*, Alverez *et al.*, Fueretes *et al.*, and Duo *et al.*, and furthermore, many of their works are referenced in subsequent chapters. While important to sulfation research, these works do not touch on the effects of changing concentrations of CO_2 or H_2O.

One of the earliest studies on direct sulfation was by Ulerich *et al.*, who used a pressurized thermogravimetric analyzer (TGA) to study the effects of CO_2 *(17)*. Using a synthetic flue gas (3000 ppm SO_2, 4% O_2, 6-9% CO_2 and N_2 balance at a total pressure of 10 atm), the authors concluded that CO_2 had a negative effect on the reaction. Since the study investigated a number of factors, the cause of such an effect was not discussed.

Later, Snow *et al.* revisited the subject, investigating CO_2 concentrations between 2-95% *(18)*. Using a thermogravimetric analyzer (TGA) with a synthetic flue gas (3000 ppm SO_2, 5% O_2, and N_2 balance at 1 bar), the authors concluded that the CO_2 partial pressure had no effect on the rate of reaction of limestone particles sized 10-12 μm. However, since it was well known to the authors that temperature had a positive effect on the reaction, and due to the delay of calcination with increasing CO_2 concentration according to the limestone-lime equilibrium relationship, the authors concluded that increasing the decomposition temperature greatly enhanced conversion. To model the reaction, the authors proposed a chemical reaction-limited shrinking-core model, which seemed to provide adequate fit for the small diameter particle sizes used. This early study concluded by underlining the advantage of avoiding limestone decomposition during sulfation, a fact which would be later leaned upon by proponents of pressurized and oxy-fuel FBC. Interestingly, the authors did not point out that, while the increased CO_2 partial pressure delayed calcination, thus increasing conversion, their data also show an increase in reaction rate after calcination with increasing CO_2 concentration, suggesting that the CO_2 may actually enhance conversion under certain conditions.

At the same time, authors Hajaligol *et al.* *(19)* were also investigating the reaction, but from a microstructural standpoint. In their work, it was suggested that the direct sulfation reaction entailed higher reaction rates than indirect sulfation due to the formation of a more porous product layer than in the case of indirect sulfation. They reported that both diffusion resistance and chemical kinetics were controlling the reaction at 50% conversion for small particles (2-12 µm), and that beyond this point, diffusion control became more dominant. The authors did not investigate the effects of varying the concentration of CO_2.

In an effort to reconcile the somewhat contradictory findings from earlier work, Tullin *et al.* performed a study entirely dedicated to investigating the effects of CO_2 on direct sulfation *(20)*. Using a similar setup to the other two studies (TGA with synthetic flue gas, 3000 ppm SO_2, 4% O_2, 30-80% CO_2 and N_2 balance at atmospheric pressure), Tullin *et al.* found that increasing the CO_2 from 30% to 80% resulted in a 26% decrease in the initial rate of reaction for particles sized 1 – 5 µm. Assuming a diffusion-limited, shrinking-core model *(21)*, the authors proposed that the influence of CO_2 on reaction rate was due to the lower diffusion coefficient of SO_2 in CO_2, but cautioned that this may actually play only a minor role in affecting the reaction rate. With the work of Tullin *et al.*, it seemed that the role of CO_2 was clearly inhibitory, and its effects on sulfation were not revisited until many years later.

In 2000, Liu *et al.* *(22)* reinvestigated direct sulfation and the effects of CO_2 and benchmarked reactions rates against indirect sulfation. In this study, the authors chose to use a quartz tube furnace (TF) with online gas analyzers, in place of the traditional TGA, allowing for a more realistic interpretation of results. Using a synthetic oxy-fuel flue gas (1920 ppm SO_2, 10% O_2, 20-80% CO_2, Ar balance at atmospheric pressure), they found that the direct sulfation reaction was up to six times faster at higher conversion levels (>45%) than the indirect reaction. Furthermore, increasing the concentration of CO_2 from 20% to 40% also resulted in increased conversion for the indirect reaction, and increased reaction rates in the latter half of the time scale investigated. Yet again a diffusion-limited shrinking core model was proposed to model the reaction, but the authors warned that since the reaction is complex, estimation of the effective diffusivity parameter would vary considerably from case to case. Unfortunately, the authors did not vary the concentration of CO_2 under direct sulfation conditions. However, this was the first study where the effects of CO_2 were shown clearly for sulfation in general: with increasing CO_2 concentration, initial reaction rates decreased, while later reaction rates increased. When these results are compared to the work of Hajaligol *et al. (19)*, it seems that the role of CO_2 during the kinetically-controlled stage is that of inhibition, while during the diffusion controlled stage, it is one of promotion.

In a series of papers published between 2006 and 2009, the Technical University of Denmark contributed substantially to the knowledge of direct sulfation, starting with a review paper on the subject by Hu et al. *(15)*. The authors identified a number of gaps in the research at the time, focusing particularly on the lack of agreement in previous work on the mechanism of reaction, applicability of models, and effects of reaction kinetic parameters, such as gas concentrations. They also countered the widely-cited suppositions that back-diffusion of CO_2 was the cause of increased porosity that in turn reduced diffusional resistance, as originally proposed by Snow *et al.* and Hajiligol *et al.*.The counter-claim was that direct sulfation required 1.5 moles of gas for each mole of CO_2 released, and thus there was a net influx of gas instead of outflow. A number of other more positive conclusions were made about other areas of interest, but in summary, the authors still concluded by stating that it seemed what was known about sulfation was far outweighed by what was not. It was this observation that prompted the same investigators to publish a paper that attempted to address the gaps identified and contradictory findings of others. In this work, a TF was used with online gas analysis and a synthetic flue gas (1800 ppm SO_2, 3% O_2, 10-60% CO_2 with N_2 balance at atmospheric pressure). At 823 K, it was found that *average* conversion rates decreased with increasing CO_2 concentration, once again casting doubt on earlier work that showed enhancement. However, it was not mentioned over what period of time average conversion rates were measured. As such, measurements could have been made mostly during the kinetically-controlled regime where increased CO_2 would push the equilibrium reaction away from the products, thus skewing the data. Furthermore, since the authors performed the work with the intention of studying direct sulfation in the cyclone preheater of a cement kiln process, the temperatures employed were much lower than for FBC combustion processes. Even so, with this work, it seemed the effects of CO_2 on sulfation were less clear than ever.

On the other hand, the authors set forth a strong argument for the invalidity of the shrinking-core model: direct sulfation involves a nucleation-grain growth process (as observed by SEM) and that the reaction is very strongly affected by solid-state diffusion processes, both of which are ideas not treated by the shrinking-core model. They even proposed their own model in its place which the authors later applied to the results of another study in 2008 *(24)*. This time, the investigation was on the initial kinetics of the reaction, the idea being that the most accurate picture of sulfation would come at the lowest of conversion levels. The authors devised an interesting entrained flow reactor that was able to measure conversions as low as 0.001 at times between 0.1 and 0.6s. This was the first time that conversion rates at such low conversions had been measured. With a synthetic flue gas (1800 ppm SO_2, 3% O_2, 8-15% CO_2 and N_2 balance at atmospheric pressure) at 873K, it was shown yet again that the effect of CO_2 was clearly that of inhibition in the early stages of sulfation.

The most recent research on direct sulfation comes from Chen *et al. (25,26)*. In the interest of furthering oxy-fuel pulverized fuel sulfation, a drop tube furnace capable of achieving accurate conversion measurements at as low as 0.25 s was used. With a synthetic flue gas (3000 ppm SO_2, 20% O_2, 20-80% CO_2 and N_2 balance at atmospheric pressure), Chen *et al* .performed tests similar to Hu *et al.*, but with an important difference in temperature: the tests of Chen *et al.* were performed in the range of 1073 K to 1473 K, a temperature range more in line with that of fluid bed combustion. The authors found that increasing the concentration of CO_2 from 20% to 80% had the effect of decreasing the reaction rate during the kinetically controlled stage, while increasing the rate in the diffusionally-controlled stage, for a substantial net increase in reaction rate over a longer period of time, similar to the findings of Liu *et al.*, but contrary to the work of Hu *et al.*.

Using methods of microstructural analysis of the limestone particles, the authors concluded that the enhanced conversion during direct sulfation was due to the continuous formation of nascent CaO sites, and because of a decreased resistance to diffusion related to the continuous formation of CO_2 (back-diffusion). The authors also adopted the solid-state diffusion model of Hu *et al.* to represent the reaction.

However, the fast reaction times employed by the authors do not give a clear picture of what would happen over the course of hours. While a few seconds of reaction time is important in the cement and pulverized coal combustion industries, FBC boiler residence time can be hours. Thus for FBC, the study of sulfation well into the diffusionally-controlled regime is of interest, especially since most studies only investigate the reaction at times up to 1 – 2 h. Moreover, it seems that all of the direct sulfation studies are in disagreement with at least one or more study, likely due to the lack of a common benchmark time scale. Since CO_2 affects the reaction rate in opposite ways depending on how far the reaction has progressed, different windows in which reaction rates are measured can easily result in the observation of conflicting trends (see Table 1-1 for a summary of the effects of CO_2).

Table 1-1 Summary of past studies on the effects of CO_2 on indirect and direct sulfation.

Reference	**Conditions**	**Apparent Effect on Rate**
Hu *et al. (23)*	Apparatus: Tube furnace (differential reactor) Mode: Direct T & P: 823 K, 1 bar SO_2: 1800 ppm, O_2:3 %, CO_2: 10 – 60% H_2O: 0% Reaction time: 1-2 h	[↓] Inhibition due to decreased number of carbonate ion vacancies in crystal lattice resulting in slower ion diffusion.
Chen *et al. (26)*	Apparatus: Drop-tube furnace Mode: Direct T & P: 1073 – 1473 K, 1 bar SO_2: 3000 ppm, O_2:0 – 20%, CO_2: 20 – 80% H_2O: 0% Reaction time: 0.25 - 4 s	[↓↑] Inhibition at low temperature, promotion at high temperature due to continuous formation of nascent CaO and porous layer.
Hu *et al. (24)*	Apparatus: Tube furnace (differential reactor) Mode: Direct T & P: 873 – 973 K, 1 bar SO_2: 1800 ppm, O_2: 3%, CO_2: 8 – 15% H_2O: 0% Reaction time: 0 – 0.6 s	[↓] Inhibition due to decreased number of carbonate ion vacancies in crystal lattice resulting in slower ion diffusion.
Ulerich *et al. (17)*	Apparatus: TGA Mode: Direct T & P: 1088 K, 10 bar SO_2: 5000 ppm, O_2:10.5 – 14%, CO_2: 6– 9% H_2O: 0% Reaction time: unknown	[↓] Inhibition. Mechanism not described.
Tullin *et al. (20)*	Apparatus: TGA Mode: Direct T & P: 1023 – 1123 K, 1 bar SO_2: 3000 ppm, O_2:4 %, CO_2: 30 – 80 % H_2O: 0% Reaction time: 1 – 2 h	[↓] Inhibition due to decreased gas diffusion coefficient of SO_2 in CO_2.
Suyadal *et al. (28)*	Apparatus: TGA Mode: Indirect T & P: 1173 K, 1 bar SO_2: 6000 ppm, O_2:5 %, CO_2: 2 – 10 % H_2O: 5% Reaction time: 2 h	[↑] Promotion. Mechanism not described.
Dennis *(10)*	Apparatus: FBC Mode: Indirect T & P: 1073– 1248 K, 1 bar SO_2: 2300 ppm, O_2:1 %, CO_2: 0 – 20 % H_2O: 0% Reaction time: 1 – 2 h	[↓] Inhibition due to back diffusion of CO_2.
Liu *et al. (22)*	Apparatus: Tube furnace Mode: Indirect/Direct T & P: 1123 K, 1 bar SO_2: 1920 ppm, O_2:10 %, CO_2: 20 – 80% H_2O: 0% Reaction time: 30 min	[↓↑] Inhibition at conversions below 0.45, promotion thereafter, due to decreased pore blocking.

Chen *et al. (25)*	Apparatus: TGA Mode: Indirect/Direct T & P: 1123 – 1173 K, 1 bar SO_2: 3000 ppm, O_2:0 – 20%, CO_2: 20 – 80% H_2O: 0% Reaction time: 1-2 h	[↑] Promotion due to back-diffusion of CO_2 resulting in porous layer.
Snow *et al. (18)*	Apparatus: TGA Mode: Indirect/Direct T & P: 1073 – 1373 K, 1 bar SO_2: 3000 ppm, O_2:5 %, CO_2: 2 – 95 % H_2O: 0% Reaction time: 30 min	[−↑]Null effect at low temperature, promotion at high temperature due to delay of onset of calcinations.
Hajaligol *et al. (19)*	Apparatus: TGA Mode: Indirect/Direct T & P: 973 – 1173 K, 1 bar SO_2: 3000 ppm, O_2:5 %, CO_2: 95 % H_2O: 0% Reaction time: 75 min	[↓↑] Inhibition at low temperatures (973 K), promotion at high temperatures (1173 K) due to back diffusion of CO_2.

Influence of $H_2O(g)$ on the Sulfation of Limestone

Whether it is the combustion of biomass, coal or petroleum coke, and no matter the technology in which the combustion takes place, $H_2O_{(g)}$ is ubiquitous in combustion flue gasses. A simple calculation can show that a typical flue gas concentration of $H_2O_{(g)}$ for coal is around $15\%_V$. In the case of oxy-fuel combustion, this number rises to upwards of 30% if the recycled flue gas is not cooled to the point of condensation. Thus, the investigation of the effects $H_2O_{(g)}$ on sulfation is logical for air-fired sulfation, and essential for oxy-fuel combustion.

However, unlike CO_2, reports on the effects of $H_2O_{(g)}$ on sulfation are generally absent from the literature, most likely due to some of the early workers in the subject area giving indication of a null effect. In his PhD dissertation, Dennis *(10)* studied indirect sulfation with steam concentrations ranging between 0 and 6.5%. Using a small (78 mm diameter) bubbling bed combustor and synthetic flue gas (2300 ppm SO_2, 0.5 – 6.5% O_2, 0 – 6.5% $H_2O_{(g)}$ with the balance N_2 at atmospheric pressure) at 1073K, he noted no systematic effect of H_2O. The timescale investigated for the $H_2O_{(g)}$ tests was about 2 h and the maximum conversion achieved was roughly 0.35. Dennis noted that his findings were in agreement with work by Johnson *et al.* *(27)*, the only other study at the time that investigated the effects of $H_2O_{(g)}$.

However, in another study, using a pilot-scale internally circulating fluidized bed desulfurization unit to study limestone attrition, Chu *et al.* *(29)* showed that increasing the relative humidity of the fluidizing gas (air) from 1% to 3% resulted in an increase in calcium utilization by about 15% after 6 h. The concentration of SO_2 in these tests was 500 ppm and the authors did not report the reaction temperature. However, it should be noted the temperature was likely much lower than that seen in FBC. The authors developed a model for limestone attrition that took into account the effects of $H_2O_{(g)}$ as a parameter in their model. However, no sulfation model was developed. Perhaps one difference that could help explain the significantly divergent findings conclusions of Chu's work and Dennis' is the time scale that was investigated. For Chu, typical sulfation times were up to 10 h, whereas Dennis' tests were in line with most TGA studies at only 2 h.

Despite a handful of studies showing strong effects of steam on sulfation, there are few papers that investigate the effects explicitly, especially for indirect sulfation. Moreover, a review of 43 studies on sulfation that either had the sole intention of developing a sulfation model or included a modelling component revealed that there is only one model in the open literature that includes the effects of $H_2O_{(g)}$ on calcium utilization *(28)* (it should be noted that this model predicts a *negative* impact of $H_2O_{(g)}$ on sulfation). If the findings of some works are correct about the significant changes effected by small changes steam concentration then it appears that a crucial factor in the sulfation reaction may have been missed.

Attacking this issue head-on, Wang *et al.* recently published a study on the effects of $H_2O_{(g)}$ on indirect sulfation *(30)*. Using a TGA, the authors found a significant enhancing effect of $H_2O_{(g)}$ at concentrations of up to 10%. Although a differentiation between regimes was not made at the time, it was clearly shown that water had no effect during the initial kinetically-controlled regime, and enhancement only occurred during the diffusionally-controlled regime, indicating a reduction in gas-phase diffusion resistance or enhancement of solid-state ion mobility. However, the authors suggested that the formation of $Ca(OH)_2$ was the cause for enhancement, which is problematic since the compound is not thermodynamically favourable at FBC temperatures. Moreover, if the intermediate product was present, it should also be so during the kinetically controlled regime thus enhancing the reaction throughout both regimes.

The conflicting conclusions from a number of different investigators (see Table 1-2 for a summary) demand a rigorous investigation of the effects of $H_2O_{(g)}$ under varying conditions and for longer timescales than those investigated previously. Furthermore, if there is in fact an effect of $H_2O_{(g)}$ on the sulfation reaction, an attempt should be made to explain the mechanism through which the effect is produced, since no satisfactory mechanism has yet been produced.

Table 1-2 Summary of past studies on the effects of H_2O on indirect and direct sulfation.

Reference	**Conditions**	**Apparent Effect on Rate**
Dennis *et al. (10)*	Apparatus: BFB Mode: Indirect T & P: 1073 K, 1 bar SO_2: 2300 ppm, O_2: 0.5 – 6.5%, H_2O: 0 – 6.5% Reaction time: 1 – 2 h	[–] Null. Mechanism not discussed.
Chu *et al. (29)*	Apparatus: CFB Mode: Indirect T & P: unknown (low) temperature K, 1 bar SO_2: 500 ppm, H_2O: 1 – 3% Reaction time: 0 - 20 min	[↑] Promotion. Mechanism not discussed.

Suyadal *et al. (28)*	Apparatus: BFB (batch) Mode: Indirect T & P: 1173 K, 1 bar SO_2: 6000 ppm, O_2: 6%,CO_2: 10% H_2O: 0 – 5% Reaction time: 0 - 120 min	[↓] Inhibition. Mechanism not discussed.
Johnson *et al. (27)*	Apparatus: TGA Mode: Indirect T & P: Unknown SO_2: 3000 ppm, O_2: 5%,CO_2: unkn. % H_2O: unkn.% Reaction time: unknown	[−] Null. Mechanism not discussed.
Wang *et al. (30)*	Apparatus: TGA Mode: Indirect T & P: 923 K, 1 bar SO_2: 1750 ppm, O_2: 3%,CO_2: 15% H_2O: 0 – 10% Reaction time: 0 - 80 min	[↑] Promotion due to formation of $Ca(OH)_2$ intermediate.
Hajaligol *et al. (19)*	Apparatus: TGA Mode: Direct T & P: 1173 K, 1 bar SO_2: 3000 ppm, O_2: 5%,CO_2: 95% H_2O: 0 – 12% Reaction time: 0 - 3 h	[↑] Promotion. Mechanism not discussed.
Hu *et al. (23)*	Apparatus: Tube furnace Mode: Direct T & P: 923 K, 1 bar SO_2: 1800 ppm, O_2: 3%,CO_2: 30% H_2O: 0 – 7.5% Reaction time: 0 - 20 min	[↑] Promotion due to improvement of solid-state diffusion.
Yhang *et al. (31)*	Mode: Direct Unknown conditions	[−] Null. Mechanism not discussed.

Research Outline

When this work was undertaken, the primary objective was to investigate the process of sulfation under oxy-fuel firing conditions at the bench scale. Specifically, since oxy-fuel combustion connotes elevated CO_2 and $H_2O_{(g)}$ concentrations in the flue gas, an investigation of the influence of these elevated concentrations on the sulfation reaction was necessary. Furthermore, amongst conflicting reports of the effects of $H_2O_{(g)}$ in the open literature, a satisfactory explanation of the mechanism of action was absent. Thus, the experiments were designed with this goal in mind. However, as the data were gathered and results analyzed, other phenomena were discovered and investigated, adding to and expanding on the original objectives of this thesis.

The work started at the lab-scale with an investigation of the microstructural phenomena associated with sulfation. To remove as many confounding factors as possible, the first tests were done in the simplest manner: using a TGA with bottled flue gasses, the influence of $H_2O_{(g)}$ on the indirect sulfation reaction was studied (direct sulfation tests would come later). This study was augmented with experimental tests using a tube furnace (more realistic environment) to generate samples of sufficient size to be analyzed at the microscopic scale, using scanning electron microscopy (SEM), nitrogen adsorption techniques (BET), and helium pycnommetery, with the objective of elucidating the mechanism. The influence of $H_2O_{(g)}$ and a possible mechanism of action is described in Chapter 2, entitled "**Enhancement of Indirect Sulfation of Limestone by Steam Addition**". The findings of this study were important not just for sulfation, but limestone phenomena, in general. Thus, the results of this study, along with the findings of Manovic *et al. (32)* were presented at the international CaOling conference on Calcium looping technology at Imperial College, London (www.CaOling.eu).

The significance of the findings described in Chapter 2 prompted the investigation into a related, but distinct phenomenon: agglomeration. From the tube furnace tests described in Chapter 2, it was observed that the sulfated samples were severely agglomerated after a comparatively short sulfation time. In the past, sulfation times of up to 100 days were required to produce significantly agglomerated deposits, while the work of Chapter 2 demonstrated significant agglomeration after just 3 days. This observation prompted the study of the effects of $H_2O_{(g)}$ on agglomeration of sulfated deposits and fouling of industrial boilers in Chapter 3, entitled "**Agglomeration of Sorbent Particles during the Sulfation of Lime in the Presence of Steam**". In this work, the same tube furnace is used with the aid of SEM methods to demonstrate the effects of $H_2O_{(g)}$ and CO_2 on agglomeration during sulfation, and to strengthen arguments made for the mechanism described in the previous work.

The next step was to extend the work started in the TGA and tube furnace on the effects of $H_2O_{(g)}$ on sulfation to include oxy-fuel combustion conditions. These tests determined the effects of changing the sulfation mode from indirect to direct (effect of CO_2) as well as the effects of $H_2O_{(g)}$ on the direct sulfation reaction. These results are discussed in Chapter 4, entitled "**Oxy-fuel Combustion in a Circulating Fluidized Bed Combustion Pilot Plant**". This chapter presents the results on a more practical backdrop with a review of the pilot-scale test unit and results of past oxy-fuel combustion tests at CanmetENERGY. This paper was presented alongside some preliminary pilot-scale test results with $H_2O_{(g)}$ addition at the international conference on Impacts of Fuel Quality in Lapland, Finland. The results of these tests spurred another parallel investigation into the impacts of elevated $H_2O_{(g)}$ concentrations on limestone activity in NO_X production in a fluidized bed.

A major limitation of bench-scale tests is that the results are often irreproducible in practice. In Chapter 5, entitled "**Effects of Steam on the Sulfation of Limestone and NO_X Formation in an Air- and Oxy-Fired Pilot-Scale CFB Combustor**", the pilot-scale CFBC at CanmetENERGY was used to verify the results from the work in Chapters 1 to 4. This work includes a deeper investigation of the bench scale results presented in Chapter 4, as well as a discussion on the mechanism of action of CO_2 and $H_2O_{(g)}$ on direct sulfation. Furthermore, as it was identified in some of the preliminary pilot-scale tests that NO_X formation was also greatly influenced by the presence of additional $H_2O_{(g)}$, the impacts and mechanism of action are discussed. This chapter ties together the discussion of the other chapters into a unified mechanism that describes their results and concludes by suggesting that the practical benefits of steam injection be tested in a commercial boiler.

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CHAPTER 2 : ENHANCEMENT OF INDIRECT SULPHATION OF LIMESTONE BY STEAM ADDITION

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Abstract

The effect of water ($H_2O_{(g)}$) on *in-situ* SO_2 capture using limestone injection under (FBC) conditions was studied using a thermobalance and tube furnace. The indirect sulphation reaction was found to be greatly enhanced in the presence of $H_2O_{(g)}$. Stoichiometric conversion of samples occurred when sulphated with a synthetic flue gas containing 15% $H_2O_{(g)}$ in under 10 h, which is equivalent to a 45% increase in conversion as compared sulphation without $H_2O_{(g)}$. Using gas pycnometry and nitrogen adsorption methods, it was shown that limestone samples sulphated in the presence of $H_2O_{(g)}$ undergo increased particle densification without any significant changes to pore area or volume. The microstructural changes and observed increase in conversion were attributed to enhanced solid-state diffusion in $CaO/CaSO_4$ in the presence of $H_2O_{(g)}$. Given steam has been shown to have such a strong influence on sulphation, whereas it had been previously regarded as inert, may prompt a revisiting of the classically accepted sulphation models and phenomena. These findings also suggest that steam injection may be used to enhance sulphur capture performance in fluidized beds firing low-moisture fuels such as petroleum coke.

Introduction

Sulphation can be used for the capture of SO_x from the flue gases of fossil fuel-fired power generation facilities. A number of processes and technologies, such as wet scrubbing and fluidized bed combustion (FBC), employ limestone for low-cost sulphur capture. FBC technology, including circulating FBC (CFBC), is particularly well suited for limestone addition due its ability to use limestone *in situ* without significant grinding or processing. Alternatives to *in situ* addition include downstream flue gas desulphurization as employed in pulverized coal combustors; however, these alternatives lack the simplicity and cost effectiveness of *in situ* sulphur capture by limestone addition for FBC technology, especially for high-sulphur coals (*1*).

Atmospheric pressure air-fired FBC sulphation can be represented by two global reactions, first calcination (2-1) and then sulphation (2-2) of the resulting porous lime product. Collectively these two reactions are known as indirect sulphation.

$$CaCO_3 = CaO + CO_2 \qquad (2\text{-}1)$$

$$CaO + SO_2 + 1/2O_2 = CaSO_4 \qquad (2\text{-}2)$$

Reaction (2-1) is endothermic (ΔH = 182.1 kJ/mol) while Reaction (2-2) is exothermic (ΔH = -481.4 kJ/mol); overall the two reactions are regarded as thermo-neutral at the Ca:S molar ratios usually employed.

Sulphation is characterized by two distinct reaction regimes: a first regime in which the rate is controlled by kinetics of chemical reaction and intra-pore gas diffusion; and a second one where the rate drops substantially as the control switches to a diffusion-limited process once a product layer ($CaSO_4$) forms and covers the inner surface of larger pores, and plugs smaller pores, due to the higher molar volume of $CaSO_4$ (*2-4*). Depending on initial porosity of the calcined material, the difference in molar volumes between the product and reactant results in an idealized maximum of conversion between 55-65% (*4,5*), assuming that the particle does not expand. However, only 30-40% conversion is normally seen in actual FBC units (*1*).

