Characterization of Sulfur Products on CaO at High Temperatures for Air and Oxy-Combustion

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Abstract

Oxy-coal combustion is a novel technology that seeks to reduce carbon dioxide emissions from electricity generating units, but the unique combustion environment could potentially affect the manner in which the flue gas and fly ash interact. Of particular interest is the ability of fly ash to reduce SO_x emissions, a source of concern in implementing oxy-coal technology. This study seeks to examine the way SO_x interacts with calcium oxide, an important fly ash metal oxide, under a variety of flue gas conditions and temperatures. Using DRIFTS and XRD, the major products under the various reaction conditions were analyzed. The dominant sulfur containing product was found to be calcium sulfate. However, a secondary calcium carbonate product was formed under certain oxy-fuel conditions. Additionally, EDX was employed to examine the temperature dependence for sulfur retention.

Keywords: Oxy-combustion, calcium oxide, sulfur oxides, DRIFTS, XRD, EDX

Introduction

Rising atmospheric levels of carbon dioxide (CO_2), which are currently approaching 400 ppm, are a cause for concern (Dlugokenchy and Tans). As of 2012 one of the main emitters of CO_2 in the United States are power plants burning fossil fuels, accounting for nearly 38% of the total CO_2 emitted or roughly 2.0 billion tons of CO_2 . One way power plants can lower their CO_2 emissions is by incorporating carbon capture and sequestration (CCS) technologies. One such CCS technology that has shown promise as being both scalable and economically feasible is oxy-fuel combustion (Stanger et al., 2015; Wall et al., 2009; Wall, 2007). It operates by combusting the fuel in a mixture of oxygen (O_2) and carbon dioxide resulting in a relatively pure CO_2 stream after combustion that can then be treated and prepared for storage. The mixture is made by mixing recycled flue gas with O_2 separated from air to reach a desired O_2/CO_2 ratio. In addition to lowering CO_2 emissions, oxy-combustion has shown promise in lowering nitrogen oxide (NO_x) emissions while the final sulfur oxide (SO_x) emissions on a mass of S to coal basis have been shown to either be lowered or remain unaffected (Croiset et al., 2000; Croiset and Thambimuthu, 2001; Kiga et al., 1997; Klostermann, 2008; Liu et al., 2005; McCauley et al., 2009; Wall et al., 2009; Woycenko et al., October 1995; Zhuang and Pavlish, 2012). Of the pollutants present in coal combustion, SO_x species are particularly important. Due to the presence of a possibly untreated recycled flue gas stream and the decreased flue gas volume from the exclusion of N_2 , sulfur dioxide (SO_2) concentrations within the flue gas will increase dramatically. The rise in SO_2 concentrations leads to a corresponding increase in sulfur trioxide (SO_3) in the flue gas (Croiset et al., 2000; Croiset and Thambimuthu, 2001). This increase is one of the main challenges facing oxy-coal combustion as SO_3 is a precursor to sulfuric acid (H_2SO_4), which would form when flue gas temperature drops below 500°C and potentially

corrode equipment increasing operating costs (Francis, 1952; Hardman and Stacy, 1998). While much research has gone into examining homogeneous SO_x reactions during oxy-combustion, research is still lacking in heterogeneous reactions that occur between SO_x species and the coal fly ash, which can play an important role limiting SO_x emissions (Cheng et al., 2003; Davis and Fiedler, 1982; Sheng et al., 2000; Spörl et al., 2013; Sturgeon et al., 2009; Yu et al., 2011).

Fly ash is a solid mixture of the non-volatile components of coal that remain after the combustion reaction. It primarily consists of a variety of metal oxides, whose individual weight percentages can vary greatly depending on the source and type of coal being utilized. Silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) are generally the most abundant with weight percentages of 37-60%, 17-30% and 5-29% respectively (Hower et al., 1996; Stanton et al., 2002; Stimpson et al., 2013; Yu et al., 2011). However, fly ash is comprised of many other oxides to lesser degrees, most notably calcium oxide (CaO) at 1-40 wt%, magnesium oxide at 0-10 wt%, sodium oxide (Na_2O) at 0-6 wt% and potassium oxide (K_2O) at 0-4 wt% respectively (Ahmaruzzaman, 2010; Hower et al., 1996; Stanton et al., 2002; Stimpson et al., 2013). These various oxides can play an important role in the reactions that take place between the gas phase SO_x and the coal fly ash. The sulfur retention in coal fly ash has been shown to strongly correlate with the alkali and alkaline earth metal oxide composition, with increased weight percentages leading to greater retention (Belo et al., 2014; Cheng et al., 2003; Davis and Fiedler, 1982; Raask, 1982; Sheng et al., 2000; Spörl et al., 2013; Sturgeon et al., 2009; Yu et al., 2011). While the actual fly ash composition is not dependent on the combustion environment (air or oxy) in which it is formed, oxy-combustion studies exhibit greater sulfur capture than air-combustion (Croiset and Thambimuthu, 2001; White et al., 2010; Yu et al., 2011). To a lesser degree the Fe_2O_3 may play an important role in retention as it can oxidize SO_2 to SO_3 , which

may facilitate increase in sulfur retention on the alkaline oxides (Marier and Dibbs, 1974). While it seems clear that oxy-combustion enhances sulfur capture on the coal fly ash, there is still a lack of understanding of how the reaction changes at high temperatures under different gas environments. Many existing studies concerning the characterization of surface sulfur species on CaO are from experiments operated under more controlled conditions, such as lower temperatures, in inert/air environments, or low pressures (Allen and Hayhurst, 1996a, b; Baltrusaitis et al., 2007; Goodman et al., 2001; Goodsel et al., 1972; Ishihara et al., 1992; Low et al., 1971; Martin et al., 1987; Rodriguez et al., 2000a; Rodriguez et al., 2000b; Rodriguez et al., 2001).

The current mechanism presented in the literature suggests that the SO₂ reacts with CaO through reactions 1 and 2(a-c) (Allen and Hayhurst, 1996a, b; Martin et al., 1987).

Thermodynamic calculations predict that calcium sulfate (CaSO₄) will be the dominant product as calcium sulfite (CaSO₃) is unstable at temperatures above 727°C. This temperature dependence is confirmed via Fourier transform infrared (FTIR) spectroscopy, where higher temperatures led to the conversion of the sulfite to the more stable sulfate on CaO (Goodsel et al., 1972; Ingraham and Marier, 1971; Low et al., 1971). While calcium sulfide (CaS) is shown as a possible intermediate in reaction 2b, it has also been shown to be oxidized at 800°C in favor of either the sulfate or the oxide (Song et al., 2007). The sulfide and sulfite become more pronounced in oxygen free conditions, such as N₂, He, or Ar, where multiple sulfur products can