Limestone sulphation studies generally involve testing samples of lime particles in a fixed bed combustor, tube furnace, drop-tube furnace, or thermogravimetric analyzer (TGA). Samples are subjected to conditions designed to mimic combustion conditions and the time allowed for sulphation ranges anywhere from seconds for drop-tube furnaces to 3-6 h for TGA studies, although the maximum time is usually 2 h or less (*1*).

In a FBC, the particle's residence time depends on its size. Particles below 75 µm escape the cyclone in seconds to minutes, while larger particles can have mean residence times of tens of hours. In one study performed on a commercial-scale FBC (*6*), it was found that particles in the 100-200 µm size range have residence times of 4-20 h. Abanades *et al.* (*2,7*) have suggested that this longer residence time is an important factor which was ignored by classical studies and shown that several percent of additional conversion can be attributed to "residual sulphation", which is not commonly investigated in typical laboratory-scale tests. However, the present work demonstrates that an extension of reaction time accounts for more than just a few percent of conversion when using $H_2O_{(g)}$ in bench-scale tests.

$H_2O_{(g)}$ is a substantial constituent of flue gases from both coal and biomass combustion. It can be shown by a simple calculation for a bituminous Western Kentucky coal (10 wt% moisture) that there is 16% $H_2O_{(g)}$ in the flue gas when the coal is burned in 20% excess air with no recycle. $H_2O_{(g)}$ in the flue gas is higher still when a lower-rank coal, or biomass is burned and even higher still when circulating or oxy-fired FBC with flue gas recycle is employed. On the other hand, for some high-rank coals and petroleum cokes, the concentration of $H_2O_{(g)}$ in the flue gas may drop below 5%. Despite its large presence in combustion environments, the effects of

$H_2O_{(g)}$ are not well covered in the literature (*8,9*). Furthermore, classical sulphation models do not take the effects of $H_2O_{(g)}$ into consideration (*6,10*). It is, therefore, important to characterize the effects of $H_2O_{(g)}$ on sulphation in simulated FBC combustion environments in order to predict sulphur capture efficiency in real combustion systems if using tools like TGA.

For the few investigators who examined the influence of H_2O on sulphation, the effects and actual mechanism are subjects of contention. In early research Dennis reported no effect of $H_2O_{(g)}$ in the concentration range 0-7% (*11*), which agreed with the findings of Johnson *et al.* (*12*). Hajaligol *et al.* (*13*) suggested that $H_2O_{(g)}$ does not affect sulphation at the gas-solid interface, but their results show that it has a clear positive effect on the conversion of small limestone particles (10-12 μm) under high CO_2 partial pressures (direct sulphation). It was found that a $H_2O_{(g)}$ partial pressure of 0.06 bar. increased conversion after 3 h by ~15%, while increasing the concentration of $H_2O_{(g)}$ further had diminishing returns. It is not clear whether the other gas concentrations such as SO_2 were kept constant while changing H_2O partial pressure, nor did these workers provide any explanation for the observed effects. Recently, Wang *et al.* (*9*) clearly showed a very positive influence of $H_2O_{(g)}$ on indirect sulphation for different temperatures and particle sizes for up to 80 min sulphation. The observed increase in reaction rate was tentatively explained by the formation of transient $Ca(OH)_2$ (thermodynamically unstable at the reaction temperatures investigated). However, a weakness of the proposed mechanism relates to the authors' observation that $H_2O_{(g)}$ has a minimal effect during initial sulphation. Namely, if transient $Ca(OH)_2$ forms under the investigated conditions, and reacts more rapidly than CaO, then there should be an observed increase in the rate of initial sulphation, not just during the diffusion-limited stage. Thus, although there has been substantial investigation into the process of sulphation, there are still many uncertainties as well as disagreements on the numerous factors that influence the reaction, as well as the mechanism itself. Furthermore, sulphation performance in real FBC environments remains difficult to predict from laboratory-scale tests and models (*14*).

The purpose of the present study is threefold: first and foremost, to investigate the effects of $H_2O_{(g)}$ on the indirect sulphation reaction under conditions similar to the bulk concentrations and temperatures seen in FBC environments both macroscopically and microscopically in order to reconcile conflicting findings in the literature; secondly, to propose a physical basis and possible mechanism to help explain the observed effects; and finally, it is the authors' hopes that some of the newly developed fuel processing technologies will be deployed such that they may take advantage of the increased sulphur capture performance due to the phenomena described herein. One such technology, calcium looping combustion can enjoy the benefits of increased sulphur capture performance of spent CO_2 sorbents in a separate vessel. The interested reader is referred elsewhere (*10,15-17*) for more information on the subject.

Experimental Methods

Sulphation tests of two limestones using a synthetic flue gas with a varying concentration of $H_2O_{(g)}$ (temperature and gas composition, Table 2-1) were performed in a Cahn TGA over the course of 10 h of reaction time. The conversion of the samples was determined according to equation (2-3), where $m(t)$ is the sample mass, $m°$ is the calcined sample mass, MM_y is the molar mass of species y, and x_e is the mass fraction of CaO in the sample.

$$X = \frac{m(t) - m^o}{\left(\frac{MM_{CaSO4}}{MM_{CaO}} - 1\right)(x_e m^o)} \tag{2-3}$$

The experimental apparatus consists of a hanging tube furnace with inner diameter of 25 mm, compressed gases, and a syringe pump and steam generator. The reactor is heated externally with a heating jacket capable of a typical heating rate of 25°C/min. Temperatures are monitored throughout the system with K-type thermocouples to control reaction temperature and ensure that no condensation of $H_2O_{(g)}$ occurs.

Table 2-1 Operating conditions for TGA and TF tests.

Temperature (°C)	850
Reaction time (h)	10
CO_2 (%)	12.75
O_2 (%)	2.53
SO_2 (ppm)	3800
H_2O (%)	0/7.5/15
N_2	balance

Two limestone sorbents were used: Cadomin and Kelly Rock having 97 and 90% purity, respectively. X-ray fluorescence (XRF) analysis of the sorbents can be found in Table 2-2. The samples (34-37 mg), particle size 75-115 µm, were spread evenly in a thin layer over a 10 mm-diameter flat platinum pan and placed within the TGA. The samples were first calcined in a N_2 atmosphere; from the onset of calcination, the step was usually complete in less than 5 min. The difference between the original sample mass and that after calcination was used to calculate the purity of each particular sample, as opposed to using the average XRF value. A total N_2 gas flow of 100 cm^3/min was introduced at the bottom of the TGA. All gas flows were controlled with electronic mass flow controllers using LabView software.

Table 2-2. Limestone sorbent composition by X-ray Fluorescence, ASTM D3426 method.

Component	Kelly Rock	Cadomin	Katowice
CaO, Wt%	50.83	54.59	54.10
SiO_2, Wt%	5.27	1.20	0.85
Al_2O_3, Wt%	1.61	0.41	0.24
Fe_2O_3, Wt%	0.39	0.17	0.09
TiO_2, Wt%	0.07	<0.03	<0.03
P_2O_5, Wt%	<0.03	<0.03	<0.03
MgO, Wt%	0.50	<0.20	0.89
SO_3, Wt%	<0.10	<0.10	<0.10
Na_2O, Wt%	<0.20	<0.20	<0.20
K_2O, Wt%	0.35	0.05	0.06
Barium, ppm	459	516	
Strontium, ppm	265	166	
Vanadium, ppm	<50	<50	
Nickel, ppm	<50	<50	
Manganese, ppm	1089	1137	
Chromium, ppm	<50	<50	
Copper, ppm	51	<30	
Zinc, ppm	63	56	
Loss on Fusion, Wt%	40.72	43.21	43.6
Sum, Wt%	99.93	99.62	99.83

Once calcination was complete, the N_2 was shut off and the synthetic flue gas and $H_2O_{(g)}$ were introduced at a total flow rate of 100 cm^3/min. Sulphation proceeded for 10 h from the time the synthetic flue gas was switched on. After 10 h, the system was purged with N_2 for 1 h to allow the system to cool down. All samples were stored in air-tight jars upon removal from the TGA so that no reaction of CaO with atmospheric moisture/CO_2 would occur prior to further analytical tests. Some authors such as Oberoi and Abbasian (*18*) have suggested that external factors such as sample size, gas flow rate and sample pan orientation do not permit scale up of TGA experiments due to their effects on observed reaction rates. However, under conditions employed here, the reaction was not appreciably affected by limitations of mass transfer from the bulk phase to the particle surface. Nor was the reaction affected by inter-particle mass transfer. These conclusions were reached by doubling the total gas flow rate, and by altering the sample size (no difference in initial sulphation rate in either case).

A quartz tube furnace (TF) was used to replicate the conditions employed in the TGA and generate sufficient sample mass for XRF and nitrogen adsorption analyses. The ancillary equipment to the TF (gas control, steam generation and data monitoring) was the same as that of the TGA experiments. The total gas flow rate during both calcination and sulphation was 380 cm^3/min. Other conditions were the same as those employed using the TGA. It was not possible to operate the TF such that the reaction proceeded without intra-particle mass transfer limitations. Therefore, sulphation was prolonged to compensate for this effect. However, it was determined by scanning-electron microscopy (SEM) that very similar sorbent morphology was obtained in the fixed bed tests as that in the TGA tests for sulphation both with and without the presence of $H_2O_{(g)}$.

Limestone samples (1.4-1.5 g) were evenly spread in two ceramic sample boats 50 mm in length. These sample boats were placed end to end within the 25 mm-diameter quartz tube and heated to 850°C for 1 h. For the first test, complete calcination was confirmed by sample weighing after an additional 10 min of calcination. In subsequent tests, complete calcination was assumed after 1 h, and the synthetic flue gas was introduced and allowed to react for 3, 6, and 14 h. After the samples were cooled to handling temperature using N_2, they were promptly placed inside a Micromeritics AccuPyc Helium Gas Pycnometer for density determination. All samples were stored in air-tight sample vials before being sent for SEM, XRF and nitrogen adsorption analyses. Finally, sample morphologies were observed with a Hitachi S3400 SEM with 20 kV of accelerating voltage under high vacuum. The samples were coated with 3 nm gold/palladium before SEM examination and images obtained by secondary electrons are presented here.

Results and Discussion

Figure 2-1 shows the effects of $H_2O_{(g)}$, limestone origin and limestone impurity fraction on the progress of sulphation for calcined samples over the course of 10 h (an expanded view for the first 100 min is given in Figure 2-2). Figure 2-1a shows that $H_2O_{(g)}$ has a clear positive influence on the indirect sulphation for Cadomin beyond the initial stage. In comparison to the baseline conversion of 65.9% (0% H_2O), 7.5% H_2O results in an increase in conversion of 15.4%. Remarkably, concentrations of 15% H_2O results in stoichiometric conversion after 10 h, equivalent to an increase in conversion of ~45%.

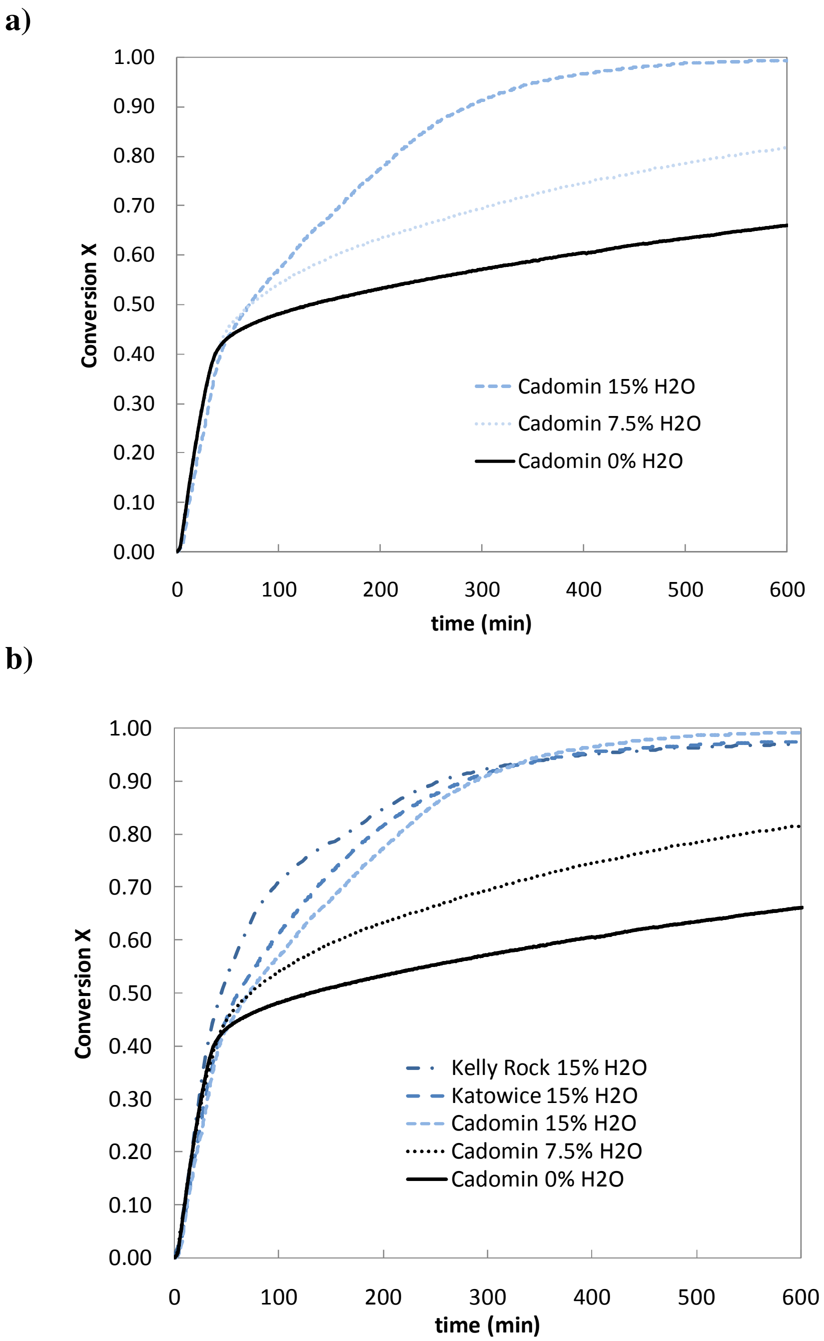

Figure 2-1 Sulphation conversion profiles for different H2O concentrations: (a) calcined Canadian limestone, Cadomin, (b) calcined limestones of various geographical origins for different H2O concentrations.

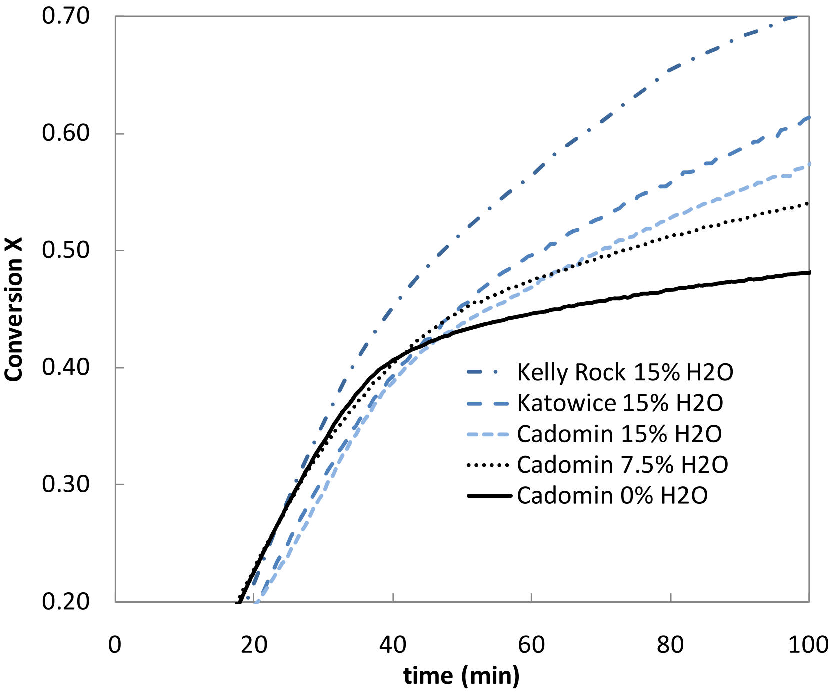

Figure 2-2 Expanded view of Figure 1 for the first 100 minutes.

Sulphation curves for Kelly Rock and Cadomin for 15% $H_2O_{(g)}$ levels (Figure 2-1b) are similar in shape and final conversion. The Kelly Rock sample achieved 98% conversion after 10 h, indicating that the difference in limestone purity does not have a large effect on the high conversions achieved with elevated concentrations of $H_2O_{(g)}$. However, it appears that Kelly Rock can achieve better conversion in shorter times, which may be due to the favorable influence of impurities leading to crystal defect vacancies (*3,5*). As both Kelly Rock and Cadomin are Canadian limestones, it was decided to determine the effects of $H_2O_{(g)}$ on a foreign stone, Katowice, a Polish (Upper Silesia) limestone. Katowice has a purity (97% CaO) similar to that of Cadomin and shows a sulphation curve that is nearly identical with a final conversion of 98%. Sulphation curves for Kelly Rock are not shown but resulted in final conversions of 76%, 90%, and 98% for $H_2O_{(g)}$ vapor concentrations of 0%, 7.5% and 15%, respectively.

Additional tests performed using Kelly Rock at concentrations of 30 and 50% H_2O showed slightly slower initial reaction rates, probably due to the lowered concentration of SO_2 (2800 and 2550 ppm, respectively, down from 3800 ppm used in all other tests); still, stoichiometric conversion was achieved in both tests after 10 h. This result indicates diminishing returns for $H_2O_{(g)}$ addition into the system beyond 30%. It appears, therefore, that there is an "optimum" $H_2O_{(g)}$ concentration (between 15 and 30%) for the present reaction conditions. This raises speculation that, for low-moisture fuels and fuels low in volatiles such as petroleum coke, simple steam injection might be employed to increase calcium utilization of limestone particles.

At least two repetitions of the tests at each condition confirmed the precision of the results presented here for Cadomin and Kelly Rock (Figure 2-3). Furthermore, since the effects of $H_2O_{(g)}$ were found to be similar for the three limestones tested in the 0–15% concentration range, subsequent experiments were performed on Cadomin limestone only and repeat tests were not run unless indicated otherwise.

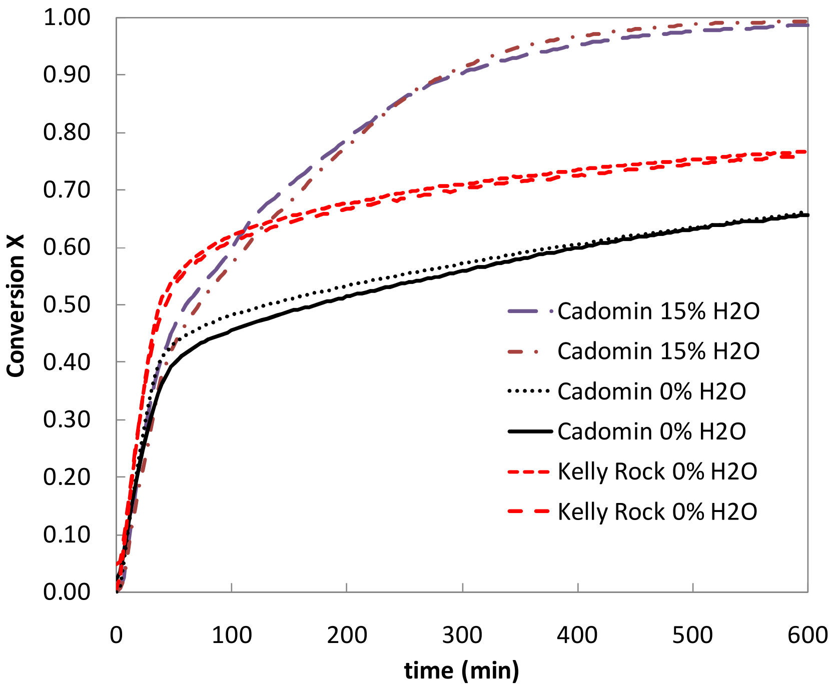

Figure 2-3 Sulphation conversion profiles for Cadomin and Kelly Rock under varying conditions of water showing the repeatability.

The transition between the kinetically-controlled and diffusion-limited regimes for the case without $H_2O_{(g)}$ is characterized by a sharp decrease in reaction rate. In the presence of $H_2O_{(g)}$, the transition becomes more gradual, making the decrease in rate in the latter period less pronounced until over 90% conversion is achieved. Furthermore, it is interesting to note that in all tests performed for all limestones, the influence of $H_2O_{(g)}$ on the initial rate of sulphation is negligible. It is for this reason that a number of investigators may have reached the conclusion that $H_2O_{(g)}$ does not affect sulphation rate. Only over longer periods of sulphation will the effects of $H_2O_{(g)}$ become appreciable. In practice, limestone particles typically sulphate well into the diffusion-controlled regime in FBCs, necessitating inclusion of the effects of $H_2O_{(g)}$ in bench-scale studies and models.

Figure 2-4 shows the conversion of Cadomin while actively controlling the addition of $H_2O_{(g)}$ in the gas phase. Sulphation in the presence of 15% $H_2O_{(g)}$ was allowed to proceed for 3 h as in the other sulphation tests. At 3 h, when the reaction was well beyond the kinetically-controlled regime, $H_2O_{(g)}$ was shut off for 2 h (replaced by 15% nitrogen), and sulphation was allowed to proceed without $H_2O_{(g)}$. After 2 h $H_2O_{(g)}$ was reinstated and sulphation continued for an additional 5 h. Here, the reaction rate decreases substantially in the absence of $H_2O_{(g)}$. When $H_2O_{(g)}$ is reintroduced, the rate increases, and 100% conversion is eventually achieved after 10 h.

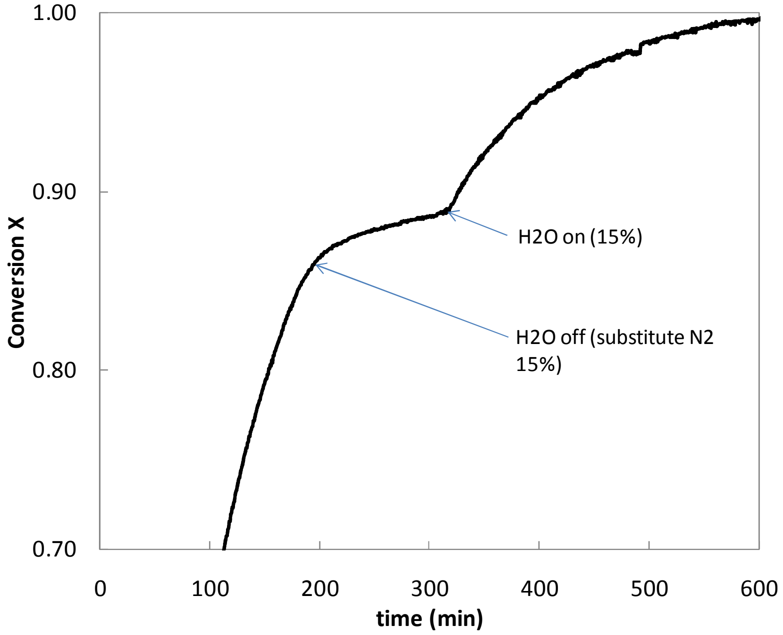

Figure 2-4 Sulphation conversion profiles of calcined Cadomin limestone while actively switching on and off the flow rate of 15% H_2O.

In comparison, an identical sample sulphated without $H_2O_{(g)}$ addition achieved only ~65% conversion after 10 h (Figure 2-1). In the result shown in Figure 2-4, when $H_2O_{(g)}$ was removed, the conversion rate did not immediately return to a level seen for the diffusion-controlled step when $H_2O_{(g)}$ was not present. This observation is indicative of a permanent physical or structural change in the lime particles, brought about by the presence of $H_2O_{(g)}$, that persists even in its absence.

Figures 2-1 and 2-2 show that the presence of $H_2O_{(g)}$ has little/no effect on the initial rate of sulphation during the kinetically-controlled regime, confirming the idea that $H_2O_{(g)}$ does not participate directly in the sulphation reaction, as suggested by Hajaligol *et al.* (*13*). With the addition (or deletion) of $H_2O_{(g)}$ beyond the kinetically controlled regime, by contrast, there is a strong effect observed. This result strongly supports the conclusion that $H_2O_{(g)}$ assists in the diffusion of gaseous reactants and/or solid-state diffusion in solid reactant/product layer ($CaO/CaSO_4$). Moreover, the evidence that the sulphation rate remains higher (in comparison with that when $H_2O_{(g)}$ was not present, Figure 2-1a) a certain time after $H_2O_{(g)}$ was shut off (Figure 2-4), indicates that $H_2O_{(g)}$ may take part in the enhancement of a solid-state diffusion mechanism.

Gas adsorption analysis using the Barrett-Joyner-Halenda (BET) pore surface area calculation method (*19*) shows a rapid decrease in surface area as sulphation proceeds, as seen in Figure 2-5. Lime pore surfaces and external CaO crystal surfaces are quickly covered in $CaSO_4$ crystals, which eventually plug the pores, eliminating their contribution to the available surface area for reaction. A “monolayer”, a layer of crystals packed tightly but not stacked, as described by Duo *et al.* (*20*), of $CaSO_4$ can be seen to cover all the visible surfaces of the lime particles, even at about 10% conversion, or 1 h sulphation time (Figure 2-6). The surface of these particles, as well as those at higher conversions, appears to be non-porous (Figure 2-7a,b). Further pore surface area and volume loss must, therefore, be attributable to a mechanism other than formation of a product layer. The rapid volume and surface area loss followed by slower rates of degradation coincide well with the transition between the kinetically- and diffusion-limited reaction regimes for the fixed bed tests shown in Figure 2-8 (at about 30-40% conversion). Loss of pore surface area and pore volume of powder compacts have been well studied and explained by sintering (*21*). These losses due to sintering can be modeled by an exponential decay relationship which also fits the data presented here.

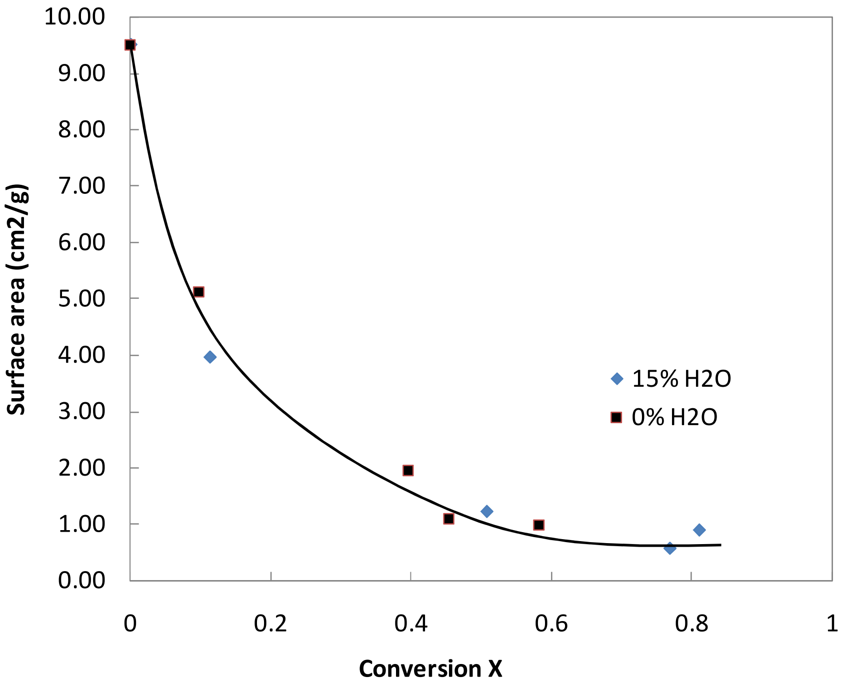

Figure 2-5 Particle surface area (BET) of samples sulphated using tube furnace.

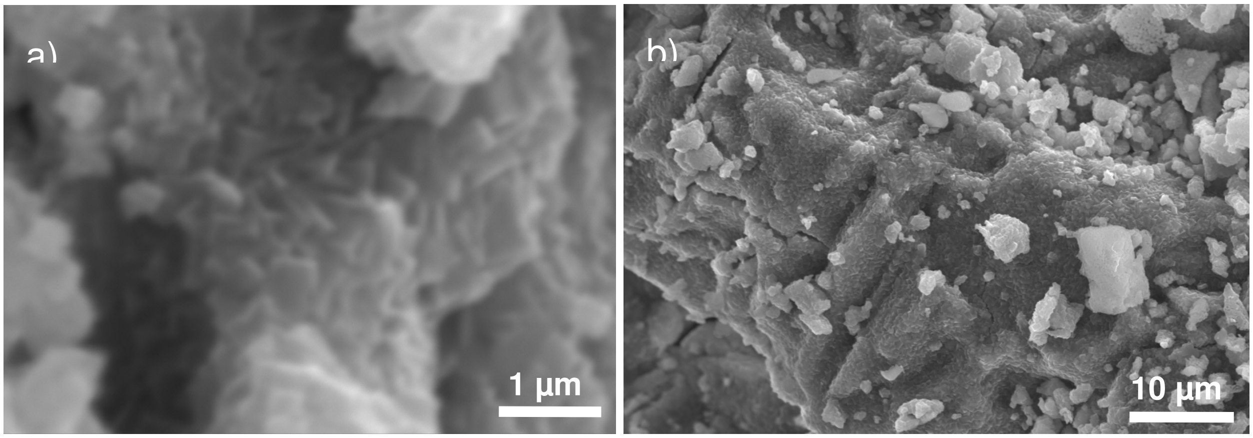

Figure 2-6. SEM images showing a monolayer of $CaSO_4$ crystals at 1 h sulphation time of Cadomin lime particles. (a) 9.8% conversion, $[H_2O] = 0\%$ and (b) 11% conversion, $[H_2O] = 15\%$.

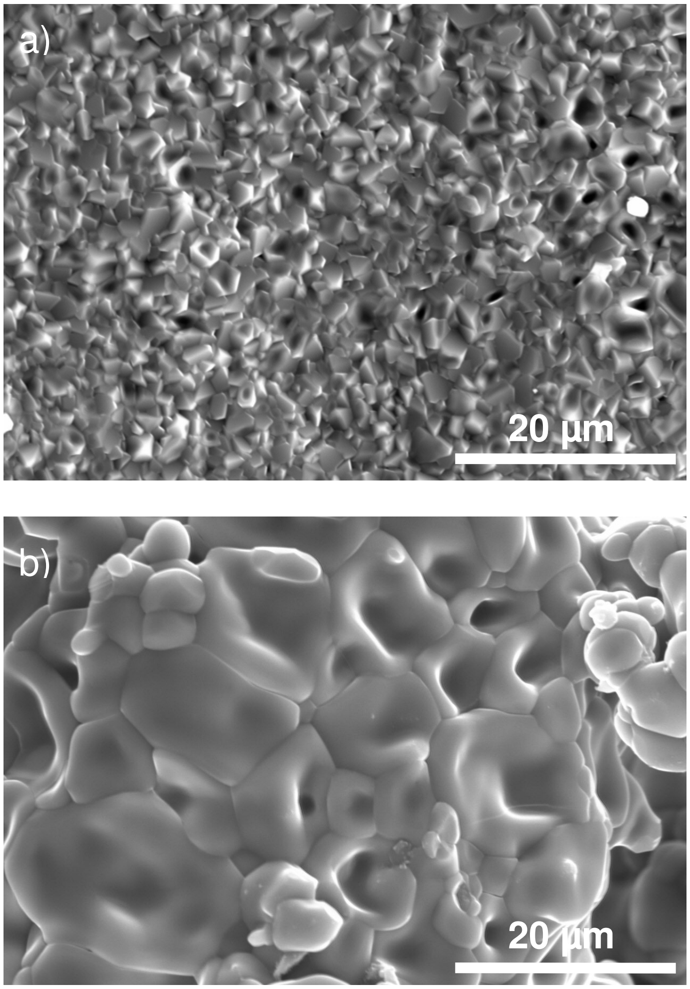

Figure 2-7 SEM images of sulphated Cadomin lime particle surface (crystal grains of $CaSO_4$) after 10 h sulphation under conditions given in Table 1: a) no water, $[H_2O] = 0\%$; b) 15% H_2O.

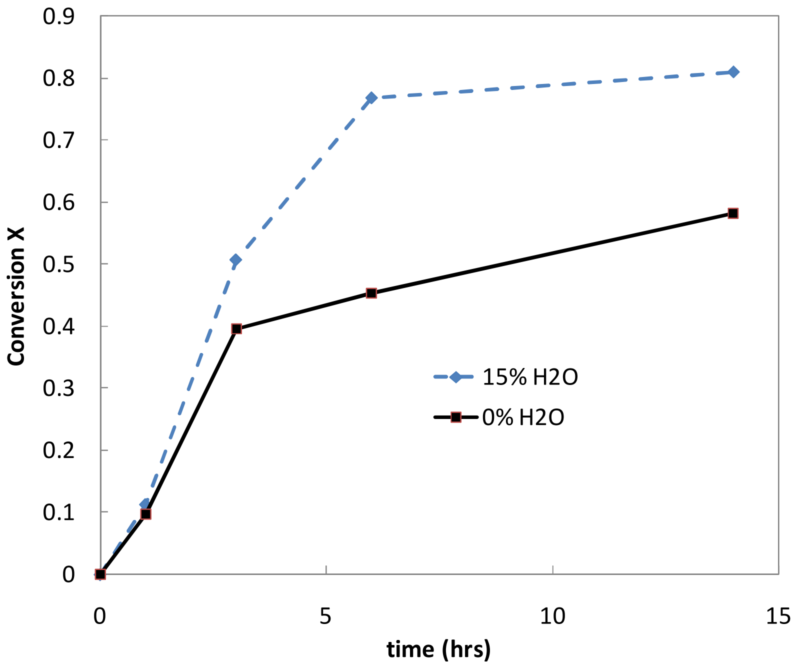

Figure 2-8 Progress of sulphation in samples generated using tube furnace.

It is also important to note that the decrease in surface area for the latter half of the reaction is 200 times smaller in magnitude than the decrease observed for the first half, yet it encompasses the same span of conversion. In other words, the reaction continues to proceed regardless of how much surface area is available. This fact, coupled with the observed indifference of the loss in surface area to the presence of $H_2O_{(g)}$, suggests that sulphation and its associated microstructural changes occur at locations and/or surfaces not accessible to the nitrogen used in surface area determination.

Using gas pycnometry, it is clear that for a given conversion, sorbent sulphated in the presence of $H_2O_{(g)}$ has a higher skeletal density than that sulphated without $H_2O_{(g)}$, as shown in Figure 2-9. As this method of density measurement gives only the volume of the solid fraction and the closed pores (*22*), pore plugging by the $CaSO_4$ must be less prominent in the presence of $H_2O_{(g)}$, and in fact, it appears that plugged pores cease to exist as conversion approaches completion. This phenomenon, and the resultant increase in reaction rate in the presence of $H_2O_{(g)}$, is attributed to the fact that sulphation in the presence of $H_2O_{(g)}$ is accompanied by an increase in average $CaSO_4$ crystal grain size 2-4 times larger in diameter than that formed without $H_2O_{(g)}$, both on the particle outer surface (Figure 2-7) and well within the bulk of the particle (Figure 2-10). In agreement with Wang *et al.* (*9*) increased $CaSO_4$ crystal size is also seen for particles sulphated in the presence of $H_2O_{(g)}$ at sulphation times as low as 1 h. Larger internal crystals promote poorer packing of the crystals, and will thus result in a more porous, partially sulphated structure that offers lower resistance to diffusion of gaseous reactants before substantial sintering of the crystals occurs.

Figure 2-11 compares the internal morphology (the particles were broken open to assist with the SEM analysis) of highly sulphated samples, showing lower crystal density inside the particle when sulphated in the presence of $H_2O_{(g)}$. Similarly, Duo *et al.* (*20,23*) attributed greater overall sulphation to the formation of a more porous product layer developed from a smaller number of larger, more stable nuclei. In the present study, the smaller $CaSO_4$ crystals formed without $H_2O_{(g)}$ may have packed well to form an impervious layer, causing pore mouth plugging. This would cause the density of particles sulphated without $H_2O_{(g)}$ to appear lower than those which were sulphated in the presence of $H_2O_{(g)}$.

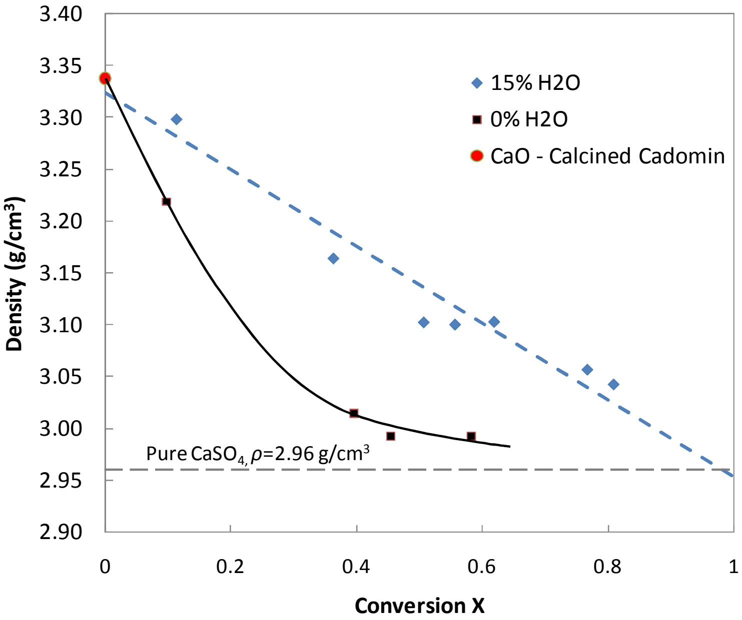

Figure 2-9 Sulphated product density (Helium pycnometry) as a function of conversion for sulphation conditions with 15% H_2O and with no H_2O present.

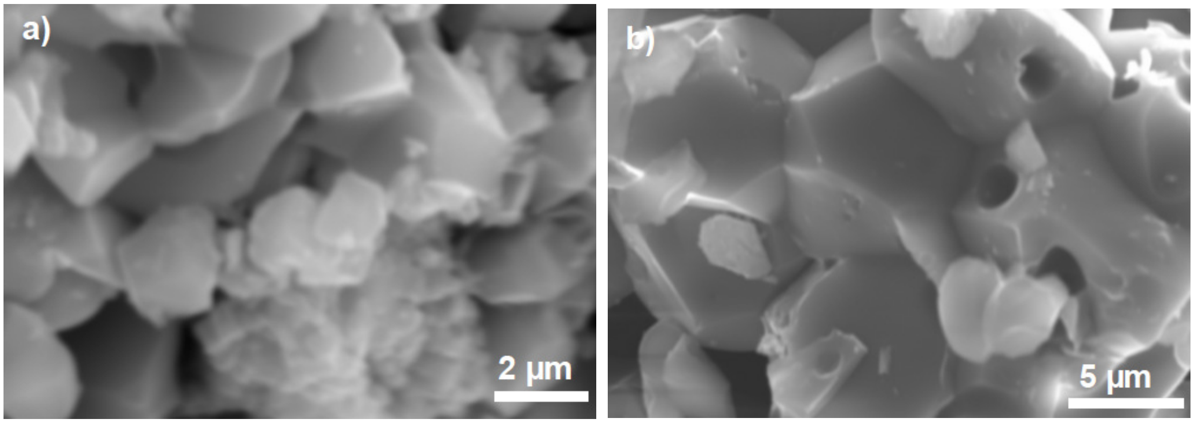

Figure 2-10 SEM images showing the difference in crystal grain size inside sulphated Cadomin lime particles after 10 h sulphation under conditions given in Table 1: a) no water, $[H_2O] = 0\%$; b) 15% H_2O.

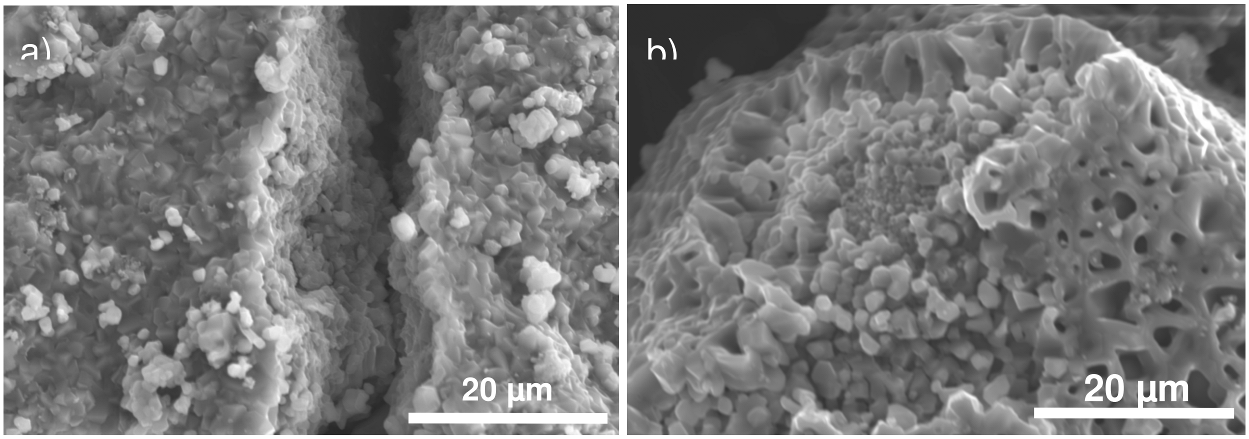

Figure 2-11 SEM images showing the packing of crystals inside sulphated Cadomin lime particles, (a) with [H_2O] = 0% and (b) with [H_2O] = 15%.

Since the reaction proceeds well beyond the point at which the majority of available pores are blocked and surface areas consumed, sulphation may proceed through a solid state diffusion mechanism, one which allows the passage of reactants through the outermost sulphated layer or shell. It is suggested that this solid-state diffusion mechanism is enhanced in the presence of $H_2O_{(g)}$, and that it is responsible for more rapid mass transfer in/between reactants and products. All else being equal, the surface morphologies of particles sulphated in the presence of $H_2O_{(g)}$ show a smoother flattened outer layer of agglomerated crystals than the surfaces of those sulphated without it, as compared in Figure 2-7a and b. Smoothing of the particle surface and agglomeration of surface crystals are well known characteristics of solid state diffusion (*21,24*). Another indicator of solid state diffusion taking place is the favorable influence of impurities in the Kelly Rock samples *vs*. the purer Cadomin (90% and 97% CaO purity, respectively). Kelly Rock sulphates to nearly 100% conversion more quickly than Cadomin, as shown in Figure 2-1b, a result seen for all investigated concentrations of $H_2O_{(g)}$.

The increased amount of impurities, and therefore crystal defects and vacancies, reduces resistance to solid state diffusion. These findings are in agreement with numerous studies that show the enhancement effects of limestone doping (*3*,*8,11,12*).

$H_2O_{(g)}$ has been shown to drastically increase the rate of sintering of metal oxides at high temperature (*24-26*). This accelerated sintering rate, *i.e.*, increased ion mobility of the CaO crystals, may follow the mechanism proposed by Anderson *et al.* (*25*) for MgO: increased surface mobility brought about by adsorption of H_2O on the crystal surface. However, this mechanism may or may not affect CaO and the $CaSO_4$ product in the same manner. Due to the difference in melting points of CaO (T_m=2845K) and $CaSO_4$ (T_m=1733K), the lower Tammann temperature (defined as half the absolute melting temperature of a solid, *(21)*) of $CaSO_4$ dictates that it sinters at a much lower temperature than CaO. For $CaSO_4$, at the temperature used in this study, the prevalence of surface diffusion diminishes in favor of volume diffusion, where vacancies migrate along crystal grain boundaries and through the crystal lattice, resulting in a reverse flow of mass into the pores. The net result of this process is particle densification accompanied by a loss in surface area, whereas surface diffusion results in a loss of surface area but fails to induce shrinkage (*21*). The data presented in Figure 2-5 and Figure 2-9 correspond well to the mechanism described here. Moreover, Borgwardt (*24*) showed that the sintering rate of CaO was enhanced in the presence of CO_2 in a similar manner as was seen with H_2O, and that their effects were additive. In the present study, a TGA test confirmed an increase in final conversion after sulphation in the presence of an additional 15% CO_2 and no $H_2O_{(g)}$ by about 8% (Figure 2-12). It is proposed that, through enhanced surface diffusion in CaO and vacancy mobility in $CaSO_4$ in the presence of $H_2O_{(g)}$ (and/or CO_2), resistance to solid state diffusion is greatly reduced, which enables enhanced sulphation.

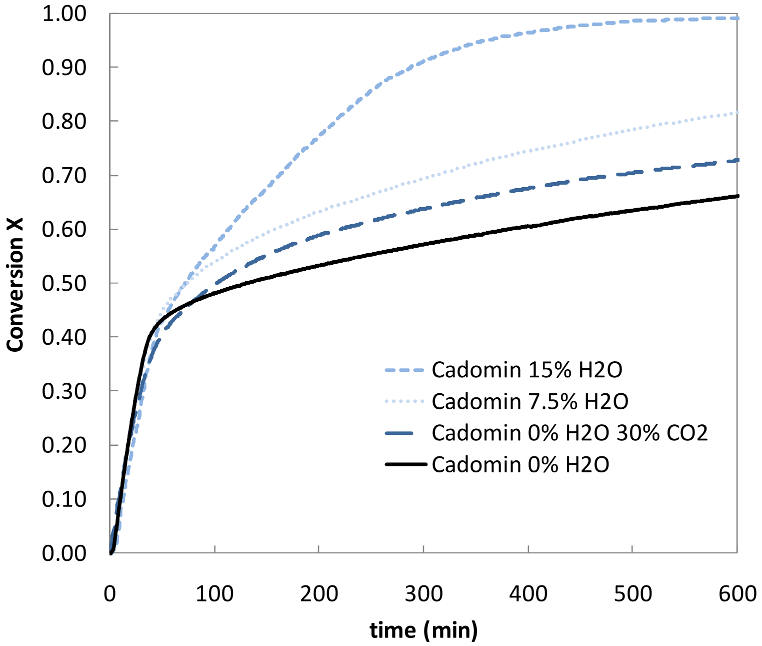

Figure 2-12. Sulphation conversion profiles of calcined Canadian limestone, Cadomin for different H_2O concentrations with one profile for an elevated (30%) concentration of CO_2.

TGA and TF sulphation tests of limestones of different geographical origin have confirmed the strong positive effect of $H_2O_{(g)}$ on sulphation. The $H_2O_{(g)}$ concentrations employed here are within the range for typical flue gas, and the presented effects are of sufficient magnitude that $H_2O_{(g)}$ should be included in future scale-up sulphation and modeling studies. Of course, one must always be cautions when attempting to generalize or scale up results from TGA experiments. Even though TF tests confirm the observed effects of $H_2O_{(g)}$ in a TGA, pilot-scale effects such as attrition, dynamic gas compositions and temperature gradients will undoubtedly influence sulphation. As such, tests on pilot-scale equipment are currently underway, using high-sulphur petroleum coke to study the effects of $H_2O_{(g)}$ on sulphation under realistic conditions. Still, at the conditions studied for particles sized 75-115 µm, regardless of limestone type, ~90%

conversion is achievable after about 5 h, an impressive result which is well within the range of CFBC retention times. This suggests that sulphation performance in real combustors firing high-rank coals can be improved by maintaining the concentration of $H_2O_{(g)}$ in the ideal range of 15-30%.

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CHAPTER 3 : AGGLOMERATION OF SORBENT PARTICLES DURING THE SULFATION OF LIME IN THE PRESENCE OF STEAM

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Abstract

Previous investigations of FBC systems utilizing limestone addition for SO_2 capture have shown that sintering due to chemical reaction (sulphation) and related solid-state diffusion are important causes for agglomeration/fouling in FBC boiler systems firing high-sulphur fuels. When the original work was done it was widely believed that steam did not affect indirect sulphation and, therefore, its effects on agglomeration were not considered. However, recent research clearly shows that steam at levels produced by burning hydrocarbon fuels can significantly improve sulphation by enhancing solid state diffusion and limestone conversion. The present study revisits the earlier studies on agglomeration but in the presence of steam. The agglomeration tendency of two limestones, Kelly Rock (Canada) and Katowice (Poland, Upper Silesia) was tested, using two particle sizes (75-115 and 250-425 μm) in pelletized and non-pelletized forms. The samples were sulphated for up to seven days in a tube furnace (TF) and thermogravimetric analyzer (TGA) by a gas mixture containing 15% of $H_2O_{(g)}$. The results were compared with those obtained with no steam present during reaction. The residues after sulphation were examined by scanning electron microscopy (SEM) and their surfaces and profiles were analyzed by energy dispersive X-ray (EDX) spectroscopy. The results showed that steam greatly affects sulphation and solid state diffusion and this caused enhanced agglomeration. Similar agglomeration effects noticed after 100 days of sulphation time in past studies were shown to occur in just one day in the presence of steam. SEM analysis showed that sulphated particles agglomerate, and connections between particles due to sulphation are often stronger than the original strength of the particles themselves. The effect of agglomeration is more pronounced in the case of smaller particles and/or pelletized samples. These results suggest that steam may play a significant role in the fouling of industrial boilers firing high-sulphur fuels.

Introduction

Lime-based sorbents are widely used for desulphurization of flue gases produced during combustion of fossil fuels such as high-sulphur coals and petroleum coke. This process is well known from fluidized bed combustion (FBC) boilers, and it is based on the heterogeneous reaction described as sulphation [1]. Depending on conditions (temperature and CO_2 partial pressure) in a combustor, sulphation may proceed *via* either the indirect or direct pathway. At higher temperature/lower CO_2 partial pressure, $CaCO_3$ calcines (Reaction 3-1) and the product, lime (CaO) further reacts with SO_2 in the presence of oxygen (Reaction 3-2) to form $CaSO_4$ (indirect sulphation):

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{3-1}$$

$$CaO_{(s)} + SO_{2(g)} + 1/2O_{2(g)} \rightarrow CaSO_{4(s)} \tag{3-2}$$

At lower temperature/higher CO_2 partial pressure, sulphation of $CaCO_3$ proceeds *via* the direct route (Reaction 3-3) [2]:

$$CaCO_{3(s)} + SO_{2(g)} + 1/2O_{2(g)} \rightarrow CaSO_{4(s)} + CO_{2(g)} \tag{3-3}$$

A wide range of reaction mechanisms for sulphation are described in the literature, including intermediary species such as $CaS_{(s)}$, $CaSO_{3(s)}$, and $SO_{3(g)}$, the formation of which depends mainly on gas concentrations and temperature [3]. However, the main characteristic of sulphation, regardless of the mechanism, is the formation of a solid product at the reacting surface, which retards further reaction [4, 5]. The solid product at the reacting surface implies additional diffusion resistance. Depending on original limestone morphology and composition, and conditions during sorbent calcination and sulphation, different partially sulphated patterns can be formed, including the formation of the core/shell pattern [6].

The sulphation product, $CaSO_4$, has a significantly larger molar volume (46 cm^3/mol) than that of CaO (17 cm^3/mol) or $CaCO_3$ (37 cm^3/mol) [1]. During sulphation the pores in sorbent particles are filled by bulky $CaSO_4$, limiting further reaction (due to a lack of room for storage of product in small pores) as well as retarding gas diffusion in sorbent particles. In the case of sorbents with predominantly small pores the formation of a product shell around an unreacted core is typical of the morphology of sulphated limestone particles, and this shell prevents diffusion of SO_2 toward the unreacted core. Therefore, it is normally assumed that gas diffusion is a limiting step for sulphation conversion. However, along with diffusion of gases in porous solids, solid state diffusion in the product layer is necessary for further conversion when the product layer is formed at the pore surface [7, 8]. The sulphation of very small sorbent particles and noted limits after the initial kinetically-controlled reaction step are further evidence that solid state diffusion is the rate-limiting step [9, 10]. Different mechanisms for this solid state diffusion were proposed including diffusion of SO_4^{2-} ions [8] or diffusion of Ca^{2+} ions [11, 12]. The main experimental evidence that solid state diffusion limits reaction rate comes from the observation of the favourable influence of impurities, *i.e.*, defects in the CaO crystal structure, and the strong temperature dependency of the rate, *i.e.*, high activation energy [8]. The typical activation energy for reactions controlled by diffusion of gases is ~20 kJ/mol, but that measured for sulphation is >120 kJ/mol, which is characteristic for ionic diffusion.