be observed (Allen and Hayhurst, 1996a, b; Munoz-Guillena et al., 1994). Thermogravimetric analysis into the oxidation of CaS by Song et al. reported significant sulfide remaining after 2 hours of exposure to 5vol% O₂ at 950°C (Song et al., 2007). After experiments where CaO exposed to SO₂ in He, Martin et al. concluded that reaction (2b) is unimportant as they do not identify any sulfide in their FTIR-PAS (photoacoustic spectroscopy) spectra even at 900°C, while also proposing that reaction 2c could occur with the resulting sulfur gas being oxidized or reacting with fresh CaO (Martin et al., 1987). Along with the crystalline products, it is important to understand the manner in which the adsorbing sulfur species binds to the surface. Martin et al. observed that SO₂ binds through a surface oxygen in a monodentate structure (Martin et al., 1987). Density functional theory (DFT) calculations for sulfur adsorption on CaO (100) surface likewise predict that a monodentate structure is the most energetically favorable where the sulfur binds to a surface oxygen site (Galloway et al., 2015; Sasmaz and Wilcox, 2008). In fact, DFT calculations predicted that this orientation is energetically favorable for NO_x, SO_x, and CO₂ on a variety of alkaline metals, not just CaO (Karlsen et al., 2003; Rodriguez et al., 2001). Once adsorbed, surface sulfur species could polymerize creating a S_xO_y structure on the surface, particularly on calcium carbonate (CaCO₃), where thiosulfate (S₂O₃) species were observed (Martin et al., 1987). It is likely that the air atmosphere allows for an oxidation reaction to readily occur at the temperatures being used despite the relatively short times the samples are exposed suggesting why no sulfide is generally observed.

As most of the previous studies investigating sulfur adsorption on CaO were done in air or an inert environment, it is important to consider the effect of other gases that the fly ash particles are likely to be exposed to. Since the application for these sulfur adsorption studies is in combustion flue gas, the effect of water is of the utmost importance as it can affect the surface

composition. DFT calculations by de Leeuw et al. show that water will dissociatively adsorb to low-coordinated surfaces of CaO like (110) or (111) planes, but only physisorb onto the more stable and abundant (100) plane (de Leeuw et al., 2000; de Leeuw et al., 1995). Furthermore, they predict that the water will create a pair of hydroxyl groups on the surface with higher coverages of water creating a more and more stable surface, possibly due to the greater stability provided by adjacent hydroxyl pairs (Carrasco et al., 2008; de Leeuw et al., 1995). Their further simulations show that water adsorbed onto various CaCO_3 surfaces can cause surface reconstructions, but not dissociation of the water molecule (H. de Leeuw and C. Parker, 1997). This agrees with an attenuated total reflection (ATR)-FTIR study by Al-Hosney and Grassian, who observed a water film covering the CaCO_3 surface, which promoted the decomposition of the carbonic acid species that would otherwise cover the surface (Al-Hosney and Grassian, 2005). Their work also proposed multiple mechanisms for calcium sulfite formation from CaCO_3 depending on if the water and SO_2 react in an Eley-Rideal or Langmuir-Hinshelwood type mechanism. Several studies have shown how increasing the partial pressure of water can increase the conversion of limestone to CaSO_4 , with increasing temperature having a similarly beneficial effect (Duan et al., 2013; Jiang et al., 2013). Baltrusaitis et al. reported similar results as x-ray photoelectron spectroscopy spectra showed significantly greater sulfite than sulfate on CaCO_3 samples when water is present (Baltrusaitis et al., 2007). The CaCO_3 formation, which becomes prevalent in oxy-combustion conditions, is itself dependent on water concentration as investigation of carbonation of lime (Ca(OH)_2) slurries by Van Balen (Van Balen, 2005) and Cizer et al. (Cizer et al., 2012) show a strong dependence on gas-phase water content in the formation of CaCO_3 . While many of the experiments investigating the effect of water were done

with CaCO_3 at ambient temperatures and not with CaO , they still illustrate the impact water plays in the sulfation reaction.

Examining the effect of sulfur and water on CaCO_3 and CaO under various inert and/or low-temperature conditions can aid in understanding the sulfation mechanism in oxy-combustion. The higher partial pressure of CO_2 in oxy-combustion allows for the carbonate to be stable at higher temperatures. CaCO_3 is stable up to $\sim 900^\circ\text{C}$ in pure CO_2 atmosphere (de Diego et al., 2013; García-Labiano et al., 2011; Reid, 1970). If the starting CaO is converted to CaCO_3 during the experiment, it is proposed that the resulting reaction mechanism changes such that SO_2 would no longer adsorb to CaO , but to CaCO_3 as shown in Reactions 3 and 4 (de Diego et al., 2013; García-Labiano et al., 2011; Reid, 1970).

At temperatures between $850\text{--}900^\circ\text{C}$, the mechanism changes from the indirect sulfation of Reaction 3 and 1 to the direct sulfation mechanism of Reaction 4. However, there are likely some kinetic limitations as analysis of fly ash showed the presence of oxide, carbonate and sulfate of calcium indicating that all of the reactions above are important to sulfur capture (Vassilev and Vassileva, 1996). Additionally, Martin et al. proposed an additional reaction whereby the sulfation of the CaCO_3 goes through a sulfite intermediate at temperatures below 550°C just as the oxide does via Reaction 5 (Martin et al., 1987).

Since carbonates can form at lower temperatures, it is important to consider the effect that its formation might have on the adsorption mechanism and consequently the total sulfur retained on

the material. Several pilot scale studies have examined the effect limestone addition (CaCO_3 with magnesium and silicon impurities) has on sulfur retention in coal combustion (Pikkarainen et al., 2014; Tan et al., 2012). Additional laboratory scale studies with limestone or pure CaCO_3 attempted to investigate the transient behavior as the material is both calcined and sulfated at higher temperatures (de Diego et al., 2011; de las Obras-Loscertales et al., 2014; Hills, 1968; Liu et al., 2000). . The formation of a CaSO_4 product is important to the transient behavior as it can create a dense product layer inhibiting mass transport of sulfur to unreacted Ca, as previously reported by researchers investigating the sulfation of both CaO and CaCO_3 (Liu et al., 2000; Liu et al., 2001; Martin et al., 1987; Sporl et al., 2016). While the extent of sulfur retention and some temperature dependence were examined previously, none of the studies investigate surface or bulk composition of the samples to more thoroughly probe the sulfation mechanism.

This paper seeks to expand upon previous research by incorporating more complex gas mixtures at elevated temperatures, representing the flue gas environment, for sulfur retention. Pure samples of CaO are exposed to SO_x -containing simulated flue gas of air and oxy-combustion at temperatures between 800-900°C. This will address one of the current gaps in the literature by directly comparing the effect of realistic gas phase compositions on adsorption and the resulting speciation of sulfur retained on the samples. The use of CaO eliminates many of the kinetic and diffusion effects that previous papers sought to investigate by starting with CaCO_3 or limestone. Furthermore, the changes in the surface sulfur species present can be monitored through x-ray diffraction (XRD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), while employing energy-dispersive x-ray spectroscopy (EDX) analysis to examine the total sulfur retention. The addition of these characteristic techniques will increase the

understanding of the sulfur reactions taking place at elevated temperatures for coal-combustion applications.