Solid state diffusion during a reaction implies related phenomena such as sintering and agglomeration of reacting particles. As a result of these phenomena, industrial boilers firing high-sulphur fuels such as petroleum coke or high-sulphur coal form solid deposits with characteristic lengths of metres on a variety of surfaces including superheaters, heat exchangers and cyclones [13, 14]. It was originally suggested that vanadium was responsible for formation of such deposits in circulating fluidized bed combustion (CFBC) boilers firing petroleum coke. However, extensive research in our laboratory on deposits from five industrial-scale CFBC boilers demonstrated that such deposits are composed of almost pure $CaSO_4$, and that sulphation and sintering are responsible for agglomeration and fouling [13-16]. In addition, careful analysis of such deposits failed to find any evidence of V_2O_5 or any low-melting-point phase but rather suggested that any vanadium present was bound up as high-melting-point magnesium or calcium vanadates [16]. More compelling still was the fact that simple sulphation of either limestone or bed ashes from these boilers, over periods of days to weeks, was in itself sufficient to produce strongly agglomerated material with characteristics similar to the original deposits. Ultimately, two mechanisms, chemical reaction sintering and "molecular cramming", were identified as responsible for forming such deposits. For a good general discussion of chemical reaction sintering, the interested reader is referred elsewhere [17] while molecular cramming is a term coined by the authors to describe the effects of intra-particle product formation, after all of the internal voids in a limestone particle are filled up with solid product and the particle must expand for further sulphation to occur (this occurs at around 70% conversion for sulphated limestone), and is in effect pressure-assisted sintering [1, 17].

What was lacking in the work done during this period was a clear idea of the timescale required for significant agglomeration to occur due to sulphation. Initially the authors carried out sulphation tests for up to 100 days to simulate the phenomena that would occur in a real boiler. Subsequently, tests were done for shorter periods of time (typically 25 days) and these timescales were also sufficient to produce strongly agglomerated materials from bed materials and original limestones. Ultimately, the primary conclusions from this body of work was that agglomeration was exacerbated by situations in which the fuel ash was low and, therefore, the authors recommended sand addition as a potential solution; they also recommended preventing dead zones in regions such as the return leg, where particles could be subjected to sulphation over longer periods, thus permitting sintering and agglomeration to occur [1]. However, no other factors were identified as being important, but given the severity of the agglomeration in commercial-scale boilers [1], it was reasonable to believe that the actual phenomena were occurring at a higher rate than modelled in the tests being done earlier by CanmetENERGY and its collaborators. However, in the absence of an obvious reason why rates should be faster in real boilers, this work went no further.

At that time, it was generally believed that the steam present in combustion gases of any boilers burning hydrocarbon fuels did not affect indirect sulphation or agglomeration and all such studies done neglected the influence of steam. This was also in line with modelling studies on sulphation presented in the open literature, as they did not consider the effect of steam or explicitly assumed that steam did not affect sulphation [18-25]. However, our recent studies on the influence of steam on both sulphation [26, 27] and carbonation [28-30] show that steam present in reactive gases greatly enhances conversion rates. The conversions obtained after >10 h of sulphation in the presence of 15% steam were typically >90%. Initially, it was speculated that sulphation and carbonation reactions were enhanced due to a catalytic effect of $H_2O_{(g)}$, *i.e.*, due to formation of transient and more reactive $Ca(OH)_2$ [26, 28, 29]. However, more detailed studies showed that steam enhances solid-state diffusion and reaction rate during the slow reaction step controlled by diffusion in the product layer, and had little effect during the kinetically-controlled regime. The enhanced solid-state diffusion was also confirmed by scanning electron microscopy (SEM) analyses of samples reacted in the presence of steam and those sulphated or carbonated with no steam [27, 30]. Significantly different morphology was seen, and in the case of sulphation typically 2-4 times larger sub-grains/crystals with smoother surfaces were obtained in the presence of steam.

The results of these recent studies on the influence of steam on sulphation and carbonation, particularly on the morphological changes of sorbent samples, led us to explore the phenomenon of agglomeration when steam is present during reaction. The aim of this study is to investigate agglomeration during sulphation at high temperature using SEM and energy dispersive X-ray (EDX) spectroscopy.

Experimental Section

Agglomeration of two limestone samples, Kelly Rock (Nova Scotia, Canada) and Katowice (Poland, Upper Silesia), and two particle sizes (75-115 and 250-425 μm) were investigated in this study. The X-ray fluorescence (XRF) elemental analysis of these limestones is given in Table 3-1. As can be seen, the main difference between these samples is the high content of silica in Kelly Rock (5.27% SiO_2).

Table 3-1 Elemental composition of limestone sorbents investigated

Component (wt%)	Kelly Rock	Katowice
CaO	50.83	54.10
SiO_2	5.27	0.85
Al_2O_3	1.61	0.24
Fe_2O_3	0.39	0.09
TiO_2	0.07	<0.03
P_2O_5	<0.03	<0.03
MgO	0.50	0.89
SO_3	<0.10	<0.10
Na_2O	<0.20	<0.20
K_2O	0.35	0.06
Loss on Fusion	40.72	43.6
Sum	99.74	99.83

The sulphation tests were done in a thermogravimetric analyzer (TGA) apparatus and tube furnace (TF) in order to simulate stationary particles resting in the dead zones of a combustor. Both experimental systems were equipped with a syringe pump and steam generator. Feed lines containing steam and the mixed gas were insulated and electrically heat-traced to prevent steam condensation. All samples were calcined in a dry nitrogen atmosphere at 900 °C. The reactive gas mixture was introduced after 30 min and sulphation was allowed to proceed for 1, 3, and 7 days at the same temperature.

A Perkin Elmer TGA-7 was used for TGA sulphation experiments. The sorbent sample (~100 mg) was suspended in a quartz tube (i.d. 20 mm) on a platinum pan (i.d. 5 mm). To ensure uniform packing of sample particles, the pan was tapped ten times to obtain a flat sample surface and constant height (~2 mm layer thickness). The gas mixture, chosen to represent a typical combustion flue gas (0.45% SO_2, 3% O_2, 15% CO_2, and N_2 balance), was introduced at a flow rate of 85 cm^3/min. The steam flow rate, controlled by injection of water (by a syringe pump) in a steam generator, was 15 cm^3/min. In the experiments with no steam the total flow of gas mixture was 100 cm^3/min. The temperature and gas used were controlled by Pyris software. Sample mass data during the experiments were monitored, which enabled us to calculate conversions. Note that all flow rates are expressed at standard temperature and pressure.

The total gas flow rate in the TF was 400 cm^3/min and about 5 g of sample was used. Samples were placed in ceramic boats (4 mm high) and tapped to obtain a flat sample surface about 2 mm high. Pelletized samples were prepared using metal cylinders (i.d. 8 mm, length 5 mm) placed on a flat metal surface. The limestone sample was placed in the cylinder and pressed with a metal disk (d = 8 mm). To control force, an Omega LCFA-250 tension/compression load cell was mounted on a drill press. The drill press was used to generate force which was the same,

~500 N, for all pellets. The resulting pellets, together with the metal cylinders, were placed in the TF and sulphated.

The morphology of agglomerated sulphated samples was observed with a Hitachi S3400 Scanning Electron Microscope with 20 kV of accelerating voltage under high vacuum. The samples were coated with 3 nm gold/palladium before SEM examination and images obtained by secondary electrons are presented here. The microscope was equipped with EDX analyzers, which enabled us to examine the elemental composition of sample surfaces.

Results and Discussion

The following discussion relates to the non-pelletized samples, while the pelletized samples are discussed below.

A significant tendency to agglomerate can be seen in samples sulphated in the presence of steam. After just one day of sulphation, the particles agglomerated so strongly that the entire sample was removed as a single mass 80 mm long (1.5 mm thick and 8 mm wide), as shown in Figure 3-1. A cross-sectional profile of a sample, sulphated for one day in the presence of steam, showing complete conversion to $CaSO_4$ along the profile, is presented in Figure 3-2a. At higher magnification (Figure 3-2b), one can clearly see agglomeration of three particles. The same sample was also sulphated for a total of 3 and 7 days in the presence of steam and agglomerates were also analyzed. Furthermore, the strength of the agglomerates increased with reaction time, as could be estimated by the effort required to section the sample. It is telling to compare these results to those of prior studies that attempted to quantify agglomeration using tests in which water was not present. A case in point is the study performed by Anthony *et al.* [13] where samples sulphated for over three months showed only "mild" agglomeration, underlining the importance of including steam in such studies.

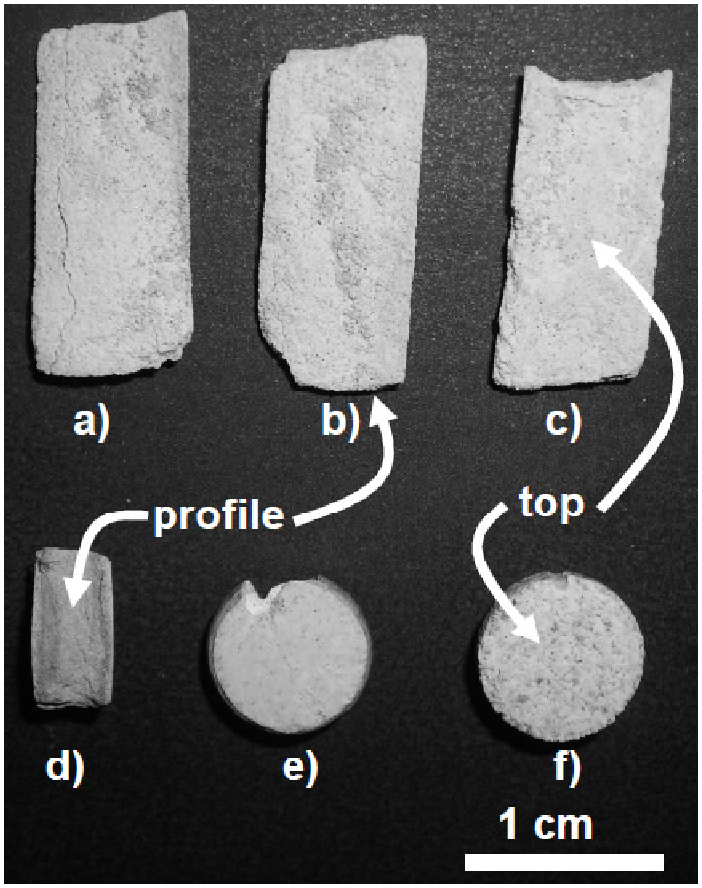

Figure 3-1 Photograph of agglomerated samples after sulphation in TF at 900 °C with a gas mixture (0.38% SO_2, 2.55% O_2, 12.75% CO_2, 15% $H_2O_{(g)}$, N_2 balance): a) Kelly Rock, 75-115 µm, sulphation for 1 day); b) Kelly Rock, 75-115 µm, 3 days; c) Kelly Rock, 75-115 µm, 7 days; d) Kelly Rock, 75-115 µm, pellet, 1 day; e) Katowice, 75-115 µm, pellet, 7 days; and f) Katowice, 250-425 µm, pellet, 7 days. (Top – the uppermost portion of the sample exposed to the gas stream, Profile – a cross section of the sample)

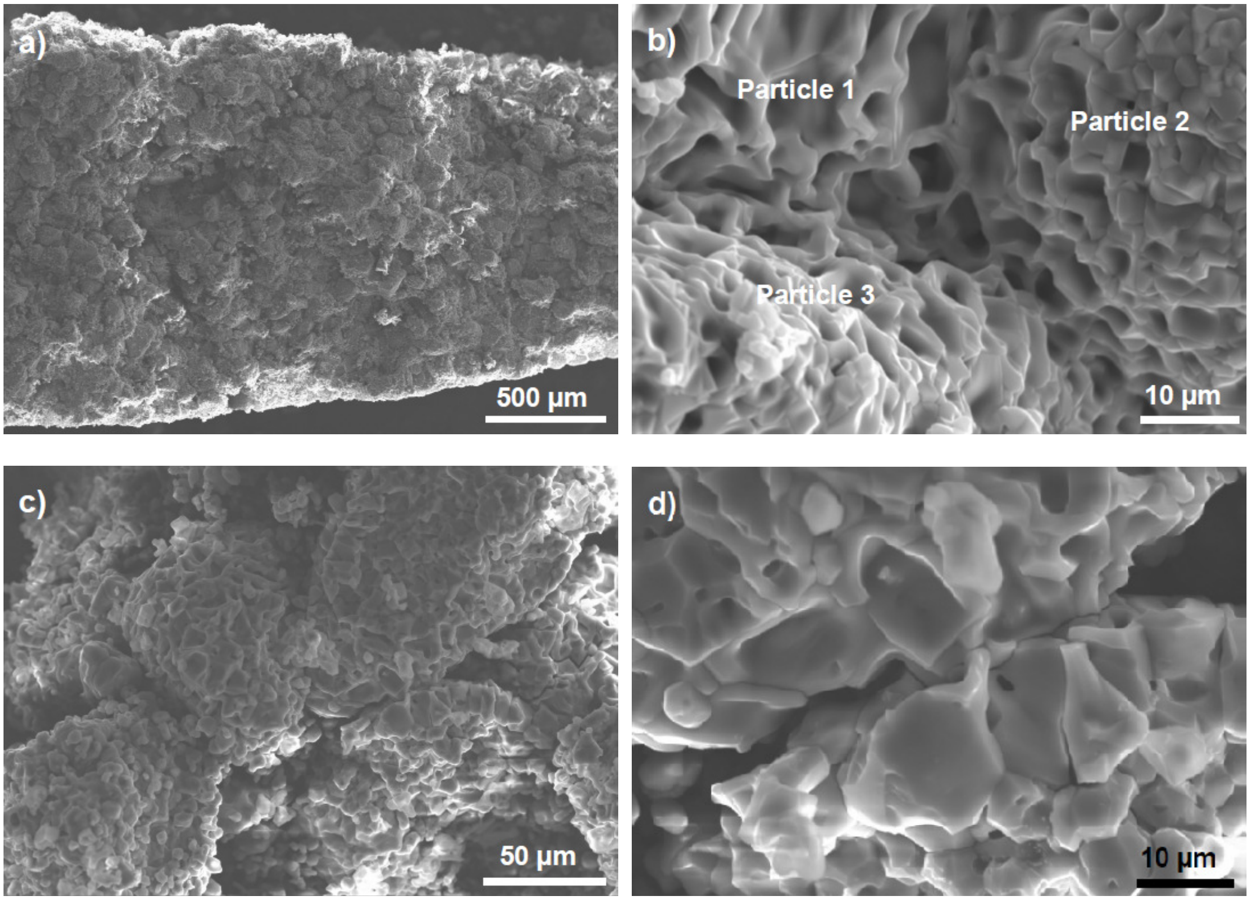

Figure 3-2 SEM images of agglomerated Katowice sample (75-115 µm) after sulphation at 900 ºC: a) and b) with steam present (0.38% SO_2, 2.55% O_2, 12.75% CO_2, 15% $H_2O_{(g)}$, N_2 balance) for 1 day; c) and d) with no steam present (0.45% SO_2, 3% O_2, 15% CO_2, 0% $H_2O_{(g)}$, N_2 balance) for 3 days.

On the other hand, the binding strength of Katowice particles after sulphation without steam was negligible. After 1 day the sample in the boat remained powdery. Sulphated particles did not stick together and it was difficult to detect any agglomeration tendency by SEM. Sulphation for at least 3 days was necessary for small clusters of agglomerated particles to become detectable (Figure 3-2c). However, the connections between particles were poor, as can be seen at higher magnification (Figure 3-2d). Moreover, their analysis by SEM was very difficult since the particles were moving under the electron beam, exposing uncoated (Au-Pd) areas. This was additional proof that particles in the clusters were only weakly bonded. A similar situation was also seen with samples sulphated for 7 days.

For larger particles (250-425 *vs*. 75-115 µm), the effect of steam on agglomeration was still clear but it became less prominent, probably due to the fewer and relatively smaller contact surfaces between particles. Thus, even after 7 days of sulphation without steam the larger particles in the Katowice sample did not agglomerate; however, they did agglomerate, albeit weakly, after 1 day in the presence of steam, and samples did not break up when handled. The 7-day, steam-sulphated agglomerate was sectioned and its profile is presented in Figure 3-3. At higher magnification, agglomeration of particles is clear (Figure 3-3b). However, it can be seen in Figure 3-3a that due to poorer packing, there are still spaces between particles, which differs from that seen in Figure 3-2a for the smaller sized sample (75-115 µm).

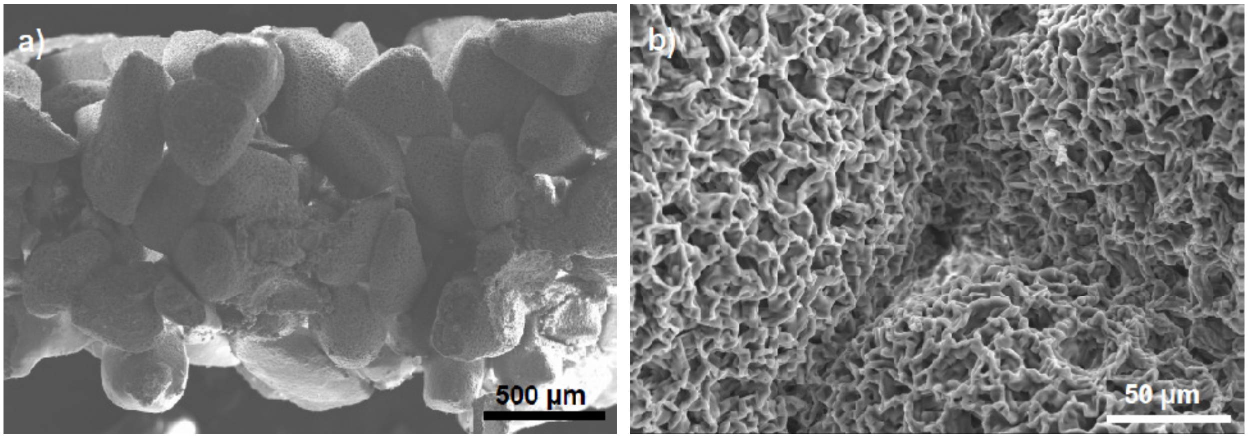

Figure 3-3. SEM images of agglomerated Katowice sample (250-425 µm) after 7 days of sulphation at 900 ºC with 15 % $H_2O_{(g)}$ present: a) 50x magnification, and b) 500x magnification.

In an attempt to determine how neighbouring particles were joined together, the agglomerates were broken and the resulting surfaces examined. Figure 3-4 shows the most interesting and characteristic images of these surfaces, obtained by SEM. The image in Figure 3-4a represents a cross section of two broken particles. It can be seen that both particles have cores with micron-size grains/crystals. Between these cores is a shared region with much larger grains, 10 µm or greater. These large grains do not belong to any one sorbent particle, and it can be assumed to have formed as a result of coalescence of smaller grains which originate from both particles. This is a classic result from chemical reaction sintering where chemical reaction at the surfaces of two particles results in the blurring of the boundary between particles.

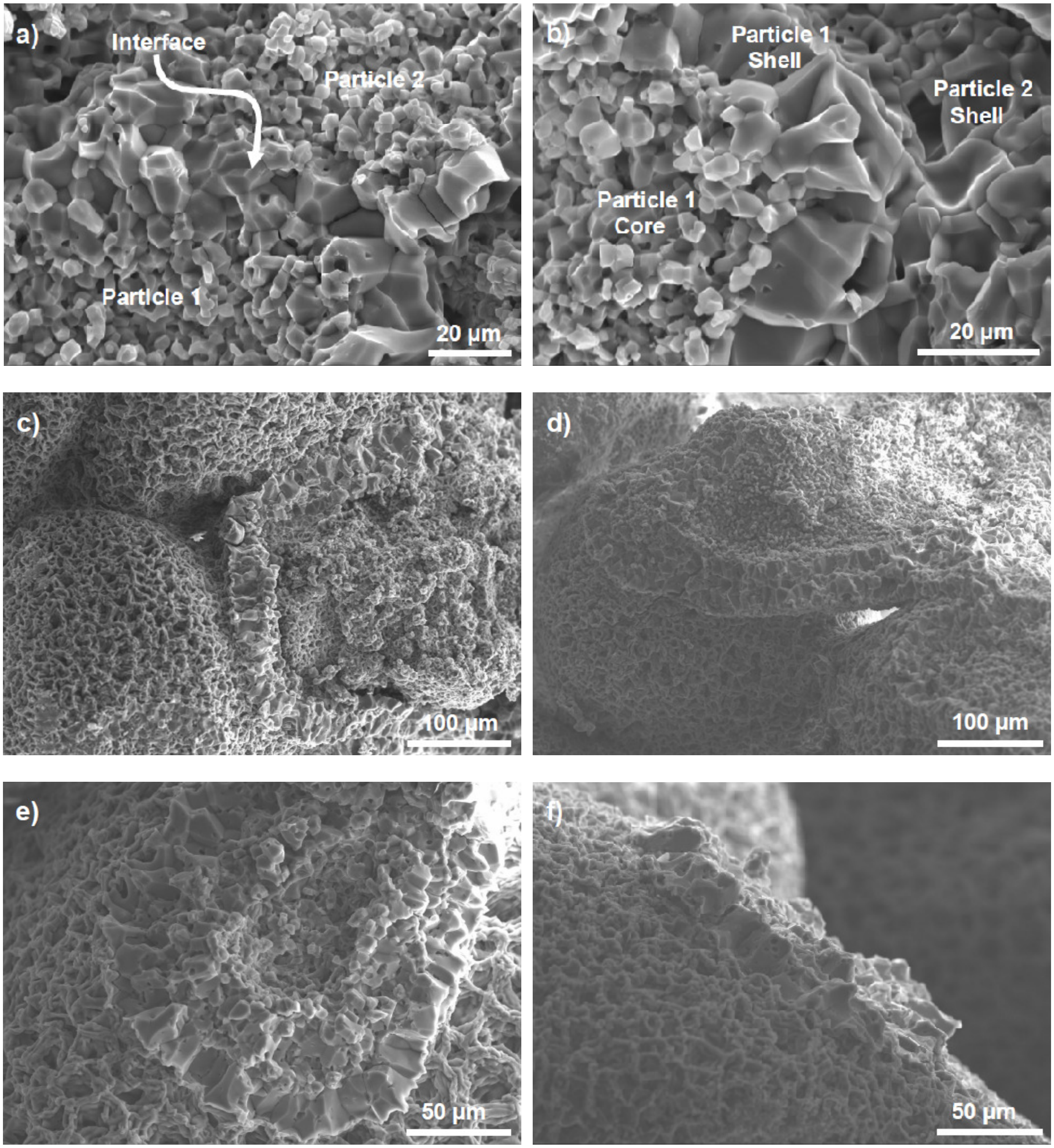

Figure 3-4 SEM images of agglomerated and broken Katowice samples after 7 days of sulphation at 900 ºC with 15% $H_2O_{(g)}$ present, particle size: a) and b) 75-115 µm; and c-f) 250-425 µm.

A further insight into this mechanism is presented in Figure 3-4b where two particles are agglomerated, but only one is broken. It can be clearly seen here that two agglomerated particles, across the joint region (Figure 3-4a), have also a joint shell formed from larger grains. It should be mentioned here that both core and shell are quantitatively sulphated; *i.e.*, sulphation did not proceed *via* the shrinking unreacted core pathway, which is confirmed by TGA results in our recent study [27], and by EDX analysis in this study. The appearance of a pure $CaSO_4$ shell here is likely due to chemical reaction sintering enhanced at the surface of the particle. This effect of enhanced sintering at the surface of the sorbent was recently discussed in the case of carbonation [31] and was explained by an effect similar to surface tension in liquids [32]. When steam is present, both improved solid state diffusion and improved conversion (*i.e.*, improved formation of bulky $CaSO_4$ product) contribute to sintering at the particle surface and formation of crystallites shared between particles, which helps explain the observed enhanced agglomeration.

An interesting result of SEM analysis of broken agglomerated samples is that the common region of agglomerated particles usually shows greater strength than the particles themselves, which is exemplified by the structures shown in Figure 3-4(c-f). From these images it is clear that particles could not be easily detached from one another. Instead, the particles fractured and the interface remained intact and part of the adjacent particle (*e.g.*, Figure 3-4f).

To investigate the effects of better particle contact on agglomeration tendency, particle pellets were prepared under pressure. A selection of the pelletized samples that were sulphated for up to 7 days, using the same gas mixture (with 15% water vapour) as in the other tests are shown in Figure 3-1. The results of SEM/EDX analysis are presented in Figure 3-5 (electron image and two examples of spectra), while the composition in terms of the three most abundant elements (Ca, S, and Si) are given in Table 3-2. It can be seen that almost total conversion occurs in the outer layer up to about 100 µm. Here it should be noted that conversion is calculated as S/Ca molar ratio, but some Ca is bound in other calcium compounds (unavailable for sulphation), which means that real conversions are higher than values given in Table 3-2. The conversion decreases towards the pellet interior and in the sixth analyzed layer, sulphation is practically negligible. This is expected because gas diffusion is limited due to pore and intra-particle spaces becoming plugged by $CaSO_4$ product in the layers nearer to the pellet surface.