Experimental

An experimental system consisting of a burner and a packed bed reactor, shown in Figure 1, is used to carry out the reactions. The system consists of multiple Brooks mass flow controllers to mix the various flue gas components to simulate the specific gas composition of interest. The gas mixture is fed to a custom quartz burner situated in a Thermcraft Split Tube Furnace that is set to 1100 °C. (It should be noted that when an experiment does not require combustion products or water, e.g., air and oxy-environment experiments, the furnace is not turned on but the gas still passes through the furnace.) After the high temperature furnace, the gas stream is split with a portion pulled to the reactor with a diaphragm pump and the excess going to the exhaust. The CaO sample is placed in a quartz reactor with a fritted disc in the center. A Pallflex quartz filter is then placed on a bed of quartz wool to provide an even surface for 200 mg of sample to lie. The whole quartz reactor tube housing the sample is surrounded by two Watlow semi-cylindrical ceramic fiber heaters, which can be heated to 950°C.

The gas compositions investigated include air, air-wet, air-flame products, oxy-environment (O_2/CO_2), and oxy-flame products with the flow rate for all samples being ~0.5LPM. The flue gas compositions used in the experiments are detailed in Table 1. The air-wet samples are created by introducing water into the heated lines after the furnace with a Shimadzu LC-10AD VP liquid pump. Combustion product compositions of both air and oxy-combustion are simulated by feeding methane, which is auto-ignited in the 1100°C furnace to create a CO_2 and H_2O mixture. For the air-flame runs, the slightly lower than stoichiometric equivalence ratio results in an O_2 concentration of 4.5vol% similar to what would be observed in

the post-combustion flue gas, where up to 5 vol% excess O₂ is common. In all experiments, the SO₂ flow is adjusted to keep its concentration constant at 2500 ppm. The presence of either the flame or higher temperature environment of the furnace allows some of the SO₂ to be oxidized to SO₃, resulting in the sulfur feed to the reactor to be an SO₂/SO₃ mixture, but still predominantly SO₂. For example, the SO₃ concentration downstream of the burner for the air-flame and oxy-flame conditions is measured to be 49±6ppm and 66±2ppm respectively.

Metal oxide samples being examined are CaO (Sigma Aldrich 99.9% purity). Prior to exposure to SO_x-containing gas mixtures, the samples are calcined at 950°C in N₂ for 1 hour. This is done to remove any residual carbonate or hydroxide species and ensure that the pure metal oxide is the only metal species present for the reaction. XRD and IR spectra obtained after this calcination procedure confirm that only the oxide was present. After the calcination pre-treatment, the reactor temperature is set to 800, 850 or 900°C in preparation for exposure to the simulated flue gas. This method ensures that the sample is not exposed to ambient atmosphere between the calcination and the reaction since the experimental system is not configured for in-situ IR measurements. After exposure, the gas mixture is switched back to N₂. The sample is then allowed to cool to room temperature before the sample is taken out for further analysis.

Characterization

After the reaction has taken place, the samples are characterized using XRD, DRIFTS, and EDX. XRD, being a bulk technique, is used to provide an approximate level of the metal oxide that is consumed during the reaction, as well as major products formed. While DRIFT spectra will give a more surface-specific picture of the mechanism taking place as the metal oxides and SO_x interact. Finally, EDX is used for the elemental analysis to determine the amount of sulfur adsorbed.

XRD measurements are taken with a Rigaku Miniflex II X-ray diffraction system. A Cu X-ray tube as the X-ray source is running at 30 kV and 15 mA, and a D/teX detector (NaI) is used. The scanning speed is maintained at 1.5 degrees per minute. DRIFTS measurements are taken using an Equinox 55; an FTIR bench provided by Bruker Optics. The bench contains a KBr beamsplitter and a DTGS detector providing a resolution of 4 cm^{-1} with a total of 640 scans. Spectra were taken at room temperature in ambient conditions. EDX spectroscopy was used to analyze the elemental composition of the samples. EDX analysis was conducted using a Tescan Vega-3 SBU variable pressure scanning electron microscope, which is equipped with a ThermoScientific UltraDry EDS detector.

Results

XRD spectra for the bulk structures of the samples before and after exposure at 800°C are shown in Figure 2(a). In all cases, the dominant peak is for the unreacted CaO (PDF#37-1497), which is used to normalize the rest of the spectra after background subtraction. Other than unreacted CaO, all samples showed the presence of anhydrous CaSO_4 (PDF#37-1496). The intensity of this peak remains fairly consistent from one condition to the next as both temperature and gas feed are changed as seen in Figure 2(b) (additional XRD data for 850°C and 900°C can be viewed in Figure S.1 (a) and (b) in the supplementary materials). Under the air, air-flame and air-wet conditions these are the only two crystal structures detectable with XRD. However, oxy-flame conditions yielded a third bulk structure, as shown in Figure 2(a). The new peak corresponds to CaCO_3 (PDF#47-1743). Unlike the sulfate peak, the carbonate peak is temperature dependent, with increasing temperature resulting in less carbonate formation. An intermediate temperature of 825°C was selected to verify that the CO_3 formation becomes less

favorable at higher temperatures. Figure 3(a) shows how carbonate formation decreases from 800°C to 825°C, with no carbonate observed at temperatures 850°C and above.

In addition to examining the bulk structure with XRD, DRIFTS was employed to thoroughly examine the species present in the samples. Figure 4(a) shows the DRIFT spectra for the same samples taken at 800°C for a variety of gas compositions whose XRD spectra are shown in Figure 2(a) (for spectra of samples exposed at 850°C and 900°C see Figure S.2 (a) and (b)). All experiments exhibited anhydrous CaSO_4 . The position of this cluster of peaks makes it ideal for identifying sulfate formation, as it is generally not obfuscated by any of the other peaks inherent to the oxide, and corroborates the sulfate peak identified in the XRD data. The only exception is when CaCO_3 is formed during the lower temperature oxy-flame experiments. Secondary bands appear in the same place with peaks at 2139 cm^{-1} and 2216 cm^{-1} . These peaks can be identified as CaCO_3 as they match the CaCO_3 standard (Alfa Aesar 99.5% purity), which was used for comparison. Not only do the sulfate and carbonate peaks overlap but the intensity of the sulfate peaks appears to decrease with the formation of the carbonate species. The formation of the carbonate also exhibits peaks at 2983 cm^{-1} and 2875 cm^{-1} , 2515 cm^{-1} with a shoulder at 2590 cm^{-1} , 1796 cm^{-1} and a smaller peak at 1960 cm^{-1} .