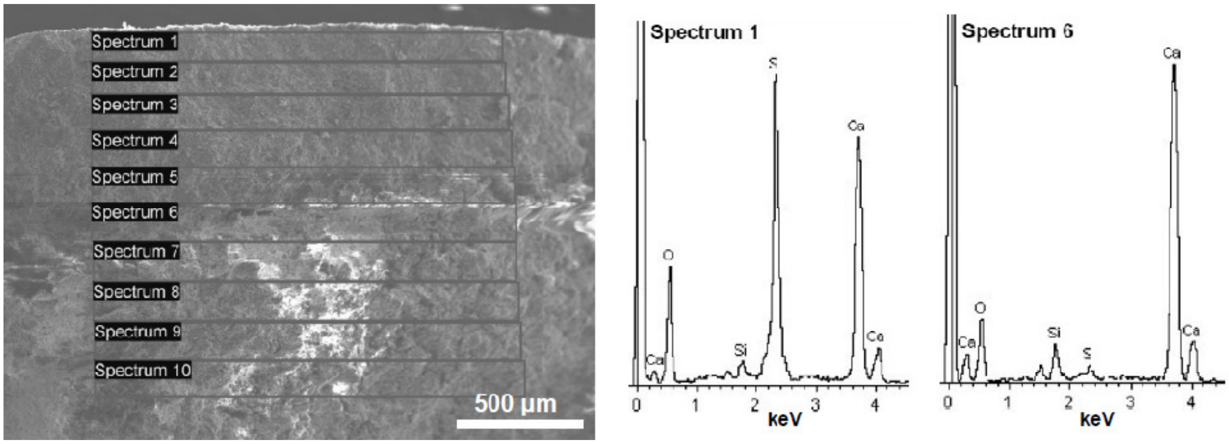

Figure 3-5 SEM/EDX analysis of pellet (Kelly Rock limestone, particle size 75-115 µm) sulphated for 1 day at 900 °C in the presence of 15% $H_2O_{(g)}$. Profile of broken pellet (Figure 3-1d) is shown in SEM image and analyzed by EDX.

Table 3-2 Results of EDX analysis of pellet profile presented in Figure 3-1 and in the SEM image in Figure 3-5.

	Spectrum (analyzed layer)									
Compound	1	2	3	4	5	6	7	8	9	10
CaO, wt%	41.11	42.52	44.33	47.24	62.44	87.59	90.14	91.04	90.38	91.81
SO_3, wt%	56.53	53.65	52.17	49.03	30.32	3.81	0.44	0.33	0.93	1.50
SiO_2, wt%	2.36	3.82	3.50	3.73	7.24	8.60	9.42	8.63	8.69	6.70
Conversion, %	96.33	88.47	82.45	72.67	34.02	3.04	0.35	0.25	0.71	1.15

A selection of characteristic SEM images taken from pellets sulphated in the presence of steam for 1 day is presented in Figure 3-6. It can be seen in both images, from the pellet surface (Figure 6a) and pellet profile near to the surface (Figure 3-6c), that the structure is very compact and there is no noticeable border between original sorbent particles. This indicates very high levels of sintering/agglomeration. As expected, this is a result of better contact between the original sorbent particles caused by pressure pelletization. This heavily sintered structure prevents diffusion of SO_2 (and also H_2O) toward the centre of the pellet particle and consequently prevents sulphation and sintering of the CaO there (Figure 3-6d). Cracks at the grain/crystal surface (Figure 3-6b) confirm the existence of tension in the layer nearest to the particle surface.

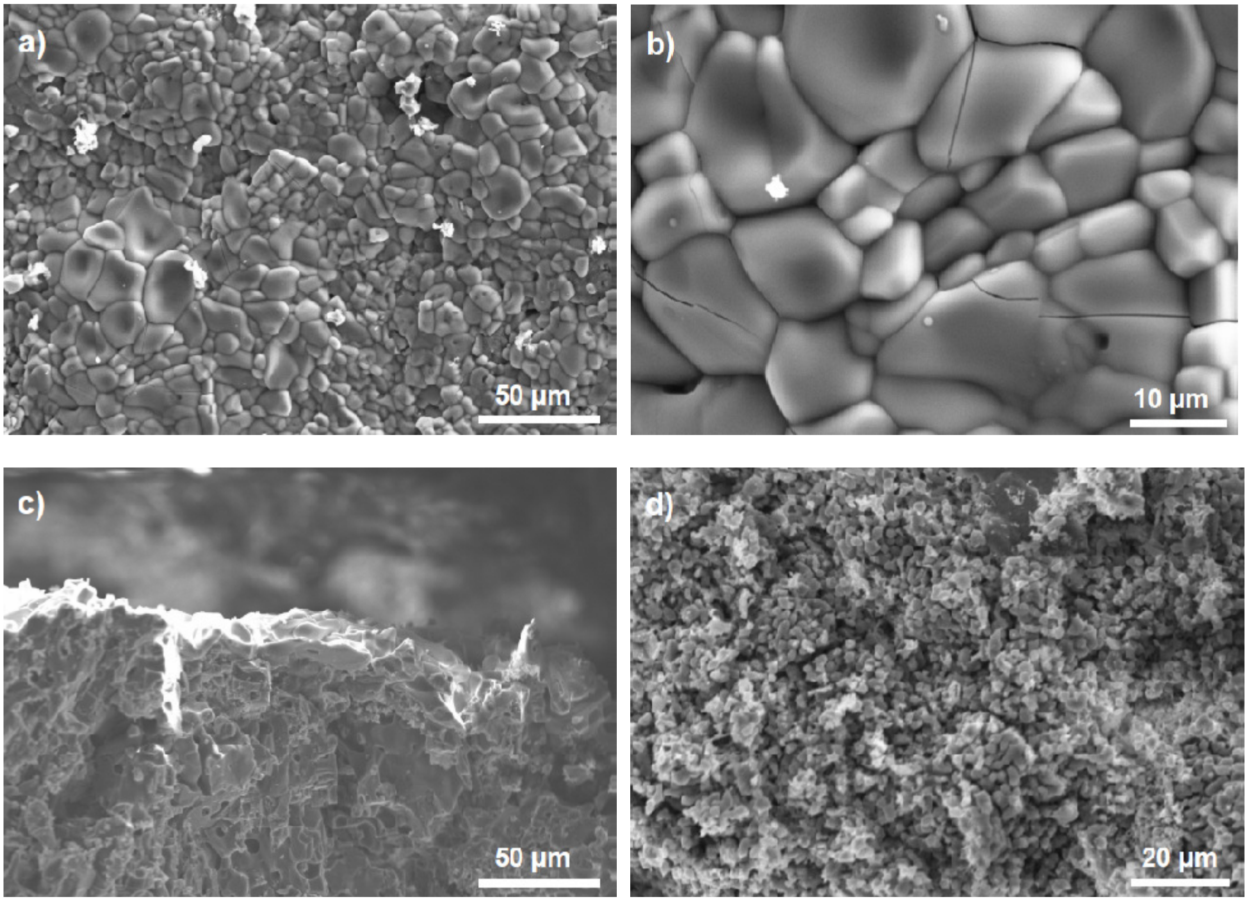

Figure 3-6 SEM images of pellet (Kelly Rock limestone, particle size 75-115 μm) sulphated for 1 day at 900 °C in the presence of 15% $H_2O_{(g)}$: a) and b) pellet surface (top); c) profile near to pellet surface; and d) unreacted pellet interior.

A similar analysis was done with pellets prepared from small and large particles sulphated in the presence of steam for 3 and 7 days. The results are not presented here in the interest of brevity, but are summarized as follows. In general, longer sulphation times lead to higher CaO-to-$CaSO_4$ conversion. With pellets prepared from smaller particles, very compact surface layers (~500-700 μm), with quantitative conversion, are formed at each end of the cylinder holding the pellet. The layers are strong, but their formation creates strain and they can be separated from the core of the pellet, leaving convex surfaces. The strain probably follows the formation of the $CaSO_4$ product in limited space, with molecular cramming. “Layer” formation did not occur with the larger particles, when there was more inter-particle space to accommodate the product better.

It appears that $CaSO_4$ formed during sulphation fills the space between neighbouring grains at the sorbent particle contacts, eventually exerting forces on the surrounding particles which in turn causes molecular cramming of adjacent grains and particles. At the higher temperatures and pressure from the cramming, these grains and particles sinter together to form the agglomerates depicted in the images. Furthermore, it seems that enhanced bulk diffusion and chemical reaction sintering in the presence of steam results in the formation of larger grains that become shared between two or more particles which were in contact or close to contact before sulphation, leading to the development of strength in $CaSO_4$ agglomerates.

The proposed mechanism of agglomeration assumes solid state diffusion in $CaSO_4$ product. To test this hypothesis, pure $CaSO_4$, sieved to obtain a sample of particle size 75-115 µm, was exposed to 15% $H_2O_{(g)}$ with CO_2 as the balance, for 1, 3, and 7 days at 900 °C in the TGA. The original sample, which was heated in N_2, and the sample treated by H_2O/CO_2 were analyzed by SEM, as presented in Figure 3-7. It can be seen that the morphology of $CaSO_4$ did not change appreciably during the test in dry nitrogen at 900 °C (Figure 3-7a and Figure 3-7b). But after one day in the steam/CO_2 atmosphere, the sample was slightly agglomerated; it formed a disk when removed from the platinum pan. Interestingly, the diameter of the agglomerated disc was ~25% smaller than the internal diameter of the pan, which means that the sample underwent densification. That disc was broken and its profile is presented in Figure 3-7c. Some of the particles were moving under the electron beam, and uncoated areas appeared, which resulted in a poor quality image (Figure 3-7c). However, at higher magnification, slight bridges between neighbouring particles were seen (Figure 3-7d). Similar morphology was seen with samples after 3 and 7 days of treatment. It was noticed that greater binding strength developed, but additional sample shrinkage and morphology changes were small.

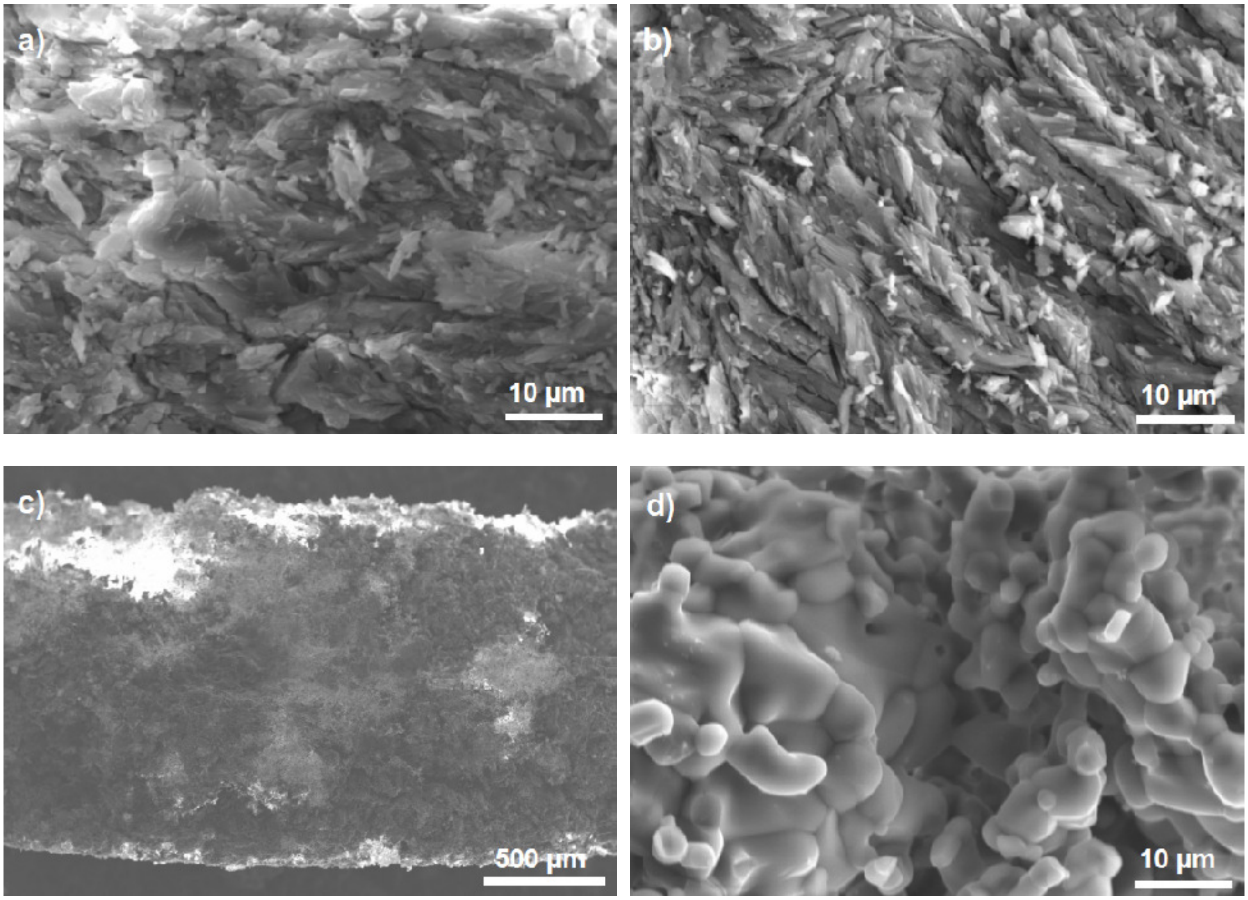

Figure 3-7 SEM images of $CaSO_4$ (anhydrite), particle size 75-115 µm: a) original sample; b) treated at 900 °C in a dry atmosphere of N_2; c) agglomerated sample after 1 day of treatment at 900 °C in 15% H_2O(g) with CO_2 as the balance; and d) the agglomerated sample at higher magnification.

These results show that steam produces changes in $CaSO_4$ morphology, *i.e.*, it enhances solid state diffusion in $CaSO_4$, a phenomenon not seen for $CaSO_4$ samples in an N_2 atmosphere.

However, when comparing the agglomeration tendency seen in Figure 3-2 to Figure 3-4 with that in Figure 3-7, it is clear that chemical reaction is necessary for substantial agglomeration to occur.

Conclusions

Steam enhances sulphation *via* the effect of enhanced solid state diffusion. More of the bulky $CaSO_4$ product is formed, which fills spaces between neighbouring CaO grains. When these belong to different sorbent particles, the particles can become bound to each other through shared $CaSO_4$ crystal grains. Steam also enhances solid state diffusion in $CaSO_4$, which results in further sintering and agglomeration. The mechanism of agglomeration can be described as sintering due to chemical reaction (sulphation), which is in this case enhanced by steam. It is found that, for the timescales investigated, both chemical reaction and steam are required for appreciable agglomeration to occur—having one and not the other does not suffice. These findings help elucidate the mechanism/cause for the formation of sulphate deposits in real FBC systems. It is clear that lime and/or limestone particles (predominantly smaller) trapped on the walls of reactors make contact and, therefore, also simultaneously sulphate and agglomerate. This process is enhanced by steam and these deposits may reach complete sulphation within 10 hours to form strong agglomerates. The results presented in this study show that the effect of steam should be taken into account in future studies, not solely on sulphation but also in the investigation of related phenomena such as agglomeration and formation of deposits, and suggest that increasing the water content in the fuel (for instance by co-firing biomass or perhaps sorbent reactivation) may easily exacerbate fouling tendencies.

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CHAPTER 4 : OXY-FUEL COMBUSTION IN A CIRCULATING FLUIDIZED BED COMBUSTION PILOT PLANT

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Abstract

Circulating fluidized bed combustion (CFBC) is particularly suited to burning a wide range of fuels, and/or co-firing fossil fuels and biomass. The technology is also well suited to oxygen-enhanced combustion for the purposes of increasing energy efficiencies and providing near-zero-emissions power production. Currently, the largest demonstration of the technology with flue gas recycle is at the 1 MWt level at CanmetENERGY in Canada. However, Foster Wheeler and other boiler companies are now working on plans to build demonstration and commercial plants. This paper will discuss emissions issues for a variety of fuels, along with results on sulphation emissions, which is a problematic area, since there is considerable disagreement in the literature about limestone performance under oxy-fuel conditions. In particular, trial results from various pilot plants will be used to elucidate peculiarities associated with limestone performance in an oxy-fuel environment.

Introduction

Anthropogenic CO_2 production is primarily driven by fossil fuel combustion and the current energy demand situation suggests that fossil fuel combustion demand will likely increase in the near future. Consequently, it is increasingly necessary to find ways to reduce CO_2 emissions when fossil fuel is used, and of the various potential reduction options, CO_2 capture and storage (CCS) appears to be among the most promising for large stationary power plants. All CCS technologies for power plants involve producing a pure stream of CO_2 either by concentrating it in some manner from flue gases, or by using effectively pure oxygen as the combustion gas [1]. The latter option, referred to as oxy-fuel combustion, has been well studied for pulverized coal combustion, but to date has received relatively little attention for oxy-fuel circulating fluidized bed combustion (CFBC), although the concept was examined over 30 years ago for bubbling FBC [2]. More recently the boiler companies, Alstom and Foster Wheeler, have explored the oxy-fuel CFBC concept using pilot-scale tests [3, 4]. Alstom's work included tests in a unit of up to 3 MWt in size, but did not involve recycle of flue gas [5]. Foster Wheeler's work [3] also involved pilot-scale testing, using a small (30-100 kW) CFBC owned and operated by VTT (Technical Research Centre of Finland) and this work along with CanmetENERGY's work with its own 100 kW CFBC appears to be the first in which units were operated with oxy-fuel combustion using flue gas recycle.

The advantages of CFBC are already well known in terms of its ability to burn a wide range of fuels, both individually and co-fired, to achieve relatively low NOx emissions, and accomplish SO_2 removal by limestone [6]. Another advantage of CFBC technology, in the context of oxy-fuel firing, is the fact that hot solids are kept in the primary reaction loop by means of a hot cyclone. This solid circulation potentially provides an effective means, in conjunction with the recycle of flue gas, to control combustion and effectively extract heat during the combustion process, thus allowing either a significant reduction of the amount of recycled flue gas or alternatively, permitting the use of a much higher oxygen concentration in the combustor. This allows the economics of oxy-fired CFBC to be significantly improved over PC or stoker firing by reducing the size of the CFBC boiler island by as much as 50% [5]. In considering the scale-up of CFBC units above 300 MWe, both Foster Wheeler and Alstom are now offering much larger units and Foster Wheeler has in operation a 460 MWe supercritical CFBC boiler [4, 7].

More difficult advantages to quantify for the technology relate to the possibility of co-firing biomass, so that with CCS, the overall combustion process may potentially result in a net reduction of anthropogenic CO_2, and the potential for this technology to be used with more marginal fuels, as premium fossil fuels become in short supply. The co-firing option offers a potentially interesting advantage of CFBC technology, since it is well established that CFBC can burn biomass and fossil fuels at any given ratio ranging from 0-100%, thus offering the possibility of using local and seasonally available biomass fuels in a CO_2 “negative” manner.

The ultimate availability of premium coal for a period of hundreds of years has also recently been called into doubt with suggestions that coal production may peak well before the end of this century. Thus, Mohr and Evans [8] for example, have developed a model which suggests that coal production will peak in 2034 on a mass basis and 2026 on an energy basis. A good general discussion of these ideas can also be found in Wikipedia [9]. In the event of such solid fuel shortages, fluidized bed combustion is ideally suited to exploit the many marginal coals and hydrocarbon-based waste streams available worldwide.

Currently R&D on oxy-fired CFBC technology is being explored in numerous countries, including Canada, Finland, Poland, China and the United States among others. However, to date most test work has been done at small scale (in the <100 kW range), and/or using bottled gases to supply a suitable combustion gas, instead of recycling flue gas to achieve the necessary gas velocity and solid circulation rate in terms of heat transfer requirement. CFBC systems can potentially accommodate recycling of less flue gases than a pulverized coal boiler, despite the inherently low temperature of the combustion process, which is required to avoid ash softening or melting in the fluidized bed combustion, and to achieve better in-bed sulphur capture. This situation arises because the hot solids that are recycled in a circulating fluidized bed can also be used to produce steam, thus cooling the fluidized bed, and hence less flue gases need be recycled than for a suspension-fired boiler. However, the minimum amount of flue gas recycling is governed by maintaining sufficient fluid velocity in the fluidized bed while at the same time providing enough water/steam-cooled surface area to provide adequate internal and external solids heat transfer. Probably, the most important advanced test programs in oxy-CFBC are the development of a number of large pilot-scale units.

Pilot Plant

CanmetENERGY has two pilot plants which are capable of being operated in the oxy-fuel mode, with full flue gas recycle: a nominal 75 kW unit and a larger 0.8 MWt unit. However, it is the smaller unit which will be discussed in detail in this paper.

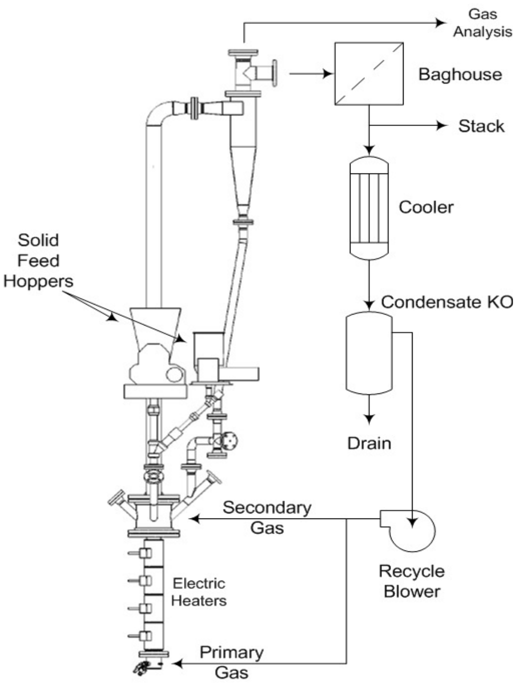

Figure 4-1. CanmetENERGY's Minibed Oxy-fired CFBC.

This unit was first described in 2006, for the tests carried out by Hughes *et al.* [10]. However, that initial work was marred by the fact that the unit still had significant leaks and high CO_2 levels were not produced in the off-gases. Completely successful results from the rig were first presented in 2007 [11].

CanmetENERGY’s mini-CFBC contains a 0.1 m ID stainless steel riser (Fig. 1) covered with 100 mm of insulation. Independent feed augers can supply multiple fuel types and a sorbent, with solid fuel feed rates of up to 15 kg/h. Oxygen, CO_2 and recycled flue gas flow rates are controlled by a combination of mass flow controllers and rotameters. Bed temperature is in the range of 750-950°C. Superficial gas velocity is up to 8 m/s, although the unit is more normally operated at around 4 m/s. The mini-CFBC has been extensively modified for oxy-fuel

CFB combustion. Modifications include the addition of an oxygen supply line and a flue gas recycle train.

Fuels and limestones primarily tested to date are given in Tables 1 and 2, respectively.

Table 4-1 Analysis of Fuels

	Eastern bituminous (EB)	**Kentucky coal**	**Highvale**	**Petroleum coke**
Proximate analysis, wt% (dry)				
Moisture, wt% (as analyzed)	1.08	2.01	10.39	0.66
Ash	8.86	11.31	19.17	1.00
Volatile matter	35.78	37.35	33.76	11.46
Fixed carbon	55.56	51.34	47.076	86.97
Ultimate analysis, wt% (dry)				
Carbon	77.81	74.05	59.78	86.91
Hydrogen	5.05	5.06	3.49	3.22
Nitrogen	1.49	1.62	0.79	1.83
Sulphur	0.95	1.56	0.22	5.88
Ash	8.86	11.31	19.17	1.00
Oxygen (by difference)	6.04	6.40	16.58	1.16
Heating value (MJ/kg)	32.51	30.93	23.27	34.71

Table 4-2. Analysis of Limestones

	Havelock	**Katowice**	**Cadomin**
CaO	53.99	54.32	54.59
MgO	0.59	0.48	<0.20
SiO_2	1.23		1.20
Al_2O_3	<0.38	0.04 - 0.09	0.41
Fe_2O_3	<0.55	0.08 - 0.11	0.17
Na_2O	<0.17	0.01 - 0.03	<0.20
K_2O	<0.08	0.02 - 0.04	0.05
MnO	0.08		
TiO_2	<0.04		
Cr_2O_3	<0.01		
P_2O_5	<0.02		
SO_3	0.20	0.08	
V_2O_5	<0.02		
SrO	0.02		
BaO	0.02		
NiO	0.01		
LOF	43.34	42.70	43.6
SUM	99.48		99.83

Results

The first discovery of the oxy-fuel program at CanmetENERGY was that it was very easy to change from air-fired to oxy-fired mode at least with the pilot-scale units and Figure 4-2, shows a typical result:

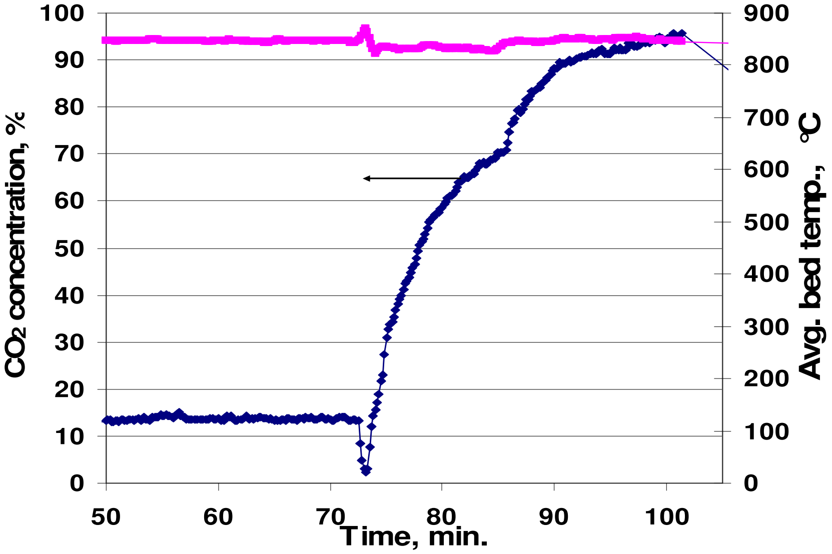

Figure 4-2 Transition from Air Firing to Oxy-fuel Firing in CanmetENERGY's Mini-CFBC during 2nd Highvale Coal Test.

Another important, albeit anticipated, result was that $CaCO_3$ was stable, at typical bed temperatures (850˚C), as is indicated in Figure 4-3, which means that sulphation can be expected to proceed *via* direct reaction with $CaCO_3$ at typical FBC temperatures of around 850˚C.