The species observed in this region of the IR spectra match well with those seen with the XRD. However, there is more information to be gleaned regarding the nature of the sulfur binding to the CaO when examining other regions of the IR spectra. Of particular interest is the region from 950 cm^{-1} to 1050 cm^{-1} as it can be used to differentiate between sulfate and sulfite products. Figure 4(b) shows this speciation region for a variety of gas compositions at 800°C. All samples show two distinct peaks at 984 cm^{-1} and 1014 cm^{-1} corresponding to the sulfite and sulfate species, respectively, based on previous literature. A generic sulfite peak is identified by

Nakamoto to be existing between $\sim 920\text{-}980\text{ cm}^{-1}$ with sulfate peaks generally arising above 1000 cm^{-1} (Nakamoto, 1997). Low et al. identify calcium sulfite species at 973 cm^{-1} with a peak around 1008 cm^{-1} belonging to calcium sulfate (Low et al., 1971). The sulfate peak reported by Low et al. matches well with the 1020 cm^{-1} for the ν_1 mode of CaSO_4 reported by Steger and Schmidt (Steger and Schmidt, 1964). It is worth noting that Evans and Bernstein reported a sulfite peak at 1010 cm^{-1} , but were examining sodium sulfite (Evans and Bernstein, 1955). While examining various sulfites, Nyberg and Larsson identified the peak around $950\text{-}1000\text{ cm}^{-1}$ as belonging to the ν_1 mode of the sulfite ion with the position of the frequency in this window giving information as to the structure (Nyberg and Larsson, 1973). Additionally, Freedman and Straughan likewise reported the IR peaks of various thiosulfate (S_2O_3) materials as having a band around 1000 cm^{-1} (Freedman and Straughan, 1971). Since they did not look specifically at anhydrous calcium thiosulfate, the identification of the peaks as being sulfate and sulfite seems justified given the agreement with the other studies already mentioned. The reference spectra for pure CaCO_3 as shown in Figure 4(b) exhibits no discernible peaks in the $950\text{-}1050\text{ cm}^{-1}$ window allowing for peaks in this region to be wholly attributed to sulfur species. Other peaks for sulfate/sulfite differentiation exist at lower wavenumbers but are not considered as they would overlap with the peak characteristic of the clean CaO .

When comparing the sulfate and sulfite peak intensities for varying gas phase compositions, several things become apparent. The first is that the sulfate peak is more intense than the sulfite one. This is true for all gas compositions except for exposure under the N_2 environment. In this case, the sulfite peak has a greater intensity than the sulfate one. Secondly, the oxy-environment (oxy- and oxy-flame) samples show slightly lower sulfate/sulfite characteristic relative to the others. Figures 5(a-c) show the speciation for a variety of gas

compositions as the temperature increases from 800°C to 900°C (spectra for air and oxy-environment from 800-900°C can be viewed in Figure S.3(a) and (b)). The ratio of sulfite and sulfate peak areas ($\text{SO}_3:\text{SO}_4$) shown in Figures 5(a-c) are given in Table 2. Figure 5(a) shows the results for the air-wet condition. With only air and H_2O present in the gas stream, the spectra show strong peaks for both sulfate and sulfite with sulfate being the more dominant one. As the temperature increases the sulfate peak remains relatively constant while the sulfite one diminishes at 850°C before eventually disappearing at 900°C. This results in a constantly decreasing sulfite to sulfate ($\text{SO}_3:\text{SO}_4$) ratio. The air-flame samples in Figure 5(b) show a similar trend with respect to the $\text{SO}_3:\text{SO}_4$ ratio decreasing with the temperature. The air-flame condition keeps the same water partial pressure as the air-wet, but includes CO_2 and more N_2 , while decreasing the O_2 partial pressure with concentration changing from 18vol% to 4.5vol%. Finally, Figure 5(c) shows the results from the oxy-flame experiments. Most notable here is that the sulfate peak appears to increase with increasing temperature, while the sulfite peak disappears at 900°C. When comparing the decreasing $\text{SO}_3:\text{SO}_4$ ratio for these samples to those of the air-wet and air-flame conditions, the same trend emerges for all gas compositions from 800 to 900°C.

It should be noted that while these will be the only two regions discussed in detail, there are other peaks that appear that are indicative of sulfur adsorption on the surface. The first is a broad multi-peak band from 1050 cm^{-1} to 1250 cm^{-1} shown in Figure 4(c). Similar to the sulfate band at 2200 cm^{-1} , this band's intensity is not greatly affected by gas composition or temperature (additional spectra similarly showing a lack of temperature dependence are shown in Figure S.4 (a-e)). There are some conflicting identifications in the literature as to what exactly the broad band centered around 1150 cm^{-1} is, as it has been attributed to amorphous sulfate, thiosulfate, or

a mix S_xO_y (Freedman and Straughan, 1971; Goodsel et al., 1972; Low et al., 1971; Martin et al., 1987). While each presents a slightly different interpretation of the band and the several peaks that appear within it, the band likely represents the incomplete reaction of the oxide to the sulfate. As the reaction proceeds, it forms a polymerizing network of linking surface SO_2 , which create an incomplete sulfation reaction from the oxide to the most stable product, the sulfate. This hypothesis would appear to be partially supported by previous DFT studies that show a strongly bound chemisorbed sulfur interacting with a surface oxygen (Galloway et al., 2015; Karlsen et al., 2003; Sasmaz and Wilcox, 2008). As the sulfur coverage increases, it is possible that a network of multi-sulfur compounds, such as thiosulfate ($S_2O_3^{2-}$), disulfite ($S_2O_5^{2-}$), and pyrosulfate ($S_2O_7^{2-}$) could form on the surface.

While XRD and DRIFTS can give information regarding the nature and speciation of adsorbed sulfur on the oxide surface, EDX analysis was employed to quantify the total amount of sulfur captured during the exposure. However, due to variations in the space velocity in the reactor, total sulfur capture can only be compared for different temperatures for a single gas composition and not across various gas compositions. The EDX results from the experiments conducted under the same conditions as those in Figure 5(a-c) are summarized in Table 3. The table shows several interesting trends not apparent from the DRIFTS or XRD results, with each gas composition behaving slightly differently. For the air-wet condition, the amount of sulfur captured slightly decreases at 850°C. Since this is within the maximum standard deviation calculated across all samples, it could be considered constant for all temperatures. The air-flame experiments also show a relatively consistent sulfur capture across all temperatures. Finally, the oxy-flame set shows a different trend by exhibiting increasing sulfur content with increasing temperature.

Discussion

The results from the DRIFTS, XRD and EDX analysis show several interesting trends with respect to the sulfur capture on CaO. It should be noted that only selected spectra are shown in the paper for brevity with the rest of the data included in the supplementary materials. The first trend is displayed in the XRD data, which shows the formation of a carbonate product during the oxy-flame experiments. What is unique about the oxy-flame experiments is that the partial pressure of CO₂ present in the gas stream is much higher than that exists during the air-flame experiments (70 vol% vs. 7 vol%). In order for the carbonate to be thermodynamically stable at 800°C, the partial pressure needs to be high. This mostly agrees with previous research that shows that 825-875°C is the thermodynamic limit before CaCO₃ decomposes back into CaO under the oxy-flame conditions, which similarly explains the decrease in carbonate as temperature increases (de Diego et al., 2004; de Diego et al., 2013; García-Labiano et al., 2011). The slight discrepancy is likely due to the fact that the reactions may not go to completion within the duration of the exposure as well as the competing sulfation reaction, suggesting kinetic limitations for carbonation under the experimental conditions. While the oxy- and oxy-flame runs have similar partial pressures of CO₂, they do not exhibit equivalent carbonate formation as expected from the thermodynamics data. While both have greater CO₂ partial pressure relative to air experiments, the added presence of water in the oxy-flame experiments also contributes to the formation of calcium carbonate. Previous research into the formation of carbonate from calcium shows a beneficial effect of H₂O partial pressure on carbonate formation (Cizer et al., 2012; Li et al., 2016; Van Balen, 2005). However, under the higher temperatures for the experiments conducted here, it is unclear how much effect, if any, water might play in carbonate formation from CaO at increased temperatures. Additional experiments conducted under the oxy-

environment without combustion, where the gas mixture passed through the high-temperature furnace at 1100°C before being fed to the reactor, exhibited CaCO₃ formation at 800°C as shown in Figure 3(b). The figure shows that less carbonate is formed and it disappears at a lower temperature when compared to the oxy-flame condition. The 1100°C temperature of the furnace possibly affects the gas-phase chemistry that could carry-over to the reactor at 800°C augmenting the surface chemistry and aiding in the carbonation reaction. Since in-situ gas or surface analysis was not available for these experiments, the reason for carbonate formation under these conditions is still unclear and should be subject to further investigation. Otherwise, carbonate formation is only present in the oxy-flame experiments suggesting that the presence of water aids in the carbonation reaction.