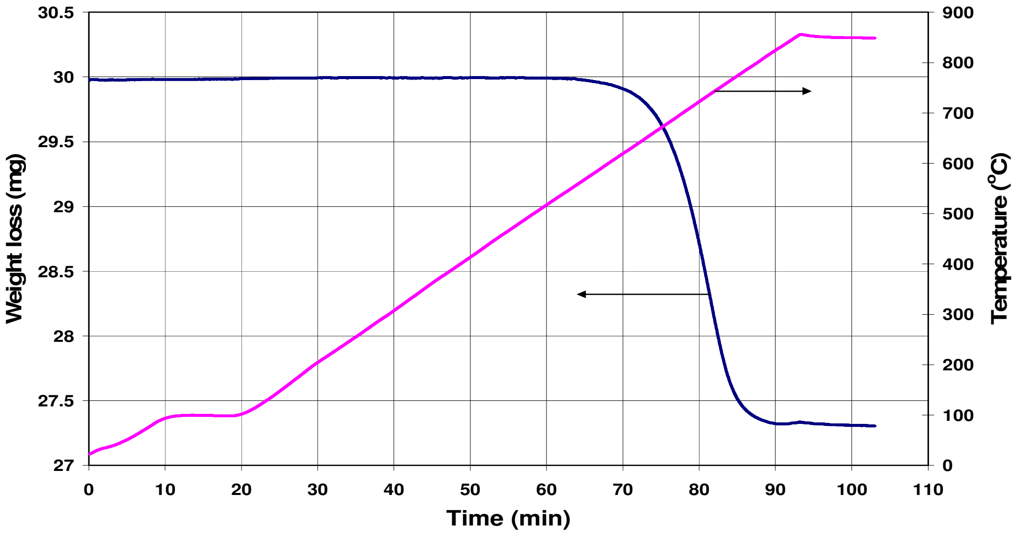

Figure 4-3 TGA Analysis of Bed Ash Generated in Oxy-fuel CFBC Combustion with EB Coal.

CO Emissions

In the initial work done by Hughes *et al*. [10], CO levels were elevated with levels of up to 0.75% and we speculated that this might be due to elevated CO_2 levels based on equilibrium considerations. However, more careful work later with much higher CO_2 levels failed to establish such behaviour, and instead showed that CO levels were extremely sensitive to cyclone temperature (see Figure 4-4) [11] which is also in good agreement with work by Knöbig *et al*. [12].

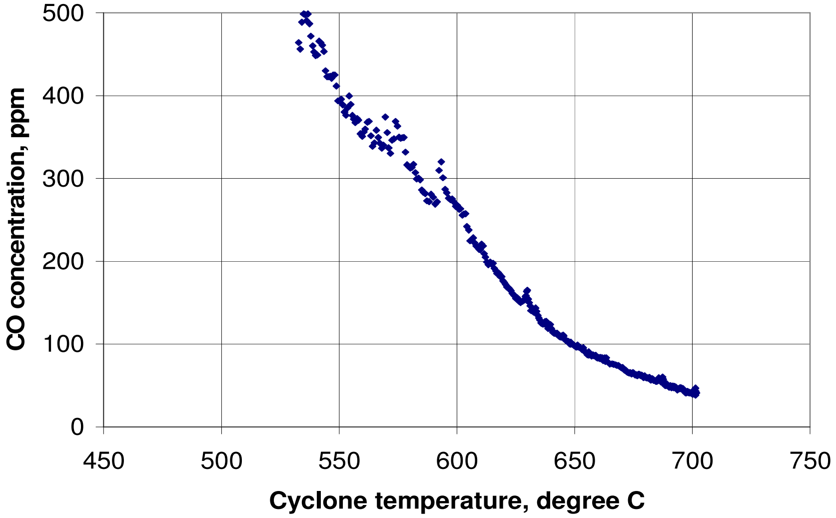

Figure 4-4 Effect of Cyclone Temperature on CO Concentration, Highvale Coal.

NOx Emissions

A series of trials [11, 13] indicated that fuel nitrogen conversions were always lower or comparable with air firing, as indicated by Table 4-3.

Table 4-3 Fuel Nitrogen Conversions at a Nominal Bed Temperature of 850˚C

Limestone	**Highvale**	**EB**	**Kentucky Coal**	**Petroleum Coke**
None	6.64 [6.61]*			
Havelock		2.83 [6.64]	3.51 [4.53]	
		1.54		
Katowice		1.76 [6.22]	1.14 [3.78]	3.35

*[] represent data for air firing

Two tests done with petroleum coke at a nominal 950˚C showed, if anything, a very similar level of fuel nitrogen conversion of 3.3 and 3.7% with Havelock and Katowice limestone, respectively, despite the fact that this temperature meant that the limestone must have calcined and, therefore, might be expected to influence fuel nitrogen conversion *via* catalytic processes as suggested by Lyngfelt and Leckner [14].

SO_2 Emissions

Table 4-4 gives Ca utilizations for various oxy-fuel tests. Unfortunately, these results do not agree with the only comparable set of studies done by VTT, which showed much higher Ca utilizations (more than double) [3, 7]; however, to date our test work has continued to show these rather low utilizations for limestone at typical Ca:S molar ratios for sulphur capture; the exception being with petroleum coke at higher temperatures, where indirect sulphation would prevail, and a typical result can be seen in Figure 4-5.

Table 4-4 Ca Utilizations (%) for Ca/S Molar Ratios of 2 to 3.

Limestone	**EB**	**Kentucky Coal**	**Petroleum Coke**	**Petroleum Coke**
	Nominal Bed Temperature of 850˚C			Nominal Bed Temperature of 950˚C
Havelock	20 [34]	21 [27]		
	26			43
Katowice	22 [25]	23 [27]	22	29

*[] represent data for air firing

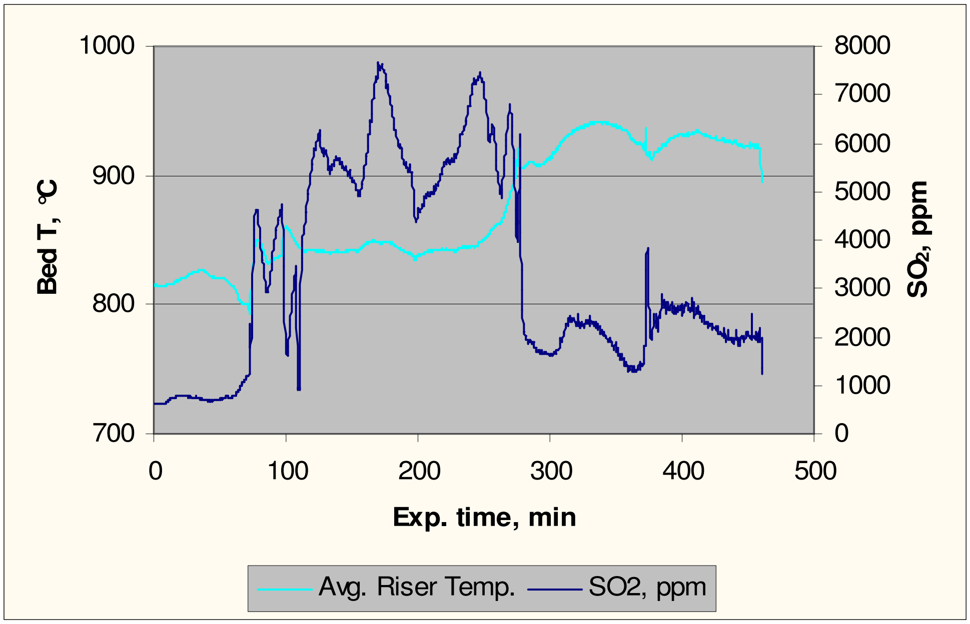

Figure 4-5 Profiles of SO_2 Concentration and Average Bed Temperature for petcoke.

To understand these results, there is substantial literature on direct sulphation conditions for pressurized fluidized bed (PFB) combustion, where sulphation normally occurs with $CaCO_3$. However, even here it is clear that the mechanisms for direct sulphation are still not completely understood [15]. Very early work suggested that direct sulphation might be more effective than indirect sulphation [16, 17] and an explanation was given that counter-diffusion of CO_2 allowed improved sorbent performance. Similar results were produced much later by Liu *et al.* [18], who studied limestone sulphation using two limestones at atmospheric pressures with different concentrations of CO_2 in the sulphation gases in a fixed bed reactor. Interesting findings from that study are that indirect sulphation is faster at low degrees of Ca conversion (<0.3), but thereafter direct sulphation becomes faster; sintering was much reduced in direct sulphation so that at higher conversions direct sulphation was faster than for indirect sulphation. Very similar arguments have been put forward recently by Chen *et al.* [19], who again note the earlier literature concerning almost complete conversion of $CaCO_3$, and mention the back-diffusion argument by CO_2. Like Liu and his co-workers [18], they find that direct sulphation becomes faster at fractional conversions of 0.3 for limestone samples sulphated in a TGA. In this context it is worth noting that while Hu and his colleagues agree with the observation that the sulphate layer is porous, they argue that this is not due to back diffusion of CO_2, but instead due to the way the product crystal grains form on the calcite surface and local porosity [15, 20]. However, to add a note of caution, it is worth remarking that results from pilot and commercial PFBC units tend to show comparable performance to air-fired FBC [21] and not the superior performance reported from fixed beds and thermogravimetric analyzer (TGA) tests for which most of the studies have been done to date, which is not altogether surprising given the various additional factors that must pertain to a real system, such as oxidizing/reducing conditions, particle loss due to attrition, *etc*.

The work of Hu *et al*. [15, 20, 22] notes that both high partial pressures of CO_2 and H_2O might cause significant sintering of the $CaCO_3$, thus impairing overall sulphation performance. In a TGA study done in a fixed bed laboratory reactor at temperatures ranging from 500-700ºC, a concentration of 7.5% H_2O produced an enhancement of sulphation behaviour [15]. In practice one would always expect H_2O to be present in a pilot-scale combustor at levels greater than that and calculations indicate, for our work, water concentrations varying from 5.8 to almost 19%; .

In a series of sulphation tests, Cadomin limestone samples sized 75-115μm were sulphated in a TGA under varying concentrations of water and CO_2 over the course of 10 h to simulate CFB conditions. Figure 6 shows that the indirect sulfation reaction is greatly enhanced in the presence of water for sulfation beyond the initial regime. In 10 h, 100% conversion is achieved, and the addition of 15% H_2O is responsible for an increase in conversion of nearly

45%. Figure 4-6 shows the conversion profiles for tests performed under both air-fired (indirect) and oxy-fired (direct) conditions (15% and 85% CO_2, respectively). In the tests performed without water, oxy-fuel conditions led to more rapid reaction rates for conversion levels >0.45, a level which is dependent on particle size and is thus comparable to the findings of Liu *et al.* [18].

It is important however to note that while the bench scale studies that show that the direct sulfation reaction is more rapid at conversions >0.3 do not include the effects of water in this determination [17, 18]. Figure 4-6 shows that water greatly enhances the direct sulphation reaction; however, the effects only become apparent after initial sulphation (~0.40). Furthermore, it appears that the indirect sulfation reaction is just as rapid as the direct sulfation reaction for conversions >0.3 in the presence of 15% water, contrary to previous findings for the reaction without water. Investigators reporting poor sulfation performance in pilot tests may be expecting to see the increased sulfation performance benchmarked against the unrealistic TGA conditions without water. Investigators would expect to see an increase in sulphation performance of their test unit similar in magnitude to that seen in the TGA when switching from air-fired to oxy-fired modes (curves 1 and 2, from the bottom of Figure 4-6). However, based on these results, the increase should in fact be minimal (curves 4 and 5, from the bottom of Figure 4-6), as water is ubiquitous in combustion systems. These effects of water observed here also have an implication on increasing the sulphur capture performance of FBCs firing high-rank/low-moisture fuels such as petroleum coke. It is conceivable that the simple addition of water into the bed at or above concentrations of 15% would result in enhanced calcium utilization. To this end, tests on CanmetENERGY's mini-CFBC are currently underway to both verify the results from the TGA and to explore the addition of steam to high-rank fuel combustion.

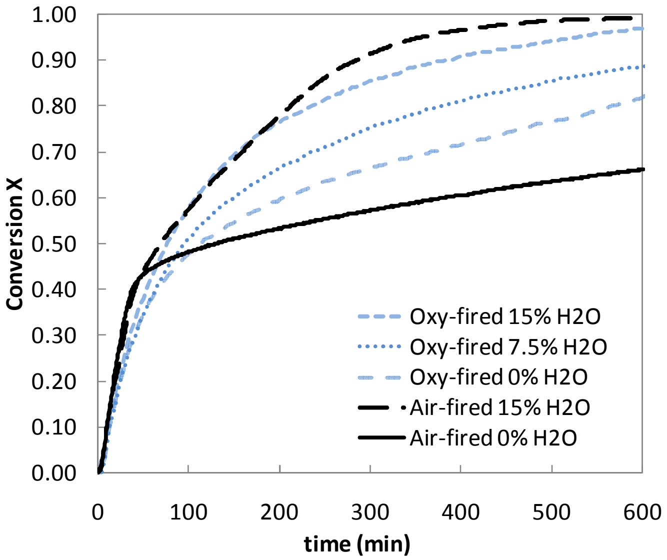

Figure 4-6 Sulphation conversion profiles under oxy-fired conditions for varying concentrations of H_2O with air-fired profiles overlaid.

Foster-Wheeler

Currently, extensive work has been undertaken in our equipment for Foster Wheeler and this will be presented later. It is perhaps sufficient to note that the results have been promising and the first discussion of these is provided elsewhere [23]. Figure 4-7 provides an example of the CO_2 emissions over a 2½ day trial under oxyfuel conditions, indicating that it is possible to maintain excellent control on CO_2 levels and combustion conditions.

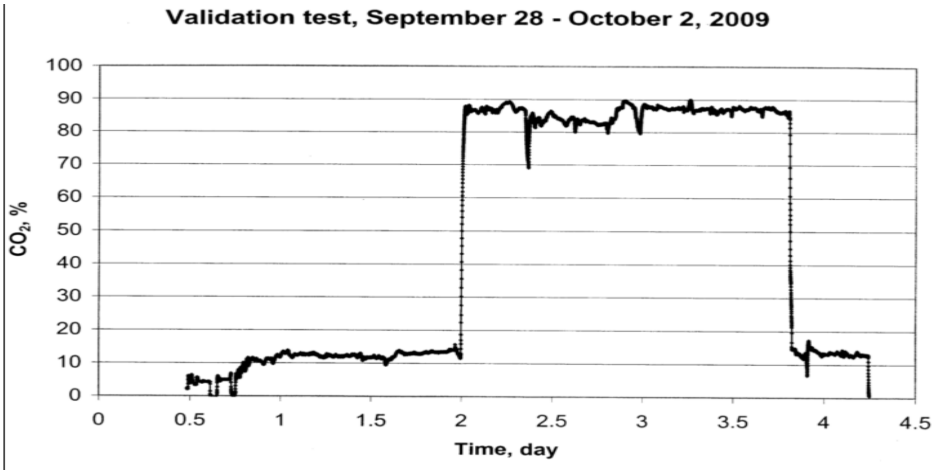

Figure 4-7 Tests on Oxy-fired Combustion in CanmetENERGY's 0.8 MWt CFBC.

Conclusions

The tests so far have proved the suitability of CFB for oxy-fuel combustion. Switchover between air- and oxygen-fired modes is easy, and the combustion process is stable in both modes. CO_2 levels can be maintained in the 80-90% range or better, and CO and NOx emissions are comparable or lower than those seen with air firing. $CaCO_3$ is also shown to be stable under the conditions of this work, suggesting that sulphation occurs *via* the direct route. However, work done at CanmetENERGY has consistently shown that sulphur capture is lower than for air-fired CFBC. Work is now underway to try and explain these results, this work also suggests that the effect of water on sulphation needs to be explored in much greater detail to better understand these phenomena.

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CHAPTER 5 : THE EFFECTS OF STEAM ON THE SULFATION OF LIMESTONE AND NO_X FORMATION IN AN AIR- AND OXY-FIRED PILOT-SCALE CFB COMBUSTOR

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Abstract

Sulfation studies have shown that above about 40% conversion, direct sulfation is always faster than indirect sulfation. However, this work demonstrates using both thermogravimetric analysis (TGA) and tube furnace (TF) experiments that direct sulfation is in fact slower than indirect sulfation for nearly all levels of conversion if steam ($H_2O_{(g)}$) is present at realistic levels for normal combustion conditions. We have also examined the effects of $H_2O_{(g)}$ on SO_2 capture and NH_3 oxidation to NO_x over calcium-containing compounds under air- and oxy-fired conditions in a pilot-scale CFBC utilizing limestone addition. For the air-firing of petroleum coke, the addition of 15%vol $H_2O_{(g)}$ resulted in decreased NO_x emissions by up to 60% as well as increased SO_2 retention. The simultaneous reduction of SO_2 and NO_x were attributed to enhanced solid-state diffusion (sintering) by $H_2O_{(g)}$. Under oxy-fuel firing conditions, $H_2O_{(g)}$ addition also resulted in decreased NO_x emissions, but the pilot-scale tests showed poorer sulfur capture performance and calcium utilization as compared to air firing when $H_2O_{(g)}$ was present, thereby reconfirming the TGA/TF results. It appears that most bench-scale work on sulfation to date has underestimated the true rate of reaction in the presence of $H_2O_{(g)}$. This conclusion explains at least in part why indirect sulfation is often greater than direct sulfation in pilot plant studies on oxy-fuel circulating fluidized bed combustion. Moreover, this work stresses the importance of including $H_2O_{(g)}$ in bench-scale experiments that attempt to simulate real combustion environments.

Introduction

Circulating fluidized bed combustion (CFBC) is a well-established combustion technology for firing biomass, waste-derived fuels and high-sulfur fuels, among others. The technology achieved commercial importance in the late 1980s and there are now several hundred large-scale utility-operated boilers worldwide *(1)*. Perhaps the most important advantages of CFBC, is its ability to utilize *in-situ* limestone addition for sulfur capture when high-sulfur fuels are burned. Upon injection into the furnace, limestone undergoes calcination (reaction 5-1) and then sulfation (reaction 5-2) to achieve 80-90% sulfur retention in practice with Ca:S molar ratios ranging from 2 to 3 *(2)*. Together, these reactions are termed indirect sulfation.

$$CaCO_3 \leftrightarrow CaO + CO_2 \tag{5-1}$$

$$CaO + SO_2 + \frac{1}{2}O_2 \leftrightarrow CaSO_4 \tag{5-2}$$

Assuming that biomass is a carbon-neutral fuel, CFBC technology provides a means to reduce anthropogenic CO_2 emissions in the power generation industry and also offers the option of co-firing more marginal fossil fuels in an environmentally benign manner. For the oxygen-fired case, so-called oxy-fuel combustion, technology offers the possibility of near perfect (90-95%) CO_2 capture, either for sequestration or enhanced oil recovery (EOR). Oxy-fuel fired pulverized fuel (PF) combustion has been extensively studied since the early 1990s (3) and demonstration units of up to 40 MW_{th} exist *(4)*. By contrast, there are no oxy-fuel CFBC demonstration plants, and the technology has only recently been tested at the pilot scale with flue gas recycle. To date, the results are available in the open literature for only two such pilot plants, operating with full flue gas recycle: a small CFBC owned and operated by VTT (Technical Research Centre of Finland) *(5,6)* and two CanmetENERGY facilities, a 0.1 MWth CFBC

(7,8,9) and a 0.8 MWth facility (10), although several others are being built or commissioned worldwide at centres in Sweden, China, Germany and the US and open domain publications from such units can soon be expected.

SO_2 Emissions under Oxy-Fuel Combustion Conditions

An important feature of oxy-fuel CFBC is its ability to utilize *in-situ* sulfur capture using limestone addition. The equilibrium relationship given by Baker *et al. (11)* indicates that, under oxy-fuel combustion in an oxy-fired CFBC at a typical operating temperature of 850ºC, sulfation proceeds *via* reaction (5-3), termed direct sulfation, at CO_2 partial pressures above 50 kPa.

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 \leftrightarrow CaSO_4 + CO_2 \qquad (5\text{-}3)$$

Early investigators, Snow *et al. (12)* and Hajaligol *et al. (13)*, suggested that direct sulfation was faster than indirect sulfation, an observation which was initially attributed to back-diffusion of CO_2, based on the results of bench-scale work. Other investigators are in agreement with this conclusion, but offer various other suggestions for the improvement *(14,15,16).* While reaction rates at lower conversion levels are characterized by an inverse relationship with the concentration of CO_2 *(15)*, Chen *et al.* found the direct sulfation reaction to be faster at conversions >0.3 *(16,17).* Since (C)FBC particle residence times far exceed the initial kinetics of sulfation, it can be inferred from early work, and it has been repeatedly shown in bench-scale work, that oxy-fuel conditions should enhance the sulfation reaction. Despite these positive results, studies on CanmetENERGY's pilot-scale CFBC showed that at 850ºC the utilization of limestone for sulfur capture under oxy-fuel conditions decreased from the air-fired case (22-23% *vs.* 25-34%) for Ca/S molar ratios of 2 to 3 *(8,9).* Furthermore, experiments performed on a small CFB at Zhejiang University in China using bottled flue gases for once-through oxy-fuel combustion also reported poorer sulfur capture efficiency under oxy-fuel conditions *(18)*, underlining the disparity between bench-scale and pilot-scale results.

Recent work by Stewart *et al. (19)* demonstrated that the presence of $H_2O_{(g)}$ during sulfation in a thermogravimetric analyzer (TGA) and tube furnace (TF) greatly enhances indirect sulfation, in agreement with the earlier work by Wang *et al. (20)*. With 15% $H_2O_{(g)}$ present, an increase in conversion of over 45% was seen in under 10 h of sulfation (which is within the typical residence time of limestone particles during CFB combustion) *(19)*. In a combustion environment, $H_2O_{(g)}$ concentration in the flue gas usually varies between 4 to over 20%. However, dozens of modeling studies from 1970's to the present have not included $H_2O_{(g)}$ as a parameter. Stewart *et al. (19)* suggested that the addition of steam to the air-fired combustion of a high-rank, low-moisture fuel such as petroleum coke (petcoke) would result in increased sulfur capture. Furthermore, since the concentration of $H_2O_{(g)}$ in the flue gas of oxy-fuel CFBC can be several times greater than that for air-fired combustion, $H_2O_{(g)}$ may have a significant effect on direct sulfation as well. A fairly recent review on the direct sulfation reaction by Hu *et al. (21)* mentions that the work of Hajaligol *et al. (13)* found a promoting effect of $H_2O_{(g)}$. Later, Hu *et al. (14)* concluded that the promoting effect was due to enhanced ion mobility in the presence of $H_2O_{(g)}$, but they did not quantify the effects nor vary the concentration. Very recently, Jia et al., *(23)* have also demonstrated that $H_2O(g)$ influences direct sulphation, but they did not provide comparisons between the two sulfation modes. As with indirect sulfation, direct sulfation models have been derived without taking into account the effect of $H_2O_{(g)}$. The failure to account for $H_2O_{(g)}$ was discussed in our earlier paper (19), but is even more remarkable when one realizes that $H_2O_{(g)}$ is well known in the corrosion and geochemistry literature to be able to affect ionic lattices, and to dissolve in various minerals and glasses at high temperature, with a resulting enhancement of ionic diffusion of other gases *(24, 25).*

Effects of H_2O on Catalytic Formation of NO_X over Calcium-Containing Compounds

Due to relatively low FBC combustion temperatures, NO_x production is lower than that for PF and is produced almost entirely from fuel nitrogen with little or no thermal NO_X *(22)*. NO_x emitted from FBC is formed though numerous pathways, although it is normally considered that the two dominant species involved in the final production of NO are NH_3 and HCN *(26).* CaO (and to a lesser extent, $CaCO_3$ and $CaSO_4$) catalyzes the oxidation and reduction of NH_3, as shown by reactions (5-4) and (5-5), which are partially responsible for the well-known increase in NO_x emissions when burning coal associated with limestone addition *(26,27,28).*

$$NH_3 + \frac{5}{4}O_2 \xrightarrow{CaO} NO + \frac{3}{2} H_2O \tag{5-4}$$

$$NH_3 + \frac{3}{4}O_2 \xrightarrow{CaO} \frac{1}{2}N_2 + \frac{3}{2}H_2O \tag{5-5}$$

At FBC temperatures, the oxidation of NH_3 is significantly affected by the concentration of $H_2O_{(g)}$ (*28,29,30*). In a study by Zijlma *et al. (28)*, the addition of $H_2O_{(g)}$ in concentrations as low as 6% resulted in the reduction of NO formation by over 80%, a result which the authors attribute to reversible deactivation of CaO by blocking of active sites by $H_2O_{(g)}$. Similar results were found in a study on the kinetics of NH_3 oxidation over CaO that showed NO_x formation to decrease monotonically with increasing $H_2O_{(g)}$ concentration over the range of 0-30% *(30).* Other studies showed that the catalytic decomposition of N_2O over CaO to form N_2 is also inhibited by the presence of either $H_2O_{(g)}$ or CO_2 *(31,32).* As it is well established that CO_2 and H_2O enhance sintering of CaO *(19,33)*, this reduction in catalytic activity was attributed both to sintering, and some adsorption of $H_2O_{(g)}/CO_2$ on the active CaO sites, resulting in a combination of reversible and irreversible deactivation *(32)*.

The effect of $H_2O_{(g)}$ on NO_x formation is well documented in small-scale tests using synthetic flue gases, but there are few studies investigating it under more realistic pilot plant conditions. However, one such study *(35)* indirectly summarized the effects $H_2O_{(g)}$ and CO_2 on NO_x production in a bubbling FBC: flue gas recirculation (in which $H_2O_{(g)}$ and CO_2 concentrations are elevated) has a large reductive effect on NO_x formation. The authors also used synthetic recirculated flue gas to alter the concentrations of $H_2O_{(g)}$ and CO_2, and they concluded that NO_x emissions decreased linearly with increasing both $H_2O_{(g)}$ and CO_2 concentrations. However, since limestone injection was not employed, no attempts to tie the results into catalytic mechanisms involving CaO were made *(35)*.

Objectives

This goal of this work is to investigate the effects of $H_2O_{(g)}$ on the emission of SO_2 and NO_x during CFB combustion with limestone addition, with a focus on oxy-fuel combustion conditions. At the bench scale, this study aims to quantify the effects of $H_2O_{(g)}$ on direct sulfation, while the pilot-scale sulfation tests were intended to resolve discrepancies between predicted capture performance under oxy-fuel conditions and actual performance. Finally, the pilot-scale tests are intended to verify the effects of $H_2O_{(g)}$ on the catalytic oxidation of NH_3 under realistic conditions during both air- and oxy-fired combustion.