While the formation of a carbonate phase does not affect the sulfate peak intensity observed in the XRD, a difference is apparent from the EDX results. As shown in Table 3, the total sulfur captured steadily increases for the oxy-flame runs as the temperature increases. This is most likely related to the carbonate formation observed at lower temperatures. While the peak intensities for sulfur products in the DRIFTS and XRD results show little change, there is a clear increase in the sulfur content in EDX. At the higher temperatures, where carbonate is no longer thermodynamically stable, sulfur no longer has to compete for adsorption sites against CO₂ leading to higher sulfur retention. As the carbonate product seems to be the only product that is temperature dependent, it makes sense that the air-wet and air-flame EDX results remain relatively constant as the temperature changes, as there is no competing product formation taking place under these conditions. This indicates that Reaction 3 is potentially competing with Reactions 1-2. It is also possible that the sulfate formation reaction is slower on carbonate

(Reaction 4) relative to the oxide (Reaction 1) limiting the total adsorption of sulfur over the duration of the experiment.

Of particular interest, when examining all of the DRIFTS spectra together, is that there is ultimately little difference as the gas composition and temperature are varied. A common trait that the proposed sulfation mechanisms, shown in Reactions 1-5, exhibit is a sulfite intermediate between the oxide and the sulfate. However, only minimal evidence of sulfite species was present in the DRIFTS results. The sulfite characteristic that is present in the DRIFT spectra shows a strong temperature dependence. This is consistent with the thermodynamic data, as the lowest temperature investigated (800°C) is already above the decomposition temperature for CaSO_3 , explaining the minimal sulfite characteristic observed (Martin et al., 1987). However, as abundant unreacted CaO is still available, kinetic limitations appear to allow for some of the sulfite characteristic to remain at the lower temperatures tested (e.g. 800°C) despite being above the thermodynamic decomposition temperature. Especially as the samples are quickly quenched and flushed with inert N_2 after exposure, the reactions may not go to completion where all the sulfite is converted to sulfate. This is further supported by the XRD results that show no evidence of the sulfite, while DRIFTS, which is a more surface sensitive technique, does, albeit much lesser extent than the sulfate. At higher and higher temperatures, only the sulfate characteristic is present regardless of the gas phase composition. Despite that minimal sulfite characteristic is observed, the $\text{SO}_3:\text{SO}_4$ ratio still increases at lower temperatures further showing the temperature dependence of the sulfite-like structure. The only exception is the oxy-flame condition where a jump in the $\text{SO}_3:\text{SO}_4$ ratio is observed between 800 to 825°C. This could be due to the slightly increasing sulfur content, as shown in the EDX data in Table 3. Additionally, the presence of the carbonate species in the DRIFT spectra could obscure the sulfur species in

this region around 2200 cm^{-1} as it was mentioned earlier. This, coupled with the minimal intensity that these peaks already exhibit, make it difficult to appropriately estimate the peak area leading to the discrepancy. Otherwise, the predominance of the sulfate characteristic in the data results from the excess O_2 present in all experiments allowing sulfite to convert to sulfate. While previous research has shown more pronounced sulfite characteristics, those were mostly conducted at lower temperatures or in inert environments, both conditions that are more conducive to the formation of a sulfite intermediate (Allen and Hayhurst, 1996a, b; Baltrusaitis et al., 2007; Goodman et al., 2001; Goodsel et al., 1972; Ishihara et al., 1992; Low et al., 1971; Martin et al., 1987; Rodriguez et al., 2000a; Rodriguez et al., 2000b; Rodriguez et al., 2001). Similarly, the conditions run here that most closely resemble those experiments are the N_2 -only ones. The N_2 -spectra in Figure 4(b) show a much more intense SO_3 peak, and therefore greater $\text{SO}_3:\text{SO}_4$ ratio, relative to the other gas samples showing the O_2 dependency on certain products. But even the N_2 experiments are run with $\sim 0.5\text{vol}\%$ O_2 , resulting in the major product still being the sulfate, as seen in the XRD data. Therefore, the only gas that affects the surface species, present during SO_2 capture, is O_2 . However, since power plants run at slightly leaner than stoichiometric conditions, with the equivalence ratio < 1 , there can be as much as $5\text{vol}\%$ of excess O_2 present in the flue gas stream. While the reactions may go through some sulfite intermediate as suggested by Reactions 2 and 5, the final product is likely to always be sulfate due to the presence of O_2 .

Conclusions

The adsorption of SO_x on CaO under a variety of gas compositions for temperatures between $800\text{-}900^\circ\text{C}$ has been investigated. The results show that the major product is CaSO_4 under all conditions with the amount of CaSO_4 also remaining relatively constant from

experiment to experiment. Only minor characteristics of thiosulfate and sulfite species were observed in the DRFITS results as secondary and tertiary sulfur products. The only other major product formed was CaCO_3 during the oxy-combustion experiments, where a high partial pressure of both CO_2 and H_2O was present. The presence of water potentially aided in the kinetics in forming the carbonate product phase for the brief duration of the experiments as carbonate formation was not observed during the oxy-environment experiments. The carbonate formation is temperature dependent with none forming above 825°C under the current experimental conditions. Additionally, the carbonate appears to inhibit sulfur adsorption either by consuming CaO or being less reactive relative to CaO . Finally, sulfite and carbonate products decrease at higher temperatures resulting in only sulfate being formed above 850°C .

Future work will investigate the effect on the CaO products by further increasing the $\text{SO}_3:\text{SO}_2$ ratio in the flue gas beyond that formed during combustion. It is important to examine the effect the greater SO_3 concentration can have on both the total amount of sulfur adsorbed and the resulting sulfur species bound to the surface. The experiments could then be expanded to other materials that comprise fly ash to investigate their interactions.

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	Flue Gas Species Concentration (vol%)				
	N ₂	O ₂	H ₂ O	CO ₂	SO _x (ppm)
N ₂	99.3	0.5	0	0	2500
Air(dry)	79	21	0	0	2500
Air(wet)	67.2	17.9	14.7	0	2500
Air-Flame	72.9	4.5	14.9	7.5	2500
Oxy-Environment	1.8	29.8	0	68.1	2500
Oxy-Flame	1.8	1.8	24.4	71.8	2500

456 Table 1. Gas-phase compositions for all conditions examined.

457

Figure 1. Schematic of the experimental setup used for SO_x exposure in flue gas.