Experimental

TGA and TF tests

The TGA and TF were used to measure sulfation rates of limestone particles under varying concentrations of $H_2O_{(g)}$ in simulated air- and oxy-fired environments. The TGA consisted of an Inconel drop tube reactor with hanging platinum pan connected to a balance with an accuracy of +/- 1 µg. Steam was supplied with a syringe pump and steam generator, and gas flows were controlled with mass-flow controllers. The quartz TF utilized the same peripheral equipment for control. Full details of the set up and operation of the TGA and TF are described elsewhere *(19)*. Both units were operated at 850°C with synthetic flue gases for the air-fired and oxy-fired tests (conditions, Table 5-1). Sulfation time was up to 10 h for the TGA. However, the TF cannot be operated without mass transfer (inter-particle) limitations, and so the sulfation time was increased to 14 h. The properties of the Cadomin limestone used in the tests are shown in Table 5-2. Density of the limestone, nascent CaO, and sulfated product were determined by gas pycnometry, while pore surface area and volume were determined *via* nitrogen adsorption methods.

Table 5-1 Operating conditions for TGA and TF tests.

	Air-firing	Oxy-firing
Temperature (°C)	850	850
Reaction time (h)	10 (14)	10 (14)
CO_2 (%)	12.75	balance
O_2 (%)	2.53	2.53
SO_2 (ppm)	3800	3800
H_2O (%)	0/7.5/15	0/7.5/15
N_2 (%)	balance	0

Table 5-2 Characteristics of Cadomin limestone used in TGA and TF tests[1]

	Calcined sample	Original sample
CaO content (wt%)	--	97.4
Particle size (µm)	--	75-115
BET specific area (m^2/g)	9.51	2.00
BJH pore volume (cm^3/g)	0.03	0.01
Density (g/cm^3)	3.34	2.73

[1] Elemental composition by XRF can be found elsewhere (Supporting Information, Ref. *(19)*).

From TGA data, conversion is calculated using eq. (5-6), where *m(t)* is the sample mass, $m°$ is the calcined sample mass, MM_y is the molar mass of species y, and x_e is the mass fraction of CaO in the sample.

$$X = \frac{m(t) - m^\circ}{\left(\frac{MM_{CaSO_4}}{MM_{CaO}} - 1\right)(x_e m^\circ)} \tag{5-6}$$

It should be noted that the term calcium utilization is often used interchangeably with conversion when discussing sulfation. Eq. (5-6) holds true for both indirect and direct sulfation, where in the latter case the molar mass of $CaCO_3$ is used in place of CaO. Eq. (5-6) cannot be applied to cases where the sample is a mixture of $CaO/CaCO_3/CaSO_4$ without first determining the content of $CaCO_3$ by calcination. Lastly, TF samples were analyzed using X-ray fluorescence (XRF) and conversion was calculated using the molar ratio of S/Ca.

Pilot-scale CFBC tests

Figure 5-1 gives a schematic drawing of the CFBC unit, which consisted of a 4.5 m stainless riser 100 mm in diameter to which supplemental heat was supplied by four 4.5 kW electric heaters surrounding the bottom 1 m of the bed. Dry flue gas recycle for oxy-fuel combustion was provided by a cyclone, baghouse, and condenser at the backend of the combustor. Full details of the unit and its operation are provided elsewhere *(7,8,9)*. For the runs with $H_2O_{(g)}$ addition, saturated steam was supplied by a 105 kW steam generator at 7 barg, then superheated in heat-traced lines that fed directly to the wind box below the bed. Oxygen purity was 99%. A charge of 5 kg of synthetic olivine sand (50:50 SiO_2:MgO, size 0.15-0.35 mm) was added before each run, and the bed sand was emptied and collected after. Bed material samples were analyzed by electron microscopy/energy dispersive X-ray (SEM/EDX) to determine Ca utilization. Limestone and fuel were premixed before adding to the feed hopper. Fuel mixture feed rates started slow (0.3 kg/h) and were ramped up until steady state was achieved (1-2 h from starting feed) at which point the feed remained constant for the duration of the run. From startup to shutdown, each run lasted between 7 and 8 h in order to minimize variances in Ca utilizations from test to test.

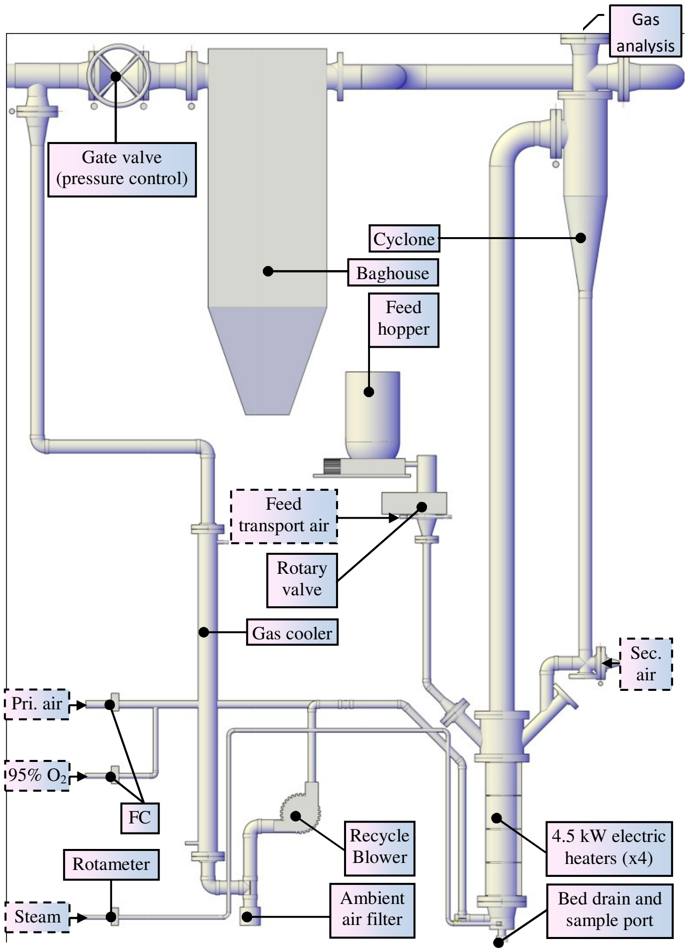

Figure 5-1 Schematic diagram of CanmetENERGY's 100 kW mini-CFBC as configured for the pilot-scale oxy-fired and air-fired tests.

Two limestones were used in the CFBC tests, Katowice (from Poland, Upper Silesia) and Cadomin (from Canada). The Cadomin was the same limestone as was used in the TGA tests, but with a "large" average particle size 600 µm. Average particle size of Katowice was "small", 250 µm, while $CaCO_3$ content in this limestone was roughly equal to that of Cadomin (97%). It has been shown that these limestones perform similarly in bench-scale experiments when they are the same size *(19)*. The Ca/S feed ratios for both petcoke and bituminous coal were 2. The average particle sizes of the fuels were ~2 mm and ~1 mm, respectively. Proximate and ultimate analyses of the fuels are provided in Table 5-3.

Table 5-3 Proximate and ultimate analyses of petroleum coke and bituminous coal used in the pilot-scale CFBC tests.

Fuel	Ash (%)	Volatiles (%)	C_{fix} (%)	Moisture (%)	C (%)	H (%)	N (%)	S (%)	O (%)[1]
Petcoke	1.4	11.0	87.6	6.6	87.4	3.7	1.7	6.0	1.2
Bituminous coal	15.2	26.9	57.9	6.7	71.1	3.9	1.7	0.6	22.7

[1] by difference

The feed system used for these tests involved a feed hopper that fed fuel/limestone through a 25.4 mm ID pipe. The system was operated at slightly negative pressure throughout, which caused some air ingress into the back end, preventing 90%+ CO_2 concentrations under oxygen firing (but still achieved >70% CO_2 and direct sulfation).

An important parameter for measuring sulfur capture performance is the sulfur capture efficiency, η_{SO2}, defined as the ratio of SO_2 retained by the system to the amount of SO_2 that would be produced if all sulfur in the fuel was converted to SO_2, a value which is readily determined *via* mass balance.

$$\eta_{SO_2}[\%] = \frac{SO_{2_{no\ capture}}[ppm] - SO_{2_{emitted}}[ppm]}{SO_{2_{no\ capture}}[ppm]} \times 100\% \qquad (5\text{-}7)$$

The fuel-N to NO_x conversion ratio, $NO_X{:}N$ can be used to conveniently compare oxy-fuel NO_x emissions to air-fired emissions, since expressing oxy-fired emissions in ppm is not comparable to air-fired emissions since the gas leaving the combustor contains no air derived nitrogen. The ratio is defined as the moles of nitrogen produced as NO_x in a given time to the moles of nitrogen in the fuel fed to the combustion system during that time, *i.e.*:

$$NO_X\colon N = \frac{NO_X \; as \; NO \left[\frac{mol}{h}\right]}{Fuel \; N \; fed \left[\frac{mol}{h}\right]} \qquad (5\text{-}8)$$

Results and Discussion

TGA and TF Sulfation Tests

Figure 5-2 shows direct and indirect sulfation curves for Cadomin limestone with steam concentrations varying between 0 and 15%. Under air-fired conditions (Table 5-1), it was confirmed that sulfation proceeded via CaO after calcination (calcination step not shown), whereas calcination did not occur for the oxy-fuel tests. It can be seen that the degree to which $H_2O_{(g)}$ enhances direct sulfation is smaller than that in the indirect case. The addition of 15% $H_2O_{(g)}$ under oxy-fired conditions results in an increase in conversion of around 15% after 10 h, whereas under air-fired conditions, the same addition results in an increase of 45%. In the tests performed without steam, oxy-fuel conditions led to more rapid reaction rates for conversion levels >0.45, a level which is dependent on particle size but is comparable to the findings of other direct sulfation studies. However, the bench-scale studies that show that the direct sulfation reaction is more rapid at conversions >0.3 do not include the effects of steam in this determination *(12,13,17,34)*. Figure 5-2a shows that steam greatly enhances both direct and indirect reactions in the TGA; however, the effect only becomes apparent after initial sulfation is complete (~0.40). Furthermore, it appears that the indirect sulfation is just as rapid, if not more so, as the direct reaction for conversions >0.4 in the presence of 15% $H_2O_{(g)}$. This picture becomes even clearer from the TF tests shown in Figure 5-2b. Investigators reporting poor sulfation performance in pilot-scale might expect to see an increase in sulfation performance of their pilot unit similar in magnitude to that seen in the TGA when switching from air-fired to oxy-fired modes without $H_2O_{(g)}$ (curves 1 and 3, from the bottom of Figure 5-2a). However, based on these results, the change should in fact be minimal (curves 5 and 6, from the bottom of Figure 5-2a), or indeed be negative (curves 3 and 4, from the bottom of Figure 5-2b), as steam is ubiquitous in real combustion systems. Thus, the poorer than expected sulfation performance of CanmetENERGY's oxy-fuel CFBC in the past compared with the air-fired case, and perhaps even in pressurized FBC systems (PFBC) where direct sulfation occurs *(36)*, can be explained as due to the effects of steam produced by the combustion of a hydrocarbon fuel.

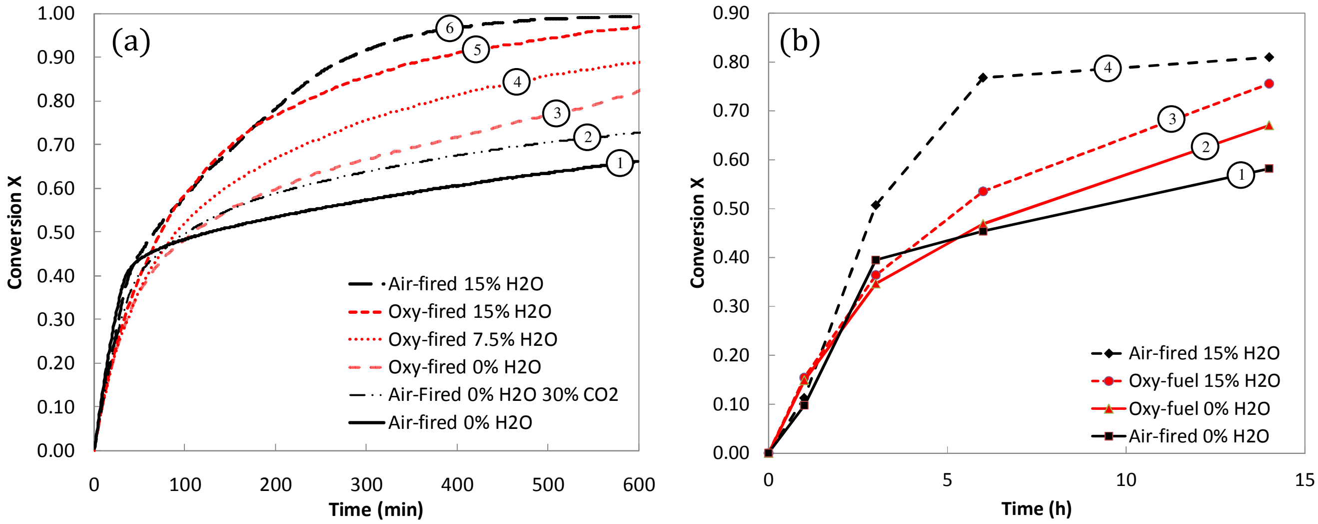

Figure 5-2. Sulfation conversion profiles of Cadomin limestone under varying CO_2 and $H_2O_{(g)}$ concentrations with 2.53% O_2 and 3800 ppm SO_2 from (a) TGA data and (b) tube furnace data.

Figure 5-2a also depicts an additional TGA test (curve 2) with $[CO_2]$ = 13% while all other conditions remained the same as in the other air-fired test (curve 1, $[CO_2]$ = 28%).While it is known that elevated CO_2 concentrations retard indirect sulfation during the kinetically-controlled stage *(15)*, it is interesting to note that curve 2 shows that CO_2 promotes the reaction beyond a conversion level of 0.4, suggesting that CO_2 may play a role similar to that of $H_2O_{(g)}$. Since the onset of direct sulfation is associated with elevated CO_2 concentrations, it seems likely that such conditions induce accelerated sintering (solid-state diffusion) and thus enhanced conversion, similar to the effects of CO_2 on indirect sulfation *(17, 34)*. The discussion on sintering by CO_2 and $H_2O_{(g)}$ is continued in section 3.3 and 3.4.

Pilot CFBC Tests: Air Firing

Operating CanmetENERGY's pilot CFB yielded the test results shown in Table 5-4. Air firing of bituminous coal (BC) and petcoke (PK) was performed with and without limestone (Ca:S molar ratio = 2, and 0), and with and without the addition of steam. For the runs firing petcoke and "small" Katowice particles (PK-KT-AF-0H_2O and PK-KT-AF-15H_2O), there was no statistically significant difference in SO_2 emissions when increasing the concentration of $H_2O_{(g)}$ from 9.4 to 17% (η_{SO2} = 79 ± 6% and 78 ± 2%, respectively); however, the Ca utilization increased from 41 to 47% when 15% steam was added - a result which is consistent with the bench-scale results presented in Figure 5-2.

Figure 5-3 depicts the portion of the 7 h run PK-KT-AF which encompasses the time during which 15% $H_2O_{(g)}$ (on a molar basis of the combined primary and secondary air) was added. Within minutes of injecting the steam, the SO_2 concentration dropped from 1250 to 848 ppm (Table 5-4). The drop in SO_2 concentration was reversed when $H_2O_{(g)}$ was cut, returning to the pre-addition level, but over a period of time that was longer than required for the response of the system to the addition of $H_2O_{(g)}$, a result parallel to the transient TGA test depicted in *(19).* η_{SO2} increased during the addition of $H_2O_{(g)}$ from 61 to 74%. It should be noted that although the average bed temperature decreased from 900 to 868°C, the average temperature of the riser was higher for the duration of $H_2O_{(g)}$ addition. This is due to the additional fluidizing gas causing expansion of the bed as well as increasing the hot solids flux. This is to say that the addition of $H_2O_{(g)}$ did not cool the bed so much as it redistributed the hottest solids along a greater length of the reactor.

For the runs firing “large” Cadomin limestone (PK-CD-AF-0H_2O and PK-CD-AF-15H_2O) the increase in η_{SO2} with the addition of $H_2O_{(g)}$ was from 53 to 57%, and Ca utilization increased only slightly (20 to 21%).

Table 5-4 Pilot-scale CFBC operating parameters and emissions. Run ID nomenclature: FUEL-LIMESTONE-FIRING MODE-H_2O ADDED

Date	4-Aug		12-Aug	13-Aug	31-Aug	23-Sep	9-Aug	2-Sep	22-Sep	6-Aug	
Run ID	PK-KT-AF[2]		PK-KT-OF-0/15H2O		PK-KT-AF-0/15H2O		PK-AF	PK-CD-AF-0/15H2O		BC-KT-AF[5]	
Emissions Data											
SO_2 (ppm)[1]	1250 ± 173	848 ± 55	4822 ± 124[4]	5189 ± 86[4]	679 ± 150	701 ± 27	2905 ± 47	1515 ± 181	1382 ± 150	33 ± 3	35 ± 1
NO_X (ppm)[1]	727 ± 46	453 ± 30	453 ± 47	319 ± 15	242 ± 93	94 ± 19	601 ± 28	447 ± 41	268 ± 41	420 ± 66	292 ± 10
CO (ppm)[1]	2394 ± 142	2976 ± 1180	49 ± 6	29 ± 8	438 ± 245	647 ± 160	665 ± 85	546 ± 159	792 ± 86	1112 ± 992	1197 ± 67
CO_2 (%)[1]	13.6 ± 0.3	13.5 ± 0.4	69.1 ± 0.2	70.2 ± 0.2	20.8 ± 2.8	19.2 ± 0.7	12.8 ± 0.3	16.3 ± 0.6	15.6 ± 0.8	12.4 ± 0.6	12.4 ± 0.3
O_2 (%)	13.3 ± 0.5	12.6 ± 0.3	3.6 ± 0.2	3.0 ± 0.3	6.6 ± 2.1	4.3 ± 0.5	4.7 ± 0.4	4.8 ± 0.6	4.6 ± 0.5	6.7 ± 1.2	6.9 ± 0.3
H_2O (%)	3.4 ± 0.2	18.3 ± 0.2	9.4 ± 0.4	17.2 ± 0.3	9.9 ± 1.1	21.3 ± 0.3	6.1 ± 0.2	7.2 ± 0.3	20.1 ± 0.2	3.8 ± 0.3	18.6 ± 0.2
NO_X:N	0.19 ± 0.12	0.12 ± 0.07	0.11 ± 0.03	0.08 ± 0.01	0.04 ± 0.04	0.02 ± 0.01	0.18 ± 0.03	0.11 ± 0.03	0.08 ± 0.03	0.21 ± 0.13	0.14 ± 0.08
Ca util. (%)[3]	--	--	40.0 ± 0.0	33.6 ± 0.0	41.2 ± 0.0	47.4 ± 0.0	--	20.3 ± 0.0	21.2 ± 0.0	--	--
Sulfur Cap. (%)	61.4 ± 6.7	73.8 ± 2.8	65.0 ± 1.9	61.9 ± 1.2	79.0 ± 5.7	78.4 ± 1.9	10.4 ± 5.2	53.2 ± 6.5	57.4 ± 5.4	91.6 ± 1.1	91.0 ± 0.8
Decrease in NO_X (%)	37.6 ± 4.9		29.5 ± 4.4		61.1 ± 36.0		--	39.9 ± 9.7		30.6 ± 5.9	
Operational Data											
Avg. Bed T (ºC)	900 ± 14	868 ± 5	842 ± 2	856 ± 1	882 ± 7	879 ± 3	890 ± 2	895 ± 8	881 ± 11	864 ± 4	834 ± 3
Fuel Feed Rate (kg/h)	1.63 ± 0.04	1.69 ± 0.03	5.02 ± 0.00	5.02 ± 0.00	3.74 ± 0.00	3.10 ± 0.00	2.46 ± 0.00	3.74 ± 0.00	3.10 ± 0.00	1.00 ± 0.00	1.00 ± 0.00
Primary Air (kg/h)	17.9 ± 0.4	17.9 ± 0.4	15.8 ± 1.3	15.6 ± 0.7	12.0 ± 1.8	13.0 ± 0.2	22.9 ± 0.1	17.7 ± 0.6	17.6 ± 0.4	14.9 ± 0.9	14.9 ± 0.9
Secondary Air (kg/h)	0.18 ± 0.01	0.17 ± 0.01	0.52 ± 0.03	0.50 ± 0.02	0.48 ± 0.05	0.53 ± 0.01	0.29 ± 0.01	0.52 ± 0.02	0.61 ± 0.02	0.35 ± 0.01	0.34 ± 0.01
Feed Transport (kg/h)	0.04 ± 0.00	0.04 ± 0.00	0.98 ± 0.05	0.66 ± 0.02	0.26 ± 0.07	0.42 ± 0.01	0.04 ± 0.00	0.21 ± 0.02	0.32 ± 0.02	0.03 ± 0.00	0.03 ± 0.00
Ca:S Molar Ratio	2 ± --	2 ± --	2 ± --	2 ± --	2 ± --	2 ± --	--	2 ± --	2 ± --	2 ± --	2 ± --
Steam Injected (kg/h)	--	1.98 ± 0.02	--	1.14 ± 0.01	--	1.52 ± 0.02	--	--	2.03 ± 0.02	--	1.67 ± 0.02
99% Oxygen (kg/h)	--	--	8.49 ± 0.09	10.43 ± 0.22	--	--	--	--	--	--	--

[1] All air-fired emissions data corrected to 6% O_2.

[2] PK-KT-AF run is a single run where the transient effects of $H_2O_{(g)}$ were tested, as depicted in Figure 5-5.

[3] By EDX analysis of Ca and S ratio in bed material.

[4] Assuming all $H_2O_{(g)}$ in recycled flue gas is condensed and drained, and that no SO_2 leaves the system in the condensate.

[5] BC-KT-AF run is also a single run.

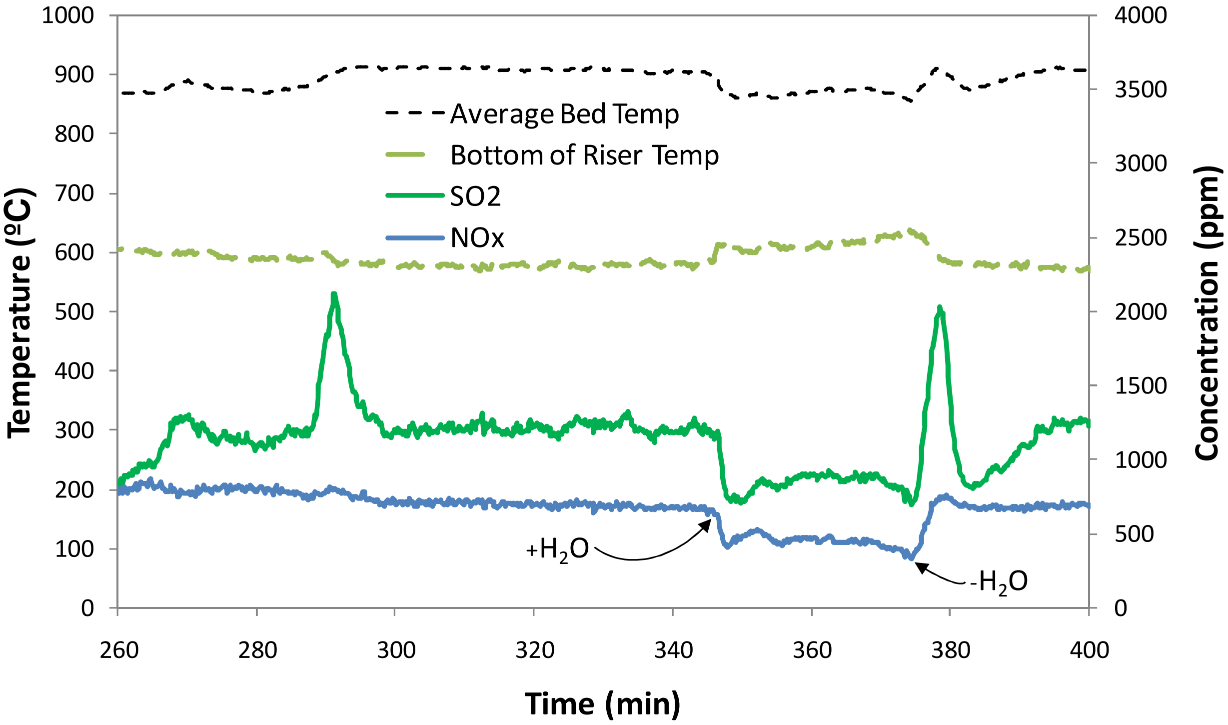

Figure 5-3 Dynamic response of 100 kW pilot CFBC to 15%vol $H_2O_{(g)}$ addition under air-fired conditions during run PK-KT-AF (see Table 5-4 for the run ID nomenclature).

Sulfur capture (η_{SO2}) during the air-firing of bituminous coal (run BC-KT) was significantly better than the petcoke runs using the same limestone. This is surprising since one would expect that the high-sulfur petcoke would promote the sulfation reaction, since it has been shown that the reaction rate is proportional to SO_2 concentration to a power between 0 and around 1 (*21*). With the addition of steam, no significant difference in sulfur capture performance was observed. It is possible that the lack of response to $H_2O_{(g)}$ addition in this case (BC-KT) is due to the high degree of sulfur capture (~91%) and relatively low SO_2 concentrations (2 orders of magnitude less than petcoke tests). Lastly, since this was a transient test, Ca utilization was not determined.

Pilot CFBC Tests: Oxy-Firing

Oxy-firing was achieved by starting the system in air-fired mode for 2 h and then changing the air feed to pure O_2, while at the same time switching the recycle blower on. After establishing steady conditions, the addition of steam to the oxy-firing of petcoke resulted in a decrease in Ca utilization from 40 to 34% (PK-KT-OF-0H_2O and PK-KT-OF-15H_2O, respectively). At the CO_2 concentrations in these tests (~70%), sulfation would proceed *via* the direct route up to 875°C *(11)***.** This was subsequently confirmed by examining the bed material in a TGA.