Figure 2. XRD spectra showing gas dependence on major product formation on CaO at 800°C with N_2 , Air, Air-wet, Air-flame, Oxy-environment, Oxy-flame. a) Spectra showing unreacted CaO, CaSO_4 and CaCO_3 b) Zoomed in sulfate peak from plot (a) for various gas compositions,

Figure 3. XRD spectra showing temperature dependence of CaCO_3 for a) oxy-flame conditions from 800°C to 900°C and b) pre-heated oxy-environment from 800°C to 850°C.

Figure 4. DRIFT spectra showing gas dependence on major product formation on CaO at 800°C. a) Spectra from 1500 to 3100 cm⁻¹. b) Spectra from 950 to 1050 cm⁻¹ showing the sulfate/sulfite speciation c) Spectra from 1050 to 1300 cm⁻¹. From bottom to top, the lines on all graphs are: calcined only, exposed to N₂ environment, air only, air-wet, air-flame, oxy-environment, oxy-flame, and CaCO₃ standard.

477 Figure 5. DRIFT spectra from 950 to 1050 cm^{-1} showing temperature dependence of
 478 sulfate/sulfite speciation for a) air-wet, b) air-flame, c) oxy-flame conditions between 800-
 479 900°C.

	Air-wet			Air-flame			Oxy-flame		
Temperature (°C)	SO ₃	SO ₄	Ratio	SO ₃	SO ₄	Ratio	SO ₃	SO ₄	Ratio
800	0.246	0.493	0.499	0.112	0.179	0.629	0.014	0.172	0.082
825	-	-	-	-	-	-	0.046	0.066	0.696
850	0.044	0.369	0.120	0.041	0.311	0.133	0.052	0.249	0.207
900	0.017	0.177	0.098	0.011	0.311	0.036	0.013	0.331	0.040

480

481 Table 2. Integrated areas for SO₃ and SO₄ peaks shown in the DRIFT spectra in Figure 5(a-c)
482 along with the calculated peak area ratio of SO₃:SO₄ for air-wet, air-flame, and oxy-flame
483 conditions between 800-900°C.

	EDX Sulfur Wt% $\pm$ Standard Deviation		
T (°C)	Air-wet	Air-flame	Oxy-flame
800	1.33 $\pm$ 0.26	0.83 $\pm$ 0.10	0.77 $\pm$ 0.04
825	-	-	0.80 $\pm$ 0.07
850	1.07 $\pm$ 0.13	0.75 $\pm$ 0.09	1.08 $\pm$ 0.15
900	1.37 $\pm$ 0.13	0.95 $\pm$ 0.12	1.69 $\pm$ 0.32

Table 3. EDX results for the sulfur weight percentages after exposure to the air-wet, air-flame, and oxy-flame conditions.

488 Bibliography

- 489 Overview of Greenhouse Gases : Carbon Dioxide Emissions U.S. Environmental Protection
490 Agency.
- 491 Ahmaruzzaman, M., 2010. A review on the utilization of fly ash. *Prog. Energ. Combust.* 36, 327-
492 363.
- 493 Al-Hosney, H.A., Grassian, V.H., 2005. Water, sulfur dioxide and nitric acid adsorption on
494 calcium carbonate: A transmission and ATR-FTIR study. *Physical Chemistry Chemical Physics*
495 7, 1266-1276.
- 496 Allen, D., Hayhurst, A.N., 1996a. Kinetics of the reaction between gaseous sulfur trioxide and
497 solid calcium oxide. *Journal of the Chemical Society, Faraday Transactions* 92, 1239-1242.
- 498 Allen, D., Hayhurst, A.N., 1996b. Reaction between gaseous sulfur dioxide and solid calcium
499 oxide mechanism and kinetics. *Journal of the Chemical Society, Faraday Transactions* 92, 1227-
500 1238.
- 501 Baltrusaitis, J., Usher, C.R., Grassian, V.H., 2007. Reactions of sulfur dioxide on calcium
502 carbonate single crystal and particle surfaces at the adsorbed water carbonate interface. *Physical*
503 *Chemistry Chemical Physics* 9, 3011-3024.
- 504 Belo, L.P., Spörl, R., Shah, K.V., Elliott, L.K., Stanger, R.J., Maier, J., Wall, T.F., 2014. Sulfur
505 Capture by Fly Ash in Air and Oxy-fuel Pulverized Fuel Combustion. *Energy Fuels* 28, 5472-
506 5479.
- 507 Carrasco, J., Illas, F., Lopez, N., 2008. Dynamic Ion Pairs in the Adsorption of Isolated Water
508 Molecules on Alkaline-Earth Oxide (001) Surfaces. *Physical Review Letters* 100, 016101.
- 509 Cheng, J., Zhou, J., Liu, J., Zhou, Z., Huang, Z., Cao, X., Zhao, X., Cen, K., 2003. Sulfur
510 removal at high temperature during coal combustion in furnaces: a review. *Prog. Energ.*
511 *Combust.* 29, 381-405.
- 512 Cizer, Ö., Rodriguez-Navarro, C., Ruiz-Agudo, E., Elsen, J., Van Gemert, D., Van Balen, K.,
513 2012. Phase and morphology evolution of calcium carbonate precipitated by carbonation of
514 hydrated lime. *J Mater Sci* 47, 6151-6165.
- 515 Croiset, E., Thambimuthu, K., Palmer, A., 2000. Coal combustion in O₂/CO₂ mixtures
516 compared with air. *Can. J. Chem. Eng.* 78, 402-407.
- 517 Croiset, E., Thambimuthu, K.V., 2001. NO_x and SO₂ emissions from O₂/CO₂ recycle coal
518 combustion. *Fuel* 80, 2117-2121.

519 Davis, W.T., Fiedler, M.A., 1982. The Retention of Sulfur in Fly Ash from Coal-Fired Boilers.
 520 JAPCA J. Air. Waste Ma. 32, 395-397.

521 de Diego, L.F., Abad, A., García-Labiano, F., Adánez, J., Gayán, P., 2004. Simultaneous
 522 Calcination and Sulfidation of Calcium-Based Sorbents. Ind. Eng. Chem. Res. 43, 3261-3269.

523 de Diego, L.F., de las Obras-Loscertales, M., García-Labiano, F., Rufas, A., Abad, A., Gayán, P.,
 524 Adánez, J., 2011. Characterization of a limestone in a batch fluidized bed reactor for sulfur
 525 retention under oxy-fuel operating conditions. Int. J. Greenh. Gas Con. 5, 1190-1198.

526 de Diego, L.F., Rufas, A., García-Labiano, F., de las Obras-Loscertales, M., Abad, A., Gayán, P.,
 527 Adánez, J., 2013. Optimum temperature for sulphur retention in fluidised beds working under
 528 oxy-fuel combustion conditions. Fuel 114, 106-113.

529 de las Obras-Loscertales, M., de Diego, L.F., García-Labiano, F., Rufas, A., Abad, A., Gayán, P.,
 530 Adánez, J., 2014. Sulfur retention in an oxy-fuel bubbling fluidized bed combustor: Effect of
 531 coal rank, type of sorbent and O₂/CO₂ ratio. Fuel 137, 384-392.

532 de Leeuw, N.H., Purton, J.A., Parker, S.C., Watson, G.W., Kresse, G., 2000. Density functional
 533 theory calculations of adsorption of water at calcium oxide and calcium fluoride surfaces. Surf.
 534 Sci. 452, 9-19.

535 de Leeuw, N.H., Watson, G.W., Parker, S.C., 1995. Atomistic Simulation of the Effect of
 536 Dissociative Adsorption of Water on the Surface Structure and Stability of Calcium and
 537 Magnesium Oxide. The Journal of Physical Chemistry 99, 17219-17225.

538 Dlugokenchy, E., Tans, P., Recent Global CO₂. National Oceanic and Atmospheric
 539 Administration - Earth Systems Research Laboratory.

540 Duan, L., Jiang, Z., Chen, X., Zhao, C., 2013. Investigation on water vapor effect on direct
 541 sulfation during wet-recycle oxy-coal combustion. Applied Energy 108, 121-127.

542 Evans, J.C., Bernstein, H.J., 1955. The vibrational spectrum of the sulphite ion in sodium
 543 sulphite. Canadian Journal of Chemistry-Revue Canadienne De Chimie 33, 1270-1272.

544 Francis, W.E., 1952. The measurement of the dewpoint and H₂SO₄ vapour content of combustion
 545 products. Gas Research Board Communication 64, 1-37.

546 Freedman, A.N., Straughan, B., 1971. Vibrational spectra and structures of some thiosulphate
 547 complexes. Spectrochimica Acta Part a-Molecular Spectroscopy A 27, 1455-&.

548 Galloway, B.D., Sasmaz, E., Padak, B., 2015. Binding of SO₃ to fly ash components: CaO,
 549 MgO, Na₂O and K₂O. Fuel 145, 79-83.

550 García-Labiano, F., Rufas, A., de Diego, L.F., Obras-Loscertales, M.d.l., Gayán, P., Abad, A.,
 551 Adánez, J., 2011. Calcium-based sorbents behaviour during sulphation at oxy-fuel fluidised bed
 552 combustion conditions. *Fuel* 90, 3100-3108.
 553 Goodman, A.L., Li, P., Usher, C.R., Grassian, V.H., 2001. Heterogeneous Uptake of Sulfur
 554 Dioxide On Aluminum and Magnesium Oxide Particles. *J. Phys. Chem. A* 105, 6109-6120.
 555 Goodsel, A.J., Low, M.J.D., Takezawa, N., 1972. Reactions of gaseous pollutants with solids. II.
 556 Infrared study of sorption of sulfur dioxide on magnesium oxide. *Environmental Science &*
 557 *Technology* 6, 268-273.
 558 H. de Leeuw, N., C. Parker, S., 1997. Atomistic simulation of the effect of molecular adsorption
 559 of water on the surface structure and energies of calcite surfaces. *Journal of the Chemical*
 560 *Society, Faraday Transactions* 93, 467-475.
 561 Hardman, R., Stacy, R., 1998. Estimating Sulfuric Acid Aerosol Emissions from Coal-Fired
 562 Power Plants, Conference on Formation, Distribution, Impact, and Fate of Sulfur Trioxide in
 563 Utility Flue-gas Streams, Pittsburgh, pp. 1-11.
 564 Hills, A.W.D., 1968. The mechanism of the thermal decomposition of calcium carbonate.
 565 *Chemical Engineering Science* 23, 297-320.
 566 Hower, J.C., Robertson, J.D., Thomas, G.A., Wong, A.S., Schram, W.H., Graham, U.M.,
 567 Rathbone, R.F., Robl, T.L., 1996. Characterization of fly ash from Kentucky power plants. *Fuel*
 568 75, 403-411.
 569 Ingraham, T.R., Marier, P., 1971. Mechanism of absorption of SO₂ by limestone. *JAPCA J. Air.*
 570 *Waste Ma.* 21, 347-&.
 571 Ishihara, M., Matsui, H., Hashizume, G., 1992. Thermal-behavior and S-O bonding state of
 572 alkaline-earth metal sulfites. *J. Therm. Anal.* 38, 1801-1815.
 573 Jiang, Z., Duan, L., Chen, X., Zhao, C., 2013. Effect of Water Vapor on Indirect Sulfation during
 574 Oxy-fuel Combustion. *Energy Fuels* 27, 1506-1512.
 575 Karlsten, E.J., Nygren, M.A., Pettersson, L.G.M., 2003. Comparative Study on Structures and
 576 Energetics of NO_x, SO_x, and CO_x Adsorption on Alkaline-Earth-Metal Oxides. *J. Phys. Chem.*
 577 *B* 107, 7795-7802.
 578 Kiga, T., Takano, S., Kimura, N., Omata, K., Okawa, M., Mori, T., Kato, M., 1997.
 579 Characteristics of pulverized-coal combustion in the system of oxygen/recycled flue gas
 580 combustion. *Energ. Convers. Manage.* 38, Supplement, S129-S134.

581 Klostermann, M., 2008. Efficiency Increase of the oxyfuel process by waste heat recovery
 582 considering the effects of flue gas treatment, #rd workshop of the IEA-GHG international oxy-
 583 combustion network, Yokohama, Japan.

584 Li, Z.-H., Wang, Y., Xu, K., Yang, J.-Z., Niu, S.-B., Yao, H., 2016. Effect of steam on CaO
 585 regeneration, carbonation and hydration reactions for CO₂ capture. *Fuel Process. Technol.* 151,
 586 101-106.

587 Liu, H., Katagiri, S., Kaneko, U., Okazaki, K., 2000. Sulfation behavior of limestone under high
 588 CO₂ concentration in O₂/CO₂ coal combustion. *Fuel* 79, 945-953.

589 Liu, H., Katagiri, S., Okazaki, K., 2001. Drastic SO_x Removal and Influences of Various Factors
 590 in O₂/CO₂ Pulverized Coal Combustion System. *Energy Fuels* 15, 403-412.

591 Liu, H., Zailani, R., Gibbs, B.M., 2005. Comparisons of pulverized coal combustion in air and in
 592 mixtures of O₂/CO₂. *Fuel* 84, 833-840.

593 Low, M.J.D., Goodsel, A.J., Takezawa, N., 1971. Reactions of gaseous pollutants with solids. I.
 594 Infrared study of the sorption of sulfur dioxide on calcium oxide. *Environmental Science &*
 595 *Technology* 5, 1191-1195.

596 Marier, P., Dibbs, H.P., 1974. The catalytic conversion of SO₂ to SO₃ by fly ash and the capture
 597 of SO₂ and SO₃ by CaO and MgO. *Thermochimica Acta* 8, 155-165.

598 Martin, M.A., Childers, J.W., Palmer, R.A., 1987. Fourier Transform Infrared Photoacoustic
 599 Spectroscopy Characterization of Sulfur-Oxygen Species Resulting from the Reaction of SO₂
 600 with CaO and CaCO₃. *Appl. Spectrosc.* 41, 120-126.