Compared to the air-fired tests of petcoke with the same limestone, both Ca utilizations and η_{SO2} were lower under oxy-fuel conditions. Without considering the effects of $H_2O_{(g)}$ on the direct sulfation, this result would be unexpected; however, when looking at the curves presented in Figure 5-2a and Figure 5-2b, a decrease in sulfur capture under oxy-firing conditions is what one should expect to see when $H_2O_{(g)}$ is present in concentrations at or above 15%.

Paradoxically, the decrease in η_{SO2} and Ca utilization with the addition of steam under oxy-fired conditions may be due to the steam addition itself. It was noted in previous work *(19)* that the enhancement of sulfation by $H_2O_{(g)}$ addition is characterized by diminishing returns and that some additional tests involving concentrations of $H_2O_{(g)}$ beyond 15% resulted in poorer conversion, possibly due to a dilution effect on SO_2. In the oxy-fuel test without steam addition (PK-KT-OF-0H_2O), the concentration of $H_2O_{(g)}$ was already 9.4%, compared to air-firing at 3.4% (PK-KT-AF-0H_20). In short, a limit is expected if excessive sintering of the sorbent occurs, and will also be brought about due to the negative effects of reducing the concentration of SO_2 through dilution. A second contributing factor may be that the further steam addition to an already elevated concentration of $H_2O_{(g),}$ combined with the sintering effects of high CO_2

concentrations, caused excessive sintering of the sorbent, thereby reducing sulfation. A similar effect and optimum value occurs when varying the reaction temperature *(2)*, a variable that also affects the rate of solid-state diffusion (sintering).

One final result of this pilot-scale sulfation study is that Ca utilizations under oxy-fuel firing, compared to CanmetENERGY's previous work, are better than previously reported from this unit, and similar to that we would expect for Ca utilizations from commercial air-fired FBCs (*i.e.*, ~40%). The better performance described in this study is attributed to the smaller limestone particle size used in the "small" limestone tests *vs.* the larger sizes used in the previous work (0-0.5 mm and 0-0.8 mm) *(7,8)*.

NO_x Emissions

NO_x formation under oxy-fuel conditions was found to be comparable to the air-fired case. Table 5-4 shows that when compared to the best performing air-fired test without steam addition, the oxy-fuel run had the same NO_x:N conversion of 0.04. Low NO_x emissions under oxy-fuel conditions have been consistently demonstrated with this CFBC unit *(7,8)*, so this discussion is primarily concerned with the effects and mechanism associated with $H_2O_{(g)}$ rather than comparing the two firing modes.

In all eight of the tests performed, the addition of $H_2O_{(g)}$ resulted in a substantial decrease in NO_x formation, ranging from 30% to 60%. The lowest decrease in NO_x formation was for the pair of PK-KT-OF runs. There are two plausible causes for smaller reduction in NO_x: first, under oxy-fuel conditions the limestone exists as $CaCO_3$ before sulfation, which has been shown to be less catalytically active for NO_x decomposition than CaO *(26)*. Secondly, if one considers that both $H_2O_{(g)}$ and CO_2 significantly sinter Ca-containing compounds, which has been previously demonstrated for CaO *(33)* and $CaSO_4$ *(37)*, and given that they enhance sulfation *(19)* and carbonation *(38)*, the high CO_2 and $H_2O_{(g)}$ concentrations inherent to oxy-fuel combustion are likely to result in significantly more sintering of Ca-containing compounds, especially since their effects are additive *(33)*. This sintering due to the composition of oxy-fuel flue gas means that catalytic NO_x formation over Ca-containing compounds is already at a reduced level, and so additional $H_2O_{(g)}$ should have a minimal impact. This effect is characteristic of the diminishing returns associated with increasing CO_2 and $H_2O_{(g)}$ concentrations on sulfation as shown in this and other work *(13,19)*, and for NO_x formation shown in other studies *(28,30,31,32)*. These findings allow for another possible interpretation of the aforementioned pilot-scale bubbling FBC (BFBC) work by Hosoda *et al. (35)*. Although the BFBC tests did not employ limestone injection for sulfur capture, presumably the coal ash (7.6%) contains some CaO which would be subject to enhanced sintering by $H_2O_{(g)}$ and CO_2, thereby giving an explanation for the authors' observation that NO_x production decreased with an increase in concentration of either component. Moreover, looking closely at their data reproduced in Figure 5-4, a negative exponential curve provides for a more accurate fit than the proposed linear response, bringing their results in line with the mechanisms discussed in the present study.

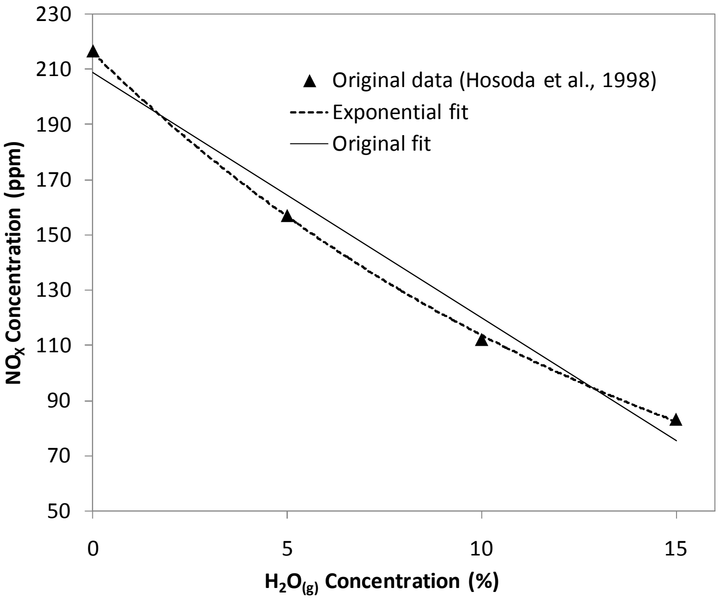

Figure 5-4 NO_x concentrations in the flue gas from a BFBC as a function of $H_2O_{(g)}$ concentration in the fluidizing gas, showing the superior fit of an exponential curve to the data from Hosoda *et al.*, 1998 *(35).*

One pilot-scale CFB test of particular interest is depicted in Figure 5-5. In the run PK-CD-AF-0H$_2$O, an additional test with $H_2O_{(g)}$ injection for a short duration was performed. Figure 5-5shows the transient response to $H_2O_{(g)}$ addition, where the (1)s represent the period of very rapid (near-instantaneous, or at the limits of the gas detector's response time) change and the (2)s represent the residual response. A rapid reduction/recovery upon steam injection/removal, likely due to blocking/unlocking of reactive sites on CaO as suggested by (*28)*, is observed. The reduction in NO_x emissions is followed by a lagged response which is likely a result of accelerated sintering of CaO in the presence of $H_2O_{(g)}$, which occurs over a longer period of time than pore-blocking, as does the extended recovery period which is dependent on the utilization of fresh, unsintered limestone from the feed over time. A result parallel to the observed effects was reported by *(31)* for N_2O decomposition.

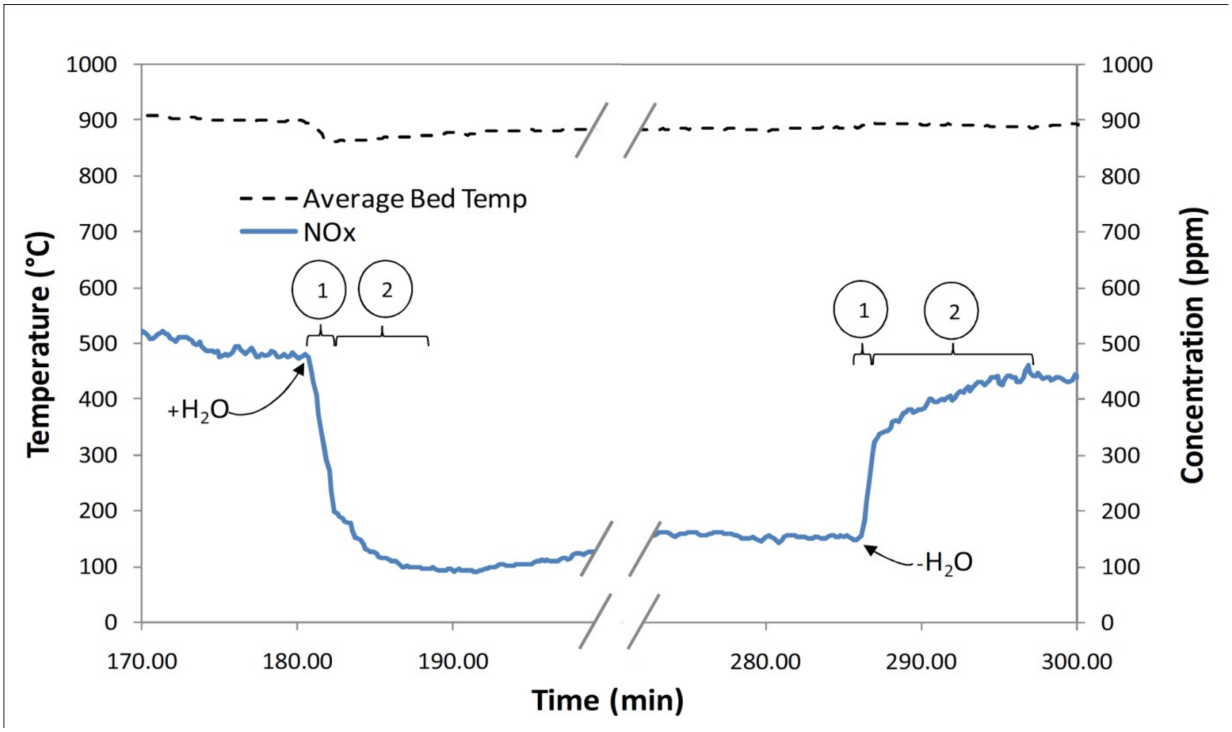

Figure 5-5 Dynamic response of 100 kW pilot CFBC to 15%vol $H_2O_{(g)}$ addition under air-fired conditions during run PK-CD-AF-0H$_2$O (see Table 5-4 for the run ID nomenclature). The regions indicated by (1) are the near-instantaneous responses to $H_2O_{(g)}$ adsorption (pore-blocking) while (2) indicates the extended response/recovery due to sintering.

Under air firing, addition of $H_2O_{(g)}$ may also reduce NO_x indirectly by enhancing Ca utilization. In an early study on the subject, Shimizu *et al. (39)* found that NO_x production correlated with the degree of sulfur capture, *i.e.*, as Ca utilizations in a fixed bed increased, NO_x emissions decreased. In support of this work, other investigators also found the degree of Ca utilization to strongly affect NH_3 oxidation to NO_x *(40,41)*. Based on our work *(19)*, and given that $CaSO_4$ is less active than CaO in the catalytic oxidation process *(26)*, the increased Ca utilizations seen in this work due to $H_2O_{(g)}$ addition may be causally correlated with the observed reductions in NO_x emissions.

Whether in air-firing or oxy-firing mode, one potential drawback of adding $H_2O_{(g)}$ may be increased N_2O emissions. Barisic *et al. (31)* showed that the reduction in activity of CaO to decompose N_2O (to N_2 and O_2) associated with adding steam may outweigh the benefits of decreased NO_x formation. They found that the presence of 15% $H_2O_{(g)}$ resulted in a 60% decrease in N_2O decomposition over a bed material containing ~10% CaO. If a similar scenario occurred during the present CFBC tests, N_2O production may have been abnormally high. Since in the present study no measurement was available for N_2O, the effect of steam on their emissions is something that needs further investigated in further pilot-scale studies.

From a practical perspective, steam is easily introduced into a combustion system; however, the effects of increased $H_2O_{(g)}$ concentration on combustion efficiency and back-end corrosion must also be taken into account. Furthermore, as this discussion suggests, N_2O production may increase. Despite potential drawbacks, it is plausible that steam addition may be an effective solution for commercial FBC units that employ limestone injection, especially those firing low-moisture, high-rank fuels, to meet more and more stringent NO_x emissions limits, or during process upsets that would otherwise result in exceeding regulatory quotas. Moreover, the differences between wet and dry recycle on the performance of an oxy-fuel FBC boiler may be explained by some of the effects described here. The authors are hopeful that steam injection will be tested at full scale in the near future to further criteria air pollutant abatement research.

Conclusions

Sulfation tests in a TGA and TF show that the addition of $H_2O_{(g)}$ enhances the direct sulfation reaction under oxy-fuel combustion conditions; however, the increase is smaller in magnitude than that for the air-fired case (indirect sulfation). In fact, when taking the presence of $H_2O_{(g)}$ into consideration at a concentration of 15%, direct sulfation is slower and less effective than indirect sulfation for most conversion levels, contrary to the conclusions formed from bench-scale experiments in the past. It is suggested here that the failure to include steam in bench-scale work may be one of the reasons why previous investigators have reported poorer than expected performance in pilot-scale oxy-fuel FBC, and commercial PFBC units.

Pilot-scale tests on a 100 kW CFBC supported TGA/TF results: namely that steam injection enhances sulfur capture performance under air-fired conditions; and oxy-fuel sulfation performance is poorer than in the air-fired case for a comparable concentration of $H_2O_{(g)}$. Moreover, despite already inherently high $H_2O_{(g)}$ concentration during oxy-firing, additional steam injection resulted in a 30% decrease in NO_x production. In the air-fired tests, steam injection also resulted in decreased NO_x production, up to 60%. The decrease in NO_x production is characterized by a reversible and irreversible effect of $H_2O_{(g)}$ on the catalytic activity of CaO which is suggested to be pore blocking and sintering, respectively. Furthermore, since $CaSO_4$ is less catalytically active for NH_3 oxidation than is CaO, enhanced Ca utilization due to $H_2O_{(g)}$ addition may also be a contributing factor to the observed decrease in NO_x emissions.

The reductive effects of CO_2 and $H_2O_{(g)}$ on both SO_2 and NO_X emissions are attributed to enhanced solid-state diffusion and while the effects seem to be additive, an excess of either CO_2, H_2O or is expected to cause excessive sintering such that the effects on sulfur capture and NOx reduction are negative.

Although potentially deleterious effects of $H_2O_{(g)}$ injection on issues such as corrosion, N_2O formation and efficiency were not investigated in this study, the possibility of simultaneous SO_2 and NO_x emissions abatement may warrant the addition of $H_2O_{(g)}$ to pilot- and commercial-scale units alike for some “dry” fuels, such as petroleum coke and high-rank coals.

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CHAPTER 6 : CONCLUSIONS

The Role of $H_2O_{(g)}$ in Limestone Phenomena in Fluidized Bed Combustion

Effects of $H_2O_{(g)}$ on Sulfation (at the bench scale)

TGA experiments using a synthetic air-fired flue gas show that the indirect sulfation of limestone is greatly enhanced in the presence of 15% $H_2O_{(g)}$, a typical concentration seen during air-fired combustion. After 10 h of sulfation time, complete conversion is achieved, indicating an increase in conversion by over 45% compared to 0% H_2O. This is an interesting result in itself, since most sulfation studies (that do not sulfate in the presence of steam) show maximum conversions of less than 0.6. More importantly, however, is the idea that water is clearly not inert for indirect sulfation despite the fact that only a handful out of hundreds of sulfation studies have taken its effects into account. Moreover, these results are presented in clear contrast to the better part of the few previous indirect sulfation studies incorporating $H_2O_{(g)}$.

The early, heavily-cited indirect sulfation studies are the cause for ignoring the effects of $H_2O_{(g)}$ in subsequent studies. Also, although it has not been discussed in this text, it is likely that the authors of subsequent sulfation studies were more than happy to have a reason not to include steam due to the more stringent equipment requirements associated with introducing steam.

Early sulfation studies noted a null effect of $H_2O_{(g)}$ on the reaction due to the short time scales investigated (typically <2 h). The highly reproducible TGA results from the present work show that $H_2O_{(g)}$ does not affect sulfation during the kinetically-controlled regime. Depending on particle size, temperature and gas conditions, this regime can extend for up to hours of sulfation time. So when the authors of early studies studied sulfation for short times, sometimes less than 1 h, the effects of $H_2O_{(g)}$ were systematically eliminated.

The tube furnace experiments that replicate the TGA work at a slightly larger scale show similar results, as expected: the presence of steam greatly enhances conversion. Microstructural analysis of samples sulfated in the tube furnace show two distinct changes in sulfated limestone morphology in the presence of steam: first, larger product crystal grains form both on the surface and on the inside of an steam-sulfated particle, thus allowing for a lowered resistance to gas diffusion; and second, particle densification without significant reduction in pore surface area and volume occurs, an observation which is highly indicative of enhanced solid-state diffusion (sintering) in the presence of steam. Although a mechanism for sulfation is not developed explicitly, it is argued that solid-state diffusion plays a major role in limiting the progress of sulfation in the diffusionally-controlled regime and thus it may make for the correct vessel to develop such a mechanism in the future.

TGA/TF experiments confirm that $H_2O_{(g)}$ also enhances oxy-fuel direct sulfation, but to a lesser degree than air-fired sulfation. In these tests, the effects of $H_2O_{(g)}$ only become apparent after the initial kinetically-controlled regime. Again, this provides an explanation for the conclusions of some workers who found $H_2O_{(g)}$ to have no effect on direct sulfation.

Oxy-Fuel Sulfation: Effects of CO_2

TGA experiments show that elevated concentrations of CO_2 result in the direct sulfation of limestone. The rate of direct sulfation is shown to be slower than that of indirect sulfation during the kinetically-controlled regime, but faster than indirect sulfation during the diffusionally-controlled regime. Moreover, since the kinetically-controlled regime appears to be shorter during direct sulfation, direct sulfation results in increased overall conversion at lengths of time that are representative for FBC sorbent particles. These results are found to be in line with a number of direct sulfation studies in the literature. However, these studies do not include the effects of steam in their determination of conversion and rates. In this work, it is shown that the presence of steam fundamentally changes these conclusions. In the presence of 15% $H_2O_{(g)}$, oxy-fuel direct sulfation is in fact slower during both regimes than its indirect counterpart, an unprecedented conclusion not found in the literature, underlining the importance of including $H_2O_{(g)}$ in sulfation studies. It is for this reason that operators of pilot- and commercial scale oxy-fuel and pressuirzed fluidized beds (which of course include the effects of steam) have noticed decreased sulfur capture performance during direct sulfation. These conclusions are shown to be even clearer with similar tests using the tube furnace.

In another TGA test, an intermediate concentration of CO_2 is applied to the indirect sulfation reaction (30%). This test shows that, while reducing the rate of reaction during the kinetically-controlled regime, reaction rates in the diffusionally-controlled regime are enhanced, leading to an overall increased conversion after 10 h. This result is also in conflict with most of the previous work on the effects of CO_2, but can again be explained in terms of reaction times. As was seen in the case $H_2O_{(g)}$, most sulfation test lengths done in the past were on the order of a few hours. Depending on conditions, the "window" of reaction time has often been chosen such that it focuses mostly on the kinetically-controlled regime. Thus, the majority of previous work has missed the dual nature effects of CO_2.

Agglomeration

As it was previously assumed that steam played no role in sulfation, its effects were ignored and it was not included in past agglomeration studies that focused on sulfation of limestone or ash deposits. In this work, a number of tube furnace sulfation tests show that, on the contrary, agglomeration of sorbent particles is greatly accelerated in the presence of steam. While previous tests of up to 100 days were required for significant agglomeration without steam, the present study shows that under similar conditions with steam (15%), severe agglomeration occurs in just one day or less.

With tests using pure $CaSO_4$ (anhydrite), it is shown that steam is necessary for agglomeration, but that chemical reaction is also necessary for significant agglomeration. The results of the agglomeration work are used to support the theory of enhanced solid-state diffusion in the presence of steam and it is suggested that steam-sulfation may play a significant role in the fouling of industrial boilers. The importance of including steam in sulfation tests of any kind is again underlined by its significant impacts on agglomeration.

Effects of $H_2O_{(g)}$ on NO_X Formation (at the pilot-scale)

Several tests in a pilot-scale 100 kW CFBC show that the addition of about 15% steam reduces the production of NO_X emissions by up to 60% for air-fired combustion, and 30% for oxy-fuel combustion. The lower reduction in NO_X for oxy-fuel is attributed to two factors: first, that $H_2O_{(g)}$ concentrations are inherently higher for oxy-fuel; and second, that direct sulfation of the less catalytically-active $CaCO_3$ takes precedence over CaO.

Decreased NO_X production in both cases is attributed to a two part deactivation of limestone-derived compounds: pore blocking and sintering. The second part is in the same vein as the enhancement of steam-sulfation: increased sintering in the presence of $H_2O_{(g)}$ rapidly reduces available surface area for the oxidation of NH_3 and HCN. With these results, well-known phenomena that have been shown at the bench scale are shown to be just as important at the pilot-scale.

Steam injection is suggested as a method for reducing NO_X emissions *in situ* with the caveat that N_2O production may be increased.

Effects of $H_2O_{(g)}$ on Sulfation (at the pilot-scale)

The observations from the bench-scale work are confirmed in CanmetENERGY's pilot-scale CFBC. The addition of 15% steam enhances air-fired sulfaion, increasing calcium utilization and sulfur capture. This demonstrates the consistency of the results from the TGA to the tube furnace to a pilot-scale test rig.

On the other hand, oxy-fuel sulfation in the pilot-scale unit shows a marked decrease in sulfur capture. But again, this is consistent with the results from the TGA: direct sulfation under oxy-fuel conditions, and in the presence of steam, results in slower reaction rates than for indirect sulfation. The most important result of this work is that it provides a concrete example and explanation for why some investigators report less-than-expected sulfation performance with oxy-fuel and pressured FBC units.

Finally, from a practical perspective, it is shown that research into oxy-fuel CFB combustion has been substantial in the recent years, with Canmet leading the task with two pilot-scale units. Operation of the oxy-fuel units has demonstrated to be largely similar to air-fired units, and it is shown that oxy-fuel meets or exceeds air-fired combustion emissions quality for all criteria air pollutants. Oxy-fuel combustion seems to benefit from the inherently increased concentration of $H_2O_{(g)}$ in the flue gas in terms of SO_2 and NO_X production; however, the effects on agglomeration *in situ* are still unknown.

Future Work & Recommendations

1. Further studies on the effects of CO_2 on both indirect and direct sulfation are needed at the bench scale. In this work, CO_2 concentration is only varied between two levels for indirect sulfation, and there was only one test performed at the elevated concentration. Furthermore, CO_2 was not varied during direct sulfation. More tests are needed to determine precisely the effects of CO_2 and the extent to which it acts on sulfation, independently of other variables. Although it can be seen in the work of a number of investigators, the dual nature effect of CO_2 has not been discussed in the open literature until now, so it would be worthwhile to fully investigate the phenomenon.
2. An appropriate model for sulfation that takes into account the influence of $H_2O_{(g)}$ as well as CO_2 should be developed. Given the results of this study, it would be difficult to justify the application of any of the existing sulfation models to the scale-up of pilot plants, or the design of a new facility. Perhaps this is most prudent for oxy-fuel CFBC if the technology is to move forward in the coming years. In developing such a model, careful attention to selecting an appropriate time scale for the particular application of the model should be made, *i.e.* a CFBC model time-scale would differ significantly than that of a pf sulfation model.
3. In light of the discoveries of how solid-state diffusion controls sulfation, a full mechanism should be described. Although some solid-state diffusion mechanisms have been proposed in the literature, there is certainly still room for improvement. Such a model may benefit from being closely linked to the discussions in the geochemistry literature, especially to those that discuss the effects of $H_2O_{(g)}$ on CaO.

4. Whether modelling is considered or not, based on this work, future studies attempting to explore limestone phenomena under combustion environments need to take the effects of $H_2O_{(g)}$ into account (*i.e.* studies not necessarily related to sulfation, such as agglomeration, NO_X chemistry, attrition, carbonation, sulfidation, calcination, etc.)
5. H_2O, CO_2 and temperature represent a triad of factors that need to be taken into account simultaneously. Thus, in developing a sulfation model or attempting to elucidate the mechanism of sulfation, the effects of temperature should be taken into account, *i.e.* varied. Since an increase in any one of the three factors will enhance solid-state diffusion, and since it will also enhance sulfation (in the diffusionally-controlled regime, and only up to a point), the three factors should be considered simultaneously. Further support of this recommendation comes from the fact that by varying one of the triad of factors, the optimum level (optimum meaning the level resulting in maximum conversion in a given period of time) of other two will change, indicating that they are not independent of each other.
6. Agglomeration: Strength development in agglomerated sulfated samples should be tested quantitatively as well as qualitatively. Furthermore, the effects of CO_2 should also be taken into account to estimate agglomeration tendency under oxy-fuel conditions. Canmet currently possesses a device and load cell that is appropriate for this task.
7. Agglomeration: Pilot-scale oxy-fuel tests designed with the intention of testing the agglomeration theories developed in this thesis should be performed. Varying the concentration of $H_2O_{(g)}$ in the pilot-scale CFBC at Canmet will strengthen arguments on agglomeration due to sintering, and would be of interest to oxy-fuel combustion research.

8. The effects of steam addition to “dry” fuels should be tested at the commercial scale. At the time of this writing, discussions are ongoing with power producer, NISCO to commission steam injection tests on a 200 MW petcoke-fired boiler. These tests could shed more light on all three of the major topics discussed in this thesis: sulfation, agglomeration and NO_X formation.
9. NO_X: The effects of $H_2O_{(g)}$ on the production of N_2O over calcium-containing compounds should be tested at the bench and pilot-scale. At the pilot-scale, this would be achieved easily with the addition of an N_2O gas analyzer, whereas at the bench scale this would be more difficult at Canmet. However, using the same gas analyzer on a tube furnace operating as a differential reactor seems feasible.

Practical considerations: for the Canmet CFB to be operated properly in oxy-fuel mode, the system needs to be leak-tested. It is known to the author that the system allows significant air ingress in and around the feed system and bag house. To achieve 90%+ CO_2, these leaks need to be addressed. However, operating the unit at a higher fuel feed rate will also suffice, but will not work at 5 kg/h or lower. Furthermore, it is the author’s suspicion that premixed fuel/limestone mixtures loaded into the feed hopper tend to separate, allowing the limestone to settle to the bottom due to the stirring action and difference in density, thus altering the rate at which limestone is introduced to the bed. Note that this does not happen for all fuels. This can be avoided with the use of a second feed hopper for limestone.