601 McCauley, K.J., Farzan, H., Alexander, K.C., McDonald, D.K., Varagani, R., Prabhakar, R.,
 602 Tranier, J.P., Perrin, N., 2009. Commercialization of oxy-coal combustion: Applying results of a
 603 large 30MWth pilot project. *Energy Procedia* 1, 439-446.

604 Munoz-Guillena, M.J., Linares-Solano, A., de Lecea, C.S.M., 1994. A study of CaO-SO₂
 605 interaction. *Applied Surface Science* 81, 409-415.

606 Nakamoto, K., 1997. Infrared and Raman Spectra of Inorganic and Coordination Compounds:
 607 Part A: Theory and Applications in Inorganic Chemistry, Sixth Edition. Wiley, New York.

608 Nyberg, B., Larsson, R., 1973. Infrared-absorption spectra of solid metal sulfites. *Acta Chemica*
 609 *Scandinavica* 27, 63-70.

610 Pikkarainen, T., Saastamoinen, J., Saastamoinen, H., Leino, T., Tourunen, A., 2014.
 611 Development of 2nd Generation Oxyfuel CFB Technology – Small Scale Combustion

Experiments and Model Development Under High Oxygen Concentrations. *Energy Procedia* 63, 372-385.

Raask, E., 1982. Sulfate capture in ash and boiler deposits in relation to SO₂ emission. *Prog. Energ. Combust.* 8, 261-276.

Reid, W.T., 1970. Basic factors in capture of sulfur dioxide by limestone and dolomite. *Journal of Engineering for Power* 92, 11-&.

Rodriguez, J.A., Jirsak, T., Freitag, A., Larese, J., Maiti, A., 2000a. Interaction of SO₂ with MgO(100) and Cu/MgO(100): Decomposition reactions and the formation of SO₃ and SO₄. *J. Phys. Chem. B* 104, 7439-7448.

Rodriguez, J.A., Jirsak, T., Freitag, A., Larese, J.Z., Maiti, A., 2000b. Interaction of SO₂ with MgO(100) and Cu/MgO(100): Decomposition Reactions and the Formation of SO₃ and SO₄. *J. Phys. Chem. B* 104, 7439-7448.

Rodriguez, J.A., Jirsak, T., Gonzalez, L., Evans, J., Perez, M., Maiti, A., 2001. Reaction of SO₂ with pure and metal-doped MgO: Basic principles for the cleavage of S-O bonds. *J. Chem. Phys.* 115, 10914-10926.

Sasmaz, E., Wilcox, J., 2008. Mercury Species and SO₂ Adsorption on CaO(100). *J. Phys. Chem. C* 112, 16484-16490.

Sheng, C., Xu, M., Zhang, J., Xu, Y., 2000. Comparison of sulphur retention by coal ash in different types of combustors. *Fuel Process. Technol.* 64, 1-11.

Song, Z., Zhang, M., Ma, C., 2007. Study on the oxidation of calcium sulfide using TGA and FTIR. *Fuel Process. Technol.* 88, 569-575.

Spörl, R., Maier, J., Scheffknecht, G., 2013. Sulphur Oxide Emissions from Dust-fired Oxy-fuel Combustion of Coal. *Energy Procedia* 37, 1435-1447.

Spörl, R., Paneru, M., Babat, S., Stein-Brzozowska, G., Maier, J., Scheffknecht, G., 2016. The influence of air and oxy-fuel combustion on fly ash and deposits. *Fuel Process. Technol.* 141, 258-265.

Stanger, R., Wall, T., Spörl, R., Paneru, M., Grathwohl, S., Weidmann, M., Scheffknecht, G., McDonald, D., Myöhänen, K., Ritvanen, J., Rahiala, S., Hyppänen, T., Mletzko, J., Kather, A., Santos, S., 2015. Oxyfuel combustion for CO₂ capture in power plants. *Int. J. Greenh. Gas Con.* 40, 55-125.

642 Stanton, K.T., Towler, M.R., Mooney, P., Hill, R.G., Querol, X., 2002. Thermal analysis of fly
 643 ashes sourced from European non-blended coals. *J. Chem. Technol. Biot.* 77, 246-250.
 644 Steger, E., Schmidt, W., 1964. Infrarotspektren von Sulfaten und Phosphaten. *Berichte Der*
 645 *Bunsen-Gesellschaft Fur Physikalische Chemie* 68, 102-109.
 646 Stimpson, C.K., Chamberlain, S., Tree, D.R., 2013. Pulverized-Coal Deposits Collected Under
 647 Staged and Unstaged Oxy-Fuel Conditions for Four U.S. Coals. *Combust. Sci. Technol.* 185,
 648 1098-1117.
 649 Sturgeon, D.W., Cameron, E.D., Fitzgerald, F.D., 2009. Demonstration of an oxyfuel
 650 combustion system. *Energy Procedia* 1, 471-478.
 651 Tan, Y., Jia, L., Wu, Y., Anthony, E.J., 2012. Experiences and results on a 0.8 MWth oxy-fuel
 652 operation pilot-scale circulating fluidized bed. *Applied Energy* 92, 343-347.
 653 Van Balen, K., 2005. Carbonation reaction of lime, kinetics at ambient temperature. *Cement and*
 654 *Concrete Research* 35, 647-657.
 655 Vassilev, S.V., Vassileva, C.G., 1996. Mineralogy of combustion wastes from coal-fired power
 656 stations. *Fuel Process. Technol.* 47, 261-280.
 657 Wall, T., Liu, Y., Spero, C., Elliott, L., Khare, S., Rathnam, R., Zeenathal, F., Moghtaderi, B.,
 658 Buhre, B., Sheng, C., Gupta, R., Yamada, T., Makino, K., Yu, J., 2009. An overview on oxyfuel
 659 coal combustion—State of the art research and technology development. *Chemical Engineering*
 660 *Research and Design* 87, 1003-1016.
 661 Wall, T.F., 2007. Combustion processes for carbon capture. *Proceedings of the Combustion*
 662 *Institute* 31, 31-47.
 663 White, V., Torrente-Murciano, L., Sturgeon, D., Chadwick, D., 2010. Purification of oxyfuel-
 664 derived CO₂. *Int. J. Greenh. Gas Con.* 4, 137-142.
 665 Woycenko, D.M., van_de_Kamp, W.L., Roberts, P.A., October 1995. Combustion of puverized
 666 coal in a mixture of oxygen and recycled flue gas. *International Flame Research Foundation*
 667 *Ijmuiden, The Netherlands*.
 668 Yu, D., Morris, W.J., Erickson, R., Wendt, J.O.L., Fry, A., Senior, C.L., 2011. Ash and deposit
 669 formation from oxy-coal combustion in a 100kW test furnace. *Int. J. Greenh. Gas Con.* 5,
 670 Supplement 1, S159-S167.

671 Zhuang, Y., Pavlish, J.H., 2012. Fate of Hazardous Air Pollutants in Oxygen-Fired Coal
672 Combustion with Different Flue Gas Recycling. *Environmental Science & Technology* 46, 4657-
673 4665.

674

